

ŽELEZARSKI ZBORNIK

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ŽELEZARSKI ZBORNIK

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Skrajševanje tehnološkega postopka od taline do žice

Shortenings of Technological Procedures from Melt to Wire

J. Rodič*

UDK: 669.181.274:621.746.047:621.771.25
ASM/SLA: D7c, D9q, D8m, A11e, 4—61

Novi materiali in materiali z izboljšanimi uporabnimi lastnostmi, ki so v ospredju strateških usmeritev razvojnih programov, zahtevajo nove ali pa spremenjene in izboljšane tehnologije z ekstremno racionalizacijo procesov, zmanjševanjem specifične porabe energije in zagotavljanjem maksimalnega materialnega izkoristka. Pojavljajo se pomembne in prav revolucionarne spremembe celo v osnovnih konceptih tehnoloških postopkov s težnjo k skrajševanju tehnoloških poti. Odločilnega pomena je optimalna kombinacija specializacije in hitre prilagodljivosti tržnim in razvojnim potrebam.

V članku je podrobneje opisan razvoj pilotne proizvodnje z vakuumsko indukcijsko pečjo ter horizontalno kontinuirno napravo za žico in palice v dimenzijskem območju $\varnothing 3$ do $\varnothing 40$ mm.

1. UVOD

Novi materiali so danes po vsem svetu v središču pozornosti strateških usmeritev razvoja. Za proizvodnjo in zagotavljanje kakovosti teh materialov je potrebna nova ali boljša tehnologija.

Spremembe tehnoloških procesov prinašajo izboljšanje materialnega izkoristka, zmanjšanje specifične porabe energije in optimalno ekonomiko proizvodnje.

Odločilnega pomena je pri tem optimalni odnos specializacije in fleksibilnosti zaradi sposobnosti hitrega prilaganja razmeram na trgu in zahtevam razvoja.

Pomembno novost v tehnološkem razvoju predstavlja horizontalno neprekinjeno litje drobnih dimenzij, žic in palic, ki je povezano tudi z novostmi v razvoju novih, tehnološko in energetsko racionalnejših procesov vroče predelave.

Razvoj pilotne proizvodnje na Metalurškem inštitutu v Ljubljani (1) je z mednarodnim sodelovanjem prinesel nekaj izvirnih novosti za nadaljnji razvoj tehnologije tega področja in novih materialov, tako da specifičnosti te nove tehnologije niso več zanimive samo za proizvajalce specialnih konstrukcijskih in orodnih jekel ter superzlitin, ampak tudi za proizvajalce manj legiranih jekel.

Izkazalo se je, da je danes že možno v proizvodni praksi uresničiti nekdanje futuristične želje po nepreki-

New materials and materials with improved properties which are in the forefront of strategic orientation of development programmes demand new or modified and improved technologies with extreme process rationalization, reduction in specific energy consumption and higher material yield. New important and revolutionary changes have appeared even in basic technological concepts with the aim of shortening technological procedures. The optimum combination of specialization and quick adaptation to market and development demands are of decisive importance.

The development of pilot plant consisting of vacuum induction furnace and horizontal continuous casting machine for wire and rods within 3—40 mm diameter range is described.

1. INTRODUCTION

Today new materials are in the focus of strategic orientation of development all over the world. The production and quality requirements of these new materials require new or better technologies.

Changes in technological procedures result in higher yield of material, reduction of specific energy consumption and optimal economy of production.

The optimal ratio between specialisation and flexibility has a decisive role due to the need for quick adaptation to market conditions and development requirements.

Horizontal continuous casting of small section rods and wires is an important innovation of technological development associated with new achievements in the development of new from energetic and technological viewpoint more rational hot working processes.

The development of pilot production at Metallurgical Institute in Ljubljana (1) with international cooperation has brought forth some original innovations for further development of this technology and new materials so that this specific technology becomes interesting not only for the producers of special constructional and tool steels, and superalloys but for the producers of low alloyed steels as well.

It has been shown that today it is possible to realize old wishes for a continuous technological process from melt to the final product — rod or wire in heat treated state.

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njenem tehnološkem postopku od taline do končnega izdelka — palice ali žice v toplotno obdelanem stanju.

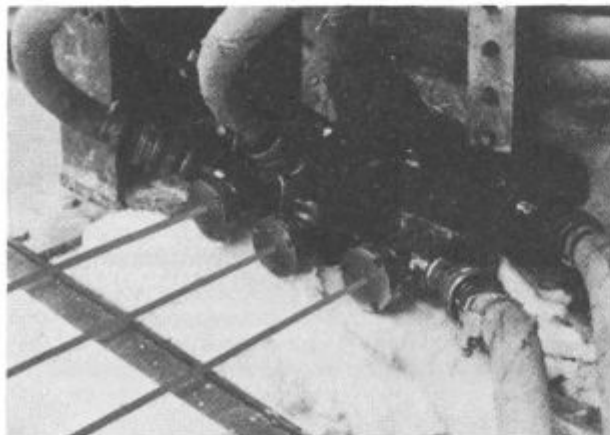
Pilotna proizvodnja je tesno povezana z matematičnim simuliranjem procesov in tako v razvoju nove tehnologije ter zagotavljanja »zanesljive ekonomske kakovosti« prevzema pomembno razvojno vlogo.

Asortiment izdelkov pilotne proizvodnje omogoča tudi ustrezno uveljavitev na tržišču, nakar ga je v polni meri treba prenesti v industrijsko proizvodnjo — učinkovito in hitro!

Prva faza razvoja pilotne proizvodnje slovenskih železarn na Metalurškem inštitutu v Ljubljani obsega vakuumsko indukcijsko peč z napravo za horizontalno neprekinjeno litje, napravo za električno pretaljevanje pod žlindro, naprave za vlečenje v hladnem in toplen stanju ter toplotno obdelavo, klasično, v vakuumu in v lebdečem sloju. Poleg tako imenovane pilotne vloge za uvajanje novih tehnoloških procesov in materialov v industrijsko proizvodnjo, bodo te naprave zadovoljevale tudi potrebe po manjših količinah posebnih materialov, katerih proizvodnja je v industrijskih pogojih ekonomsko nesprejemljiva.

2. HORIZONTALNO NEPREKINJENO LITJE ŽICE, OKROGLIH IN KVADRATNIH PALIC TER DROBNIH PLOŠČATIH PRESEKOV

Leta 1972 je firma CSE (Steel Casting Engineering) izdelala prvo napravo (2) za horizontalno neprekinjeno litje žic (Slika 1). Najpomembnejše je, da je na taki napravi možno izdelati tanke palice, premera 3 do 15 mm in dolžine ca. 6 ali tudi več metrov, iz nepredelavnih materialov na bazi kobalta in drugih zlitin za dodajne materiale pri postopkih varjenja oziroma navarjanja, katere je bilo doslej mogoče izdelovati samo z dragimi postopki sesanja v kvarčne cevke, dolžine največ do 600 mm. Z razvojem novega postopka neprekinjenega litja se je odprlo tudi novo področje tehnologije, ki je zaenkrat še omejeno na asortiment avstenitnih nerjavnih jekel in nekaterih supezlitin. Lito žico nekaterih vrst jekel in zlitin je namreč mogoče vleči v hladnem ali toplen, in to neposredno po litju, v nekaterih primerih celo brez kakršne koli predhodne toplotne obdelave. Za razvoj te tehnologije bo potrebno še veliko raziskovalno-razvojnega dela, predvsem na področju orodnih in nekaterih posebnih jekel, za ka-



Slika 1

Izhodni del trožilne naprave za horizontalno neprekinjeno litje žice

Fig. 1

Outgoing side of a three strand horizontal continuous wire caster

Pilot production is closely bound with mathematical modelling and computer simulation of processes which enables it to undertake an important role in the development of new technological procedures and obtaining "reliable economic quality".

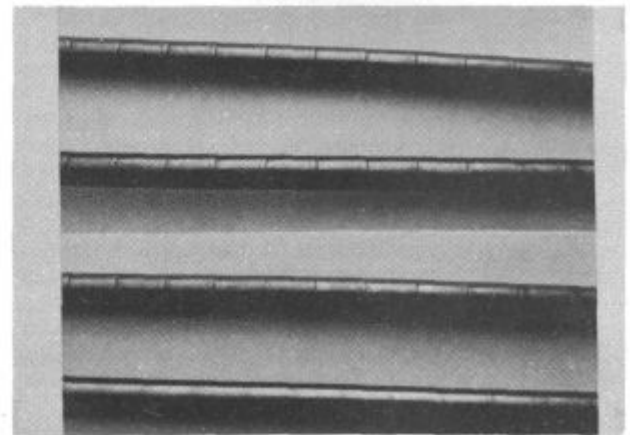
The production program of the pilot production makes it possible to reach corresponding market effect which should be followed by a quick and efficient transfer in industrial production!

The first phase of development of the pilot production of Slovenske železarne (Slovenian Ironworks) at the Metallurgical Institute in Ljubljana is made up of a vacuum induction furnace with horizontal continuous casting machine, electro-slag remelting unit, hot and cold drawing machines, and the equipment for vacuum heat treatment, classic heat treatment and heat treatment in fluidized bed. The pilot plant composed in this way will besides its development role satisfy also market demands for smaller quantities of special materials which can not be produced economically in an industrial plant.

2. HORIZONTAL CONTINUOUS CASTING OF WIRE, ROUNDED AND SQUARE BARS AND SMALL FLAT CROSS SECTIONS

In 1972 SCE (Steel Casting Engineering) built the world's first (2) horizontal continuous wire casting machine (fig. 1)

The most important is that such a caster can produce 3—15 mm diameter rods of ca 6 m or longer length from practically nonworkable materials such as cobalt based and similar alloys for welding rods which up to the present had to be produced by expensive vacuum sucking into quartz glass tubes of utmost 600 mm length. The development of the new continuous casting process opened up new field of technology also which is at present limited to austenitic stainless steel and some superalloys. Continuously casted wire of some steels and alloys can be subjected to hot or cold drawing immediately after the casting and in certain cases even without any heat treatment. The development of this technology specially for tool steel and some specialty steel will demand a lot of additional research work. However, the obtained experience confirm its feasibility and



Slika 2

Površina žice kobaltove zlitine ob frekvenci oscilacij 200, 250, 300 in 800 impulzov na minuto (od zgoraj navzdol)

Fig. 2

Surface of cobalt based wire. Stroking rates from above: 200, 250, 300 and 800 strokes per minute.

tera tehnologija še ni osvojena, izkušnje pa kažejo, da je prav gotovo možna in za kakovost zelo perspektivna. Firma SCE je tudi dobavitelj pilotnih naprav Metalurškega inštituta v Ljubljani.

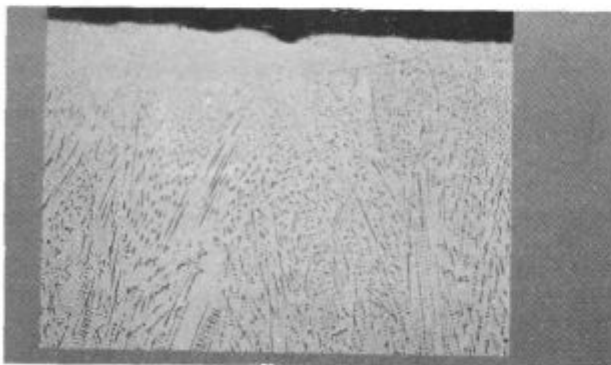
Tehnološki parametri litja (1, 2) vplivajo na izoblikovanje oziroma odpravo lunckerjev in na kakovost površine (Slika 2). Pri optimalnih pogojih je danes, ne glede na veliko hitrost litja, že mogoče zanesljivo izdelati z neprekinjenim litjem žico brez lunckerjev (Slika 3). Uvedba vmesne ponovce v izvedbi in vlogi dogrevalne ali celo talilne peči (3), ki deluje pod tlakom in ima možnost preprihovanja taline z argonom, omogoča vzdrževanje optimalnega in nespremenljivega ferostatičnega pritiska v kristalizatorju (Slika 4).

Z razvojem horizontalnega neprekinjenega litja valjarskih gredic in žice je povezan tudi razvoj horizontalnega neprekinjenega litja palic končnih dimenzij za razrez pri postopku utopnega ali prostega kovanja in polizdelkov za nadaljnje valjanje. To so palice v območju premerov 20—50 mm, ki v zadnjem času postajajo vse bolj interesanten vložek za nadaljnjo predelavo.

Izdelki iz te naprave za horizontalno neprekinjeno litje so zelo perspektivni v nadaljnjem razvoju predelave z vročim valjanjem specialnih jekel in zlitin, izdelkov in oblik, ki so v določenih primerih tudi vložek za vroče, poltoplo ali hladno kovanje. Kot primer lahko omenimo ventile, obroče krogličnih ležajev in številne druge izdelke.

Neprekinjeno litje palic v območju premerov 20—50 mm za nadaljnjo vročo plastično predelavo se je izkazalo kot zelo pomembno, predvsem pri materialih, ki se težko plastično preoblikujejo. Z manjšim vhodnim presekom je mogoče vhodno hitrost pri valjanju optimalno prilagoditi najprimernejši izhodni hitrosti ter z uravnavanjem stopenj deformacije pri posameznih prehodih zagotavljati izotermalno predelavo v ozkem temperaturnem intervalu. Tako je mogoče valjati z novo kovaško valjavsko linijo (4) tudi jekla in zlitine, ki so doslej veljale skoraj kot nesposobne za vročo plastično predelavo. Posebej je treba poudariti, da je interes za neprekinjeno vliivanje takih polizdelkov v obliki drobnih palic odprl nove probleme in zahteval nove tehnološke rešitve v tehnologiji neprekinjenega litja.

Matematično modeliranje za optimiranje tehnoloških pogojev (5, 7) daje velik prispevek k pospeševanju napredka na področjih litja in predelave.

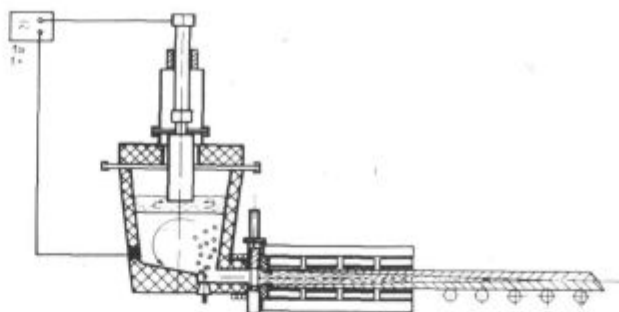


Slika 3

Vzdolžni prerez neprekinjeno lite žice nerjavnega jekla tipa 18 % Cr-11 % Ni ob izvlačanju žice s frekvenco 800 impulzov na minuto

Fig. 3

Longitudinal section of continuously cast stainless steel (18 % Cr-11 % Ni) wire. Stroking rate 800 strokes/min.



Slika 4

Tlačna vmesna ponovca, ogrevanje z električnim pretaljevanjem pod žilindro ali induktivno ogrevanje ponovce in izlivka, preprihovanje z argonom in drsno zapiralo za horizontalno neprekinjeno litje

Fig. 4

Scheme of an HCC with Electroslag Heating, Ar-purging and constant gas pressure above the bath

promising prospect regarding quality improvement. The mentioned equipment of the pilot plant of Metallurgical Institute is to be supplied by SCE.

Technological parameters of casting (1, 2) influence the internal shrinkage and surface quality (fig. 2). At optimum conditions it is possible to produce internally sound wire (fig. 3) with horizontal continuous casting irrespective of great casting rate.

The introduction of heating or even smelting type tundish (3) operating at constant gas pressure above the bath and equipped with argon purging helps to maintain optimal and constant ferostatic pressure in the mould (fig. 4).

The development of horizontal continuous casting of bars of final dimensions and cutting for die or free forging and semi products for subsequent rolling is also associated with the development of horizontal continuous casting of billets and wire. These bars of 20—50 mm diameter for further subsequent working have recently become very interesting. The products of horizontal continuous caster are very interesting for further development of hot rolling of special steels and alloys as well as profiles and shapes which in certain cases serve as semi-products for subsequent hot, semi hot or cold forging. As an example valves and ball bearing rings should be mentioned.

Continuous casting of rods of 20—50 mm diameter for further hot working has been found as very important particularly for materials of poor workability. The use of smaller section makes it possible to select the most appropriate input rolling rate to suit the optimal exit rate and to ensure practically isothermal working within a narrow temperature range by the control of deformation degree in particular rolling passes. The new combined forging-rolling procedure (4) makes it possible to process the steels and alloys which up to now were considered as practically nonworkable. However, it should be underlined that continuous casting of such semi products in the form of small size rods opened up new problems and started the search for new innovations of the continuous casting technology.

Mathematical modelling as a tool for optimization of technological conditions (5, 7) have a significant share in the acceleration of progress in the field of casting and plastic deformation.

The productivity of these machines is quite good today also, e.g. a three strand horizontal continuous caster of wire can produce

Tudi produktivnost teh naprav je danes že kar pomembna, saj na primer horizontalna kontilivna naprava za žico s tremi žilami omogoča letno proizvodnjo.

— pri \varnothing 3 mm ... ca. 200—250 t/leto

— pri \varnothing 5 mm ... ca. 400—500 t/leto

— nad \varnothing 8 mm ... nad 850 t/leto,

kar je odvisno od deleža sekvenčnega ali individualnega litja.

Enožilna naprava za palice, premera 50 mm, pa daje možnost proizvodnje od 10.000 do 20.000 ton letno, kar predstavlja dandanes najekonomičnejši postopek proizvodnje nekaterih izdelkov v določenem dimenzijskem območju.

V fazi razvoja je tudi naprava za neprekinjeno litje ploščatih presekov (3) z debelino 10 mm—15 mm in širino 150 mm—350 mm. Ta razvoj je namenjen optimiranju tehnologije za proizvodnjo nerjavnih varjenih cevi. Posebno za te namene prirejena valjavka linija se v kombinaciji z napravo za neprekinjeno litje pojavlja kot zelo resen konkurent konvencionalnemu proizvodnemu postopku za varjenje cevi.

3. NOVE PERSPEKTIVE RAZVOJA NA PODROČJU VALJANJA SPECIJALNIH JEKEL IN ZLITIN

Današnja stopnja razvoja je mogoče opredeliti z optimalno kombinacijo horizontalnega neprekinjenega litja z neprekinjeno kovaško valjavsko linijo za predelavo v vročem, ki ima prehodni kovaški stroj povezan s kontinuirno valjavsko progo (1). Taka kombinacija z regulirnim natančnim indukcijskim dogrevanjem pred vstopom v progo zagotavlja proizvodnjo homogenih in po vsem preseku zdravih izdelkov — žic in palic. Pri taki specialni liniji že stopnja predelave neprekinjeno litih polizdelkov z redukcijo 3,5:1 povsem zadošča (4).

Sekvenčno litje žice že pri majhni napravi omogoča izdelavo kolobarjev celo do dveh ton.

Vroča predelava v eni vročini od dobave vročega vložka iz jeklarne do končnega izdelka predelave, ki predstavlja normalni tehnološki postopek na področju konstrukcijskih jekel, je vsekakor ekonomsko tehnični cilj razvoja tudi na področju specialnih jekel in zlitin, orodnih jekel in superzlitin, kakor tudi visokotrdnih in ognjeodpornih, težko predelavnih materialov, kar pri današnjih standardnih pogojih ni izvedljivo.

V središču pozornosti je zato danes nov postopek vroče predelave z napravami, ki omogočajo učinkovitejšo plastično deformacijo in že pri manjši stopnji redukcije zagotavljajo zdrav presek tudi pri uporabi neprekinjeno litih gredic ali palic, zaradi optimirane porazdelitve deformacij, ki omogočajo učinkovito zapiranje lunkerjev in zgoščevanje centralne pozornosti (7).

Na osnovi praktičnih izkušenj valjanja je znano, da vhodna hitrost ne sme ali pa ne more biti manjša od 0,1 m/sek. Končna izhodna hitrost pri valjanju pa je omejena z značilnimi lastnostmi valjanega materiala.

Danes končna izhodna hitrost 50 m/sek pri premeru 6 mm ni več nikakršna posebnost in ne predstavlja tehničnih problemov valjanja. Seveda pa je ta hitrost dopustna pri običajnih konstrukcijskih jeklih, od nelegiranih do srednjelegiranih in pri malolegiranih orodnih jeklih. Pri brzoreznih jeklih ta hitrost v splošnem ne sme presegati 30 m/sek. Pri kobaltovih brzoreznih jeklih je ta hitrost omejena na maksimum 25 m/sek, a pri nekaterih superzlitinah celo na maksimum 20 m/sek.

Če upoštevamo te omejitve, lahko takoj ugotovimo, da klasično valjanje neprekinjeno litih gredic v eni vročini pri mnogih vrstah specialnih in orodnih jekel ter superzlitin sploh ni izvedljivo.

at 3 mm diameter ... ca 200—250 t/year

at 5 mm diameter ... ca 400—500 t/year

over 8 mm diameter ... over 850 t/year.

which depends on the share of sequential casting.

Single strand caster for rods of 50 mm diameter can produce 10,000 to 20,000 tons per year, which today represents the most economic production process for some products of certain dimension range. Research work is continuing on a development programme to cast flats (3) in sizes of 10—15 mm by 150—350 mm. This development programme is aimed at the optimization of the manufacture of welded stainless steel tubes. Specially adapted rolling mill combined with continuous caster appears as very serious contender with conventional manufacturing of welded tubes.

3. NEW OUTLOOK FOR DEVELOPMENT IN ROLLING OF SPECIAL STEELS AND ALLOYS

The present stage of development can be defined with the optimal combination of horizontal continuous casting with a continuous forging-rolling mill for hot working with continuous forging machine coupled with continuous rolling mill. Such a combination with accurately controlled induction heating at the start ensures a reliable manufacture of homogeneous and over all section sound rods and wires. The degree of deformation for continuously casted semi products of 3.5:1 is already sufficient (4) for such a combined production line. Sequential continuous casting makes it possible to produce even 2 ton coils already with a small caster. Hot working of hot stock as supplied by steelworks without any intermediate reheating to the end of processing, which is a normal procedure for constructional steel, is by all means the economic and technical aim of development also in the field of special steels and alloys as well as for tool steels, superalloys, hardfacing and refractory materials of poor plasticity which at present standard conditions is still impossible.

Today the activity is focused in the new hot processing method which makes it possible to perform more effective plastic deformation and ensures sound cross-section of continuously cast billets or rods already at lower degree of deformation because of the optimum distribution of deformation which helps to eliminate center line porosity (7).

Experience obtained in rolling has shown that input speed may not or can not be lower than 0.1 m/s whereas the final exit rolling speed is limited by material properties.

Today's exit speed of 50 m/s at 6 mm diameter is almost routine and does not cause technical rolling problems. Of course, such final speed is permissible for common constructional steel from unalloyed to medium alloyed grade and for low alloyed tool steel. The speed for high speed tool steel is limited to 30 m/s. For high speed tool steel containing Co the maximum rolling speed is 25 m/s whereas it is utmost 20 m/s for some super alloys.

Taking into account these limitations it can easily be concluded that conventional rolling of continuous cast billets without intermediate reheating is not possible for numerous special and tool steels and superalloys. The key for the solving of hot working problem when dealing with such a production programme lies in the radical changes of first technological phase of plastic working as brought forth by the development of new GFM forging-rolling process which has been described elsewhere (1, 4, 6).

Ključ za rešitev problemov vroče predelave na področju teh asortimentov proizvodnega programa je v zagotavljanju radikalnih sprememb v prvi tehnološki fazi plastične predelave, kakršne je prinesel razvoj novega kovaško-valjavskega postopka GFM, ki je podrobneje opisan v (1, 4, 6).

4. NADALJNI RAZVOJ

Nadaljnji razvoj prinaša bistvene novosti na področju specialnih jekel in zlitin z inovacijo nove moderne visoke tehnologije, ki se razvija z namenom izboljševanja materialnega izkoristka in zmanjševanja specifične porabe energije.

V proizvodnji specialnih jekel in superzlitin drobnih dimenzij je zaradi težav pri plastičnem preoblikovanju, ki so povezane z izkoristkom vložnega dela in materiala, a tudi zaradi splošne specifične porabe energije nesmiselno začeti predelavo s preseki vložnih materialov, ki so večji od nujno potrebnih. Dosedanje izkušnje s kovaško-valjavskim postopkom kažejo, da je pri tovrstnem plastičnem preoblikovanju že z zmanjšanjem premera vhodnega materiala na polovico mogoče zagotoviti zdravo strukturo po vsem preseku tudi pri uporabi kontinuirno vlitiga vložka.

To pomeni, da neprekinjeno litje v območju dimenzij 20—40 mm danes že predstavlja interes v industrijski uporabi in ustreza smernicam razvoja najsodobnejše vrhunske tehnologije v svetu.

Spomnimo se, da je dosednji razvoj neprekinjenega litja gredic potekal v dveh fazah. Najprej je bila izražena težnja k čimvečjim presekom neprekinjeno litih gredic, da bi s klasičnim valjanjem dosegli zdrav presek pri čimvečjih dimenzijah končnih izdelkov. Z novim kombiniranim razvojem tehnologije neprekinjenega vlivanja in intenzivnejše ter optimirane plastične predelave z novimi postopki so težnje razvoja usmerjene k zmanjševanju preseka neprekinjeno ulitih gredic, ki naj bi še zagotavljale ustrezno kakovost končnih izdelkov v čimširšem dimenzijskem območju do največjih potrebnih in tehnično ekonomsko sprejemljivih premerov. Nadaljnji razvoj je vse bolj usmerjen na področje horizontalnega neprekinjenega litja in predelave manjših dimenzij palic in žice.

Ta tehnologija daje široke možnosti intenzivni racionalizaciji proizvodnje, predvsem na področju materialov iz asortimenta specialnih visokolegiranih konstrukcijskih jekel, orodnih jekel, jekel s posebnimi lastnostmi, specialnih zlitin in superzlitin — materialov, od katerih se zahtevajo posebne lastnosti na najvišjem nivoju.

Znano je, da prinaša že dosedanje klasično in neprekinjeno litje v primerjavi s tradicionalnim litjem ingotov izboljšanje materialnega izkoristka za 10—20 %, odvisno od vrste jekla. Zmanjševanje stopnje predelave na minimalno neobhodno potrebno redukcijo omogoča posebno pri težko predelavnih materialih pomembno dodatno povečanje izkoristka, vezanega na tehnološko fazo predelave.

Skrajševanje verige celotnega tehnološkega postopka, ki predstavlja prevladujočo idejo v današnjih razvojnih prizadevanjih racionalizacije, prinaša zelo pomembne prihranke v specifični porabi energije (8).

Na današnji stopnji tehnološkega razvoja moramo posebej poudariti, da se že zelo približujemo industrijsko sprejemljivi realizaciji ideje neprekinjenega proizvodnega procesa od taline do končnih dimenzij palic ali žice v kolobarjih, kar je dolgo predstavljalo neuresničljive želje (1).

Za določeno dimenzijsko območje je mogoče razmerno veliko hitrost neprekinjenega litja prilagoditi razme-

4. FUTURE DEVELOPMENT

Further development will result in essential innovations and advancements of high technology in the field of specialty steel and superalloys which is aimed at higher material yield and energy saving.

In the production of special steel and super alloys of small cross-section the input stock should have as small cross-section as possible because of well-known difficulties in plastic deformation which are joined with corresponding poor yield of material and high specific energy consumption. The obtained experience in forging-rolling process has shown that 50 % reduction in stock diameter already can ensure soundness over all cross section of continuous cast stock also.

This means that continuous casting of products with in 20—40 mm section size range is today already interesting for industrial use and well compatible with development trend of the most advanced technology in the world.

The development of continuous casting of billets has proceeded in the two stages. The first trend was to develop continuous casting of billets of maximum possible section size to produce by conventional rolling completely sound cross-section at highest possible section size of finished products. With new combined development of continuous casting technology, with more intensive and optimum new plastic working processes the trend has changed to the reduction of cross section of continuously cast billets which should yet suffice for the corresponding quality of finished product of the widest possible dimension range up to the utmost needed and techno-economically acceptable diameters. Further development is even more oriented to horizontal continuous casting and processing of small sized rod and wire.

This technology offers wide possibilities for intensive rationalization of manufacturing particularly in the field of special high alloyed construction steel, tool steel, steel with special properties, special alloys and super alloys of top level properties.

It is well known that transition from ingot casting to conventional continuous casting resulted in 10—20 % increase in material yield depending on steel grade. The reduction in the degree of deformation to the lowest necessary amount brings forth a significant additional increase in yield particularly of material with poor workability.

The shortening of over-all technological process which is the predominant idea lying in the background of present development trend and rationalization efforts results in very important reduction of specific energy consumption (8).

It should be emphasized that today's development level is very close to the industrially acceptable continuous production process from molten steel to the final product i.e., wire coil or rod of finite dimension which has long been unrealistic wish only (1).

For a definite dimension range comparatively great rate of continuous casting can be adapted to relatively small input rate of the continuous forging-rolling line.

For a part of production programme the production line composed in this way can reach optimal techno-economic results with the minimum energy consumption, the highest yield of material and generally, the lowest production cost.

This idea of the continuous production line which has not yet been realized has become feasible thanks to the new concept. Of course, it requires the determina-

roma majhni vhodni hitrosti v kovaško-valjavsko preoblikovalno linijo.

S proizvodno linijo, ki jo oblikujemo na tak način, je mogoče za določen del programa proizvodnje dejansko doseči optimalne tehničnoekonomske rezultate z minimalno porabo energije in maksimalnim izkoristkom materiala ter v splošnem doseči minimalne možne proizvodne stroške.

Ta, doslej še ne izpolnjena ideja tehnološkega postopka, ima z novim konceptom realno možnost uresničenja z zagotavljanjem optimalnih parametrov. Pilotna proizvodnja Metalurškega inštituta v Ljubljani ima pri tem važno vlogo (1).

5. RAZVOJNE RAZISKAVE IN PILOTNA PROIZVODNJA (1, 8)

V sodobni visoko produktivni proizvodnji se izvajanje raziskav prenaša iz laboratorijskih na pilotne naprave, ki se po osnovnih karakteristikah približujejo pogojem industrijske proizvodnje. Take pilotne naprave so predrage, da bi jih izkoriščali samo za raziskave, zato morajo dajati tudi določen delež neposredne proizvodnje, s katerim je po možnosti treba pokrivati vsaj lastne stroške delovanja pilotne proizvodnje. Informacije in rezultati raziskav ter meritve na napravah pilotne proizvodnje so velikega pomena za hitrejši nadaljnji razvoj. Na ta način z izkoriščanjem pilotnih naprav ne motimo redne proizvodnje z eksperimentiranjem, ampak v njej samo občasno preverjamo modele. Poleg raziskovalnega pomena ima pilotna proizvodnja tudi velik pomen za razvoj in osvajanje tržišča, saj daje normalne proizvode v manjših količinah za neposredno uporabo. Ko količina proizvodov iz pilotnih naprav ne zadošča več potrebam, se z vsemi izkušnjami ta proizvodnja prenese v industrijske obrate.

Take usmeritve razvojnih raziskav so povsem razumljive in pilotna proizvodnja je v današnjih pogojih za učinkovit napredek neobhodno potrebna!

Pilotna proizvodnja slovenskih železarn na Metalurškem inštitutu v Ljubljani neposredno povezuje v celovit sistem naprav vakuumsko indukcijsko peč in napravo za horizontalno neprekinjeno litje žice ali palic. To je izredno fleksibilen sistem, ki omogoča najrazličnejše kombinacije tehnoloških postopkov tudi v povezavi z električnim pretaljevanjem pod žlindro, kovanjem, valjanjem, vlečenjem v hladnem ali pri povišanih temperaturah in toplotno obdelavo vseh vrst, od klasične do vakuumske. Ta koncept pilotne proizvodnje odpira široke možnosti neposredne proizvodnje določenih specialnih izdelkov v ustreznih količinah, za katere je zagotovljen plasman na tržišču. Po drugi strani pa tak sistem omogoča v povezavi s posebnimi meritvami in laboratorijskim preizkušnjem ter raziskovanjem lastnosti izvajanje programov vrhunskih aplikativnih in znanstvenih raziskav, katerih rezultati se preko simulacij z matematičnimi metodami modeliranja učinkovito prenašajo v razvoj industrijske proizvodne tehnologije. Če tovrstno pilotno proizvodnjo gledamo kot mini tovarno s potrebami prav vseh normalnih aktivnosti, od raziskav in razvoja do organiziranja proizvodnje in plasmaja na tržišču, je tak celovit sistem odlična priložnost za sistematično vzgojo mladih kadrov in za dopolnilno usposabljanje strokovnjakov — tehnologov, organizatorjev, kontrolorjev, raziskovalcev in ekonomistov.

Naprava za horizontalno neprekinjeno litje žice ima tri žile za premer žice v območju od 3—12 mm in na njej se lahko izdelujejo palice dolžine do 6 m ali pa v primeru sekvenčnega litja kolobarji do 1000 kg.

Z zamenjavo izhodnega bloka vmesne ponovce je možno napravo prilagoditi za neprekinjeno litje palic,

tion of optimum technological parameters. The pilot production of Metallurgical Institute has an important role in respect to this task (1).

5. DEVELOPMENT RESEARCH AND PILOT PRODUCTION (1, 8)

In modern production with top level productivity research and development work is transferred from laboratory to pilot plant which is by its characteristics very close to industrial works. However, such a pilot plant is expensive therefore it must be partly market-oriented to cover pilot plant production costs at least. The informations measurements and research results obtained in pilot production are very important for the rate of development. In this way research and development work do not disturb normal production which is temporarily used only for checking elaborated models. Besides this role the pilot production is very important for market development also since it offers smaller quantities of new products directly to the market. When the market demands surpasses the pilot production capacity the production moves to industrial scale together with overall experience obtained.

Such orientation of development is quite understandable. Under today's conditions pilot production is absolutely necessary for efficient progress!

The pilot production of Slovenian Ironworks at Metallurgical Institute in Ljubljana is an integral system composed of vacuum induction furnace and a horizontal continuous caster for rod and wire. This is a very flexible system which can be combined with electro-slag remelting unit, forging and rolling mills, cold drawing or drawing at higher temperatures including all sorts of heat treatment from the conventional one to the vacuum treatment. This pilot production concept opens up new possibilities for direct manufacture of certain special products in adequate quantities to satisfy the existing market demands. On the other side pilot plant in connection with special measurements and laboratory research makes it possible to carry out the most advanced scientific and applied research programme the results of which are used for mathematical modelling and computer simulation and finally utilized for development of industrial technology. The pilot plant can be considered as a mini factory including all necessary activities from research and development to the production planning and marketing so it is quite clear that such an integrated system offers excellent opportunities for systematic education of young workers and supplemental education of professionals like technologists, planners, foremen, supervisors, research workers, economists. etc.

Horizontal continuous caster is of three strand type for casting wire of 3—12 mm diameter range in coils and can be used for casting rods up to 6 m length also. In the case of sequential casting it can produce wire coils up to one tone weight.

By replacement of the exit block of tundish and pulper system the caster can be adapted to single strand continuous casting of 20—40 mm diameter rods. Similar replacement of drawing mechanism can adapt it to cast flat section products.

The continuous manufacturing process from melt to wire can be connected with further cold drawing or drawing at higher temperatures.

The mentioned flexibility includes also vacuum or open-air casting of 300 kg ingots for subsequent forging on GFM machine in Ironworks Ravne. Of course, smaller experimental ingots can also be cast. Electrodes for

premera 20—40 mm, z eno žilo. Če zamenjamo vlečne mehanizme, je s to napravo mogoče vlivati tudi ploščate preseke.

Neprekinjen tehnološki postopek od tekoče kovine do žice lahko neposredno povežemo z nadaljnjo predelavo z vlečenjem v hladnem ali pri povišanih temperaturah.

K že omenjeni prilagodljivosti tega sistema pilotnih naprav naj omenimo, da je mogoče vlivati ingote, teže 300 kg, prosto na zraku ali v vakuumu za normalno predelavo na kovaškem stroju GFM v Železarni Ravne ali pa manjše eksperimentalne ingote. Prav tako je mogoče vlivati elektrode za električno pretaljevanje pod žilindro in ulitke v kovinske, croning ali precizijske forme, in to en ulitek maksimalne teže 300 kg ali pa več manjših ulitkov ali grozdov pri precizijskem litju.

Horizontalna naprava za neprekinjeno litje žice je predvsem pomembna za osvajanje novih vrst dodajnih materialov pri postopkih varjenja in navarjanja. Največkrat je mogoče proizvesti kar celotne potrebne količine nekaterih specialnih materialov. Pomembno je to, da se v določenih primerih lahko uporabi kar kontinuirno ulita žica, kar omogoča tudi izdelavo elektrod iz nepredelavnih materialov.

Na ta način razvoj pilotne proizvodnje lahko ocenjujemo z dveh gledišč, enkrat kot nujno potrebno in racionalno osvajanje novih materialov, drugič pa kot proizvodnjo mini količin, ki v normalnem industrijskem procesu ne morejo biti sprejemljive in ekonomične.

Horizontalno neprekinjeno litje predstavlja potencialno zelo velik interes za področje proizvodnje brzoreznih in ledeburitnih orodnih jekel ter specialnih zlitin, za katere pa tehnološki parametri litja še niso osvojeni. Ta interes je vezan predvsem na finoiznato strjevanje in na skrajševanje procesov, ki je danes v splošnem v ospredju tehnološkega razvoja predelave kovin. Na teh področjih pričakujemo od raziskav v naslednjem obdobju velik pomen in številne aktivnosti zaradi široke mednarodne aktualnosti tega razvoja.

6. MOŽNOSTI ZMANJŠANJA SPECIFIČNE PORABE ENERGIJE

V okviru investicijskega projekta pilotne proizvodnje na Metalurškem inštitutu v Ljubljani smo podrobno analizirali specifično porabo energije s primerjavo različnih postopkov opisanega tehnološkega razvoja (8).

Pri tem smo upoštevali za primerjavo dva značilna tehnološka postopka klasične tehnologije in tri variante nove tehnologije. Naslednja shema na **sliki 5** nazorno prikazuje specifičnosti teh petih tehnoloških postopkov. V glavnem nas zanima primerjava specifične porabe energije v procesu vroče predelave, kajti specifična poraba energije za taljenje jekla je pri vseh variantah v bistvu enaka in se ji ne moremo izogniti.

1. varianta tehnološkega postopka se uporablja danes za zahtevnejše vrste orodnih, specialnih in visokolegiranih konstrukcijskih jekel. Specifična poraba energije za tehnološko fazo vroče predelave, približno 1500 kWh/tono, predstavlja . . . indeks 100.

2. varianta tehnološkega postopka predstavlja klasični standardni tehnološki postopek. Specifična poraba energije, približno 1350 kWh/tono, predstavlja . . . indeks 90.

3. varianta tehnološkega postopka predstavlja tehnologijo za standardni del proizvodnega programa dobro predelavnih jekel. Specifična poraba energije, približno 500 kWh/tono, predstavlja . . . indeks 33.

electro-slag remelting can also be produced as well as castings made by metall mould, shell mould or precision wax cluster proces. Casting limited to a 300 kg piece or several pieces of smaller weight is possible.

Horizontal continuous wire caster is particularly significant for development of new materials for welding electrodes. Frequently it is possible to produce the required quantity of special materials. Sometimes continuously cast wire can be directly used for welding electrodes from nonworkable materials.

Thus the development of pilot production can be estimated from the two view points. First as absolutely necessary for rational research and development of new materials and second as mini production unit for small lot production which can not be accepted by normal industrial works.

The horizontal continuous casting is potentially very interesting for high-speed tool steel, ledeburitic tool steels and special alloys. Technological parameters for continuous casting of these materials have not yet been developed. Special interest is devoted to grain refinement and shortening of technological procedures which is generally in the forefront of development of metal working. Numerous development activities can be expected in these fields because of their's importance and universal actuality.

6. POSSIBILITIES FOR ENERGY SAVINGS

Within the investment project of pilot production plant at Metallurgical Institute an analysis of specific energy consumption has been made involving the comparison of different ways of the technological development described (8).

Two characteristic procedures of conventional technology and three variants of the new technology were taken into account. The sketch on fig. 5 display specific characteristics of the five procedures.

Specific energy consumption for melting is naturally the same for all the five variants, therefore it is interesting to find out the differences in hot working stage.

1. variant has been used for high quality tool, special and high alloyed constructional steel. Specific energy consumption for hot working phase of technology amounts to 1500 kWh/ton and serves as a basis for comparison, i.e.

Index 100

2. variant is the standard technological procedure. Specific energy consumption is 1350 kWh/ton.

Index 90

3. variant represents the technology for standard part of production programme consisting of steel with good workability. Specific energy consumption is 500 kWh/ton i.e.

Index 33

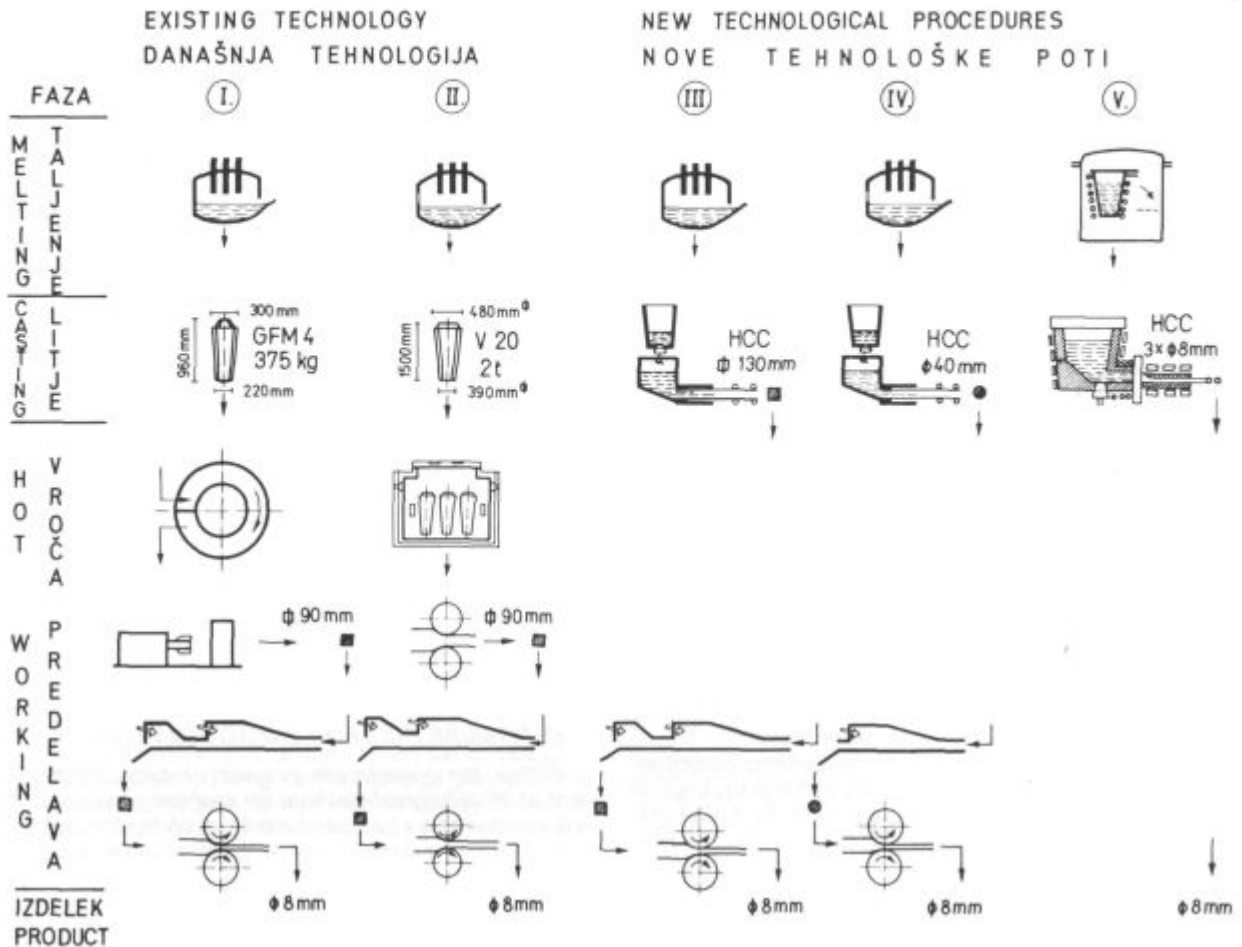
4. variant covers dimension range under 20 mm and is suited to the steels of poor workability belonging to constructional, special and tool steel group as well as to special alloys and super alloys wherein it is desired to obviate problematic hot working. Specific energy consumption is approx. 400 kWh/ton.

Index 27

5. variant represents horizontal continuous casting of 3—12 mm diameter wire. This technology completely discard hot working stage.

Index 0

It is specially interesting for the two fields of production programme:



Slika 5

Primerjava dveh klasičnih in treh novih tehnoloških postopkov za specifično porabo energije v procesu vroče predelave

Fig. 5

Comparison of specific energy consumption of hot working for two conventional and three new technological procedures.

4. **varijanta tehnološkega postopka** naj bi pokrivala dimenzijski asortiment pod 20 mm in je posebej primerena za težko predelavna konstrukcijska jekla, specialna in orodna jekla, specialne zlitine in superzlitine, pri katerih se želimo predvsem izogniti nepotrebni delu problematične vroče predelave. Specifična poraba energije, približno 400 kWh/tono, predstavlja . . . indeks 27.

5. **varijanta tehnološkega postopka** predstavlja postopek horizontalnega neprekinjenega litja žice s premerom 3—12 mm. Ta tehnologija, pri kateri vroča predelava sploh odpade (indeks 0) je interesantna predvsem za dve področji proizvodnega programa:

— za vse materiale, ki se uporabljajo v tem dimenzijskem območju in so praktično nepredelavni. Razumljivo je, da je ta tehnologija zanimiva predvsem za vse vrste dodatnih materialov za elektrode v postopkih varjenja, ker se s tem postopkom lahko popolnoma izognemo klasični predelavi, četudi bi bila izvedljiva. To prinaša pomembne ekonomske učinke v prihranku materiala, dela in porabe energije, kar končno omogoča maksimalno možno ekonomiko in izkoristek blizu 100 %;

— za vse materiale, ki so primerni za nadaljnjo predelavo z vlečenjem v hladnem ali vročem stanju. Za nekatere materiale, kot so na primer nerjavna in ognjeodporna jekla avstenitnega tipa, nekatere ventilska jekla in nekatere specialne zlitine, je postopek že v celoti osvojen in preizkušen, mnogo pa je takih jekel, za katere je

— for all practically non workable materials of the mentioned dimension range. Of course this technology is particularly interesting for welding electrodes. This brings forth considerable savings in material, work and energy making it possible to minimize the production costs and to reach almost 100 % yield.

— for all materials suitable for cold or hot drawing. For some materials of this group like austenitic stainless steels, heat resisting steels, some valve steels and special alloys the technology has been fully developed. However, the technology for numerous steel grades remain to be developed. The growing interest for this task is noted.

7. CONCLUSIONS

Technological process of continuous casting of steels and alloys in the shape of wire and rod brings forth significant quality and economic benefits as compared to conventional technology. Reduction in specific energy consumption is of great importance particularly in the field of heating and intermediate reheating in hot working.

The energy saving increases with reducing section size of the finished products.

In the field of expensive and hardly workable materials increase in yield is of particular importance. Con-

treba tehnologijb še raziskati in optimirati, interes za take rešitve pa je vse večji.

7. ZAKLJUČKI

Tehnološki postopek neprekinjenega litja jekel in zlitin v obliki palic in žice prinaša pomembne kakovostne in ekonomske prednosti v primerjavi s klasičnimi tehnološkimi postopki. Ekonomika specifične porabe energije ima velik pomen, posebno v območju ogrevanja in dogrevanja pri procesih vroče predelave. Ta ekonomika se izboljšuje z zmanjševanjem preseka gotovih izdelkov.

Pri asortimentu razmeroma dragih in težko predelavnih materialov je še posebno pomembna vloga izboljševanja izkoristkov materiala, ki že pri uvedbi klasičnega neprekinjenega litja gredic prinese 10—20 % v primerjavi s klasičnim postopkom litja v ingote, zaradi rezanja glav in nog ingotov. Velik je tudi vpliv, ki ga prinaša zmanjševanje investicijskih stroškov na področjih litja in predelave. V odvisnosti od vrste materialov ocenjujemo z novo tehnologijo možne prihranke materialov z boljšimi izkoristki 5—30 %, odvisno od sposobnosti materiala za plastično preoblikovanje v vročem. Tudi izgube s škakanjem so v primerih nove tehnologije znatno manjše.

S fizikalno-metalurškega gledišča ima jeklo, izdelano s postopkom neprekinjenega litja drobnih presekov, bistvene kakovostne prednosti, ki so povezane s hitrejšim strjevanjem.

ventional continuous casting results in 10—20 % increase in yield in comparison to ingot casting already. Highly important is a reduction in investment costs for casting and working also. Depending on hot workability of the material possible material savings through increased yield resulting from the new technology can be estimated as 5—30 %. Scale losses are also reduced as compared to the conventional technology.

From physico-metallurgical viewpoint the steel produced by horizontal continuous casting of small section size has essential quality advantages associated with increased rate of solidification.

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SLOVENSKE ŽELEZARNE
METALURŠKI INŠTITUT
LJUBLJANA, LEPI POT 6

KAJ JE METALURŠKI INŠTITUT

Metalurški inštitut je delovna organizacija v okviru SOZD Slovenske Železarne, po statutu pa je osrednja raziskovalna organizacija vse slovenske metalurgije in livarstva. Inštitut razvija vse aktivnosti, ki so potrebne za raziskovalno delo, torej raziskave osnovnega, razvojnega in uporabnega značaja, pilotno proizvodnjo posebnih materialov, je soizdajatelj strokovnega časopisa, prireja strokovna srečanja in seminarje, dela različne strokovne ad hoc usluge za industrijo s področja kakovosti in uporabe kovinskih materialov, goji stike z raziskovalnimi organizacijami pri nas in v inozemstvu, sodeluje v programih in projektih Raziskovalne skupnosti Slovenije, v projektih usmerjenih v tehnološki razvoj Jugoslavije ter v projektih mednarodnega sodelovanja z zapadno in vzhodno Evropo in ZDA.

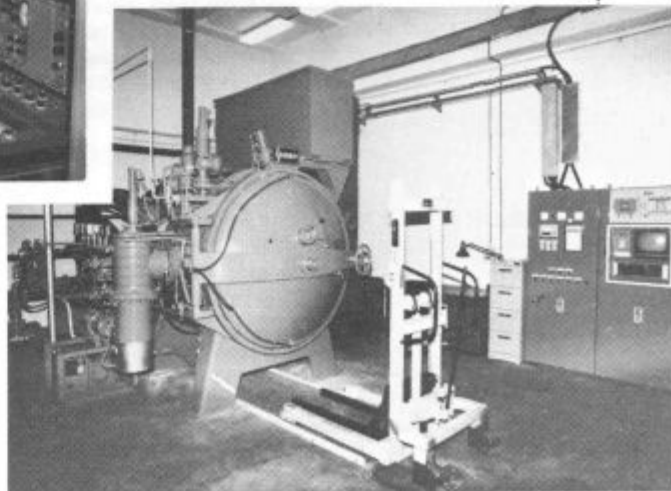
PROGRAM DELA IN OPREMA

Program raziskovalnega dela posega v naslednja področja: razvoj sodobnih masovnih kovinskih materialov in tehnologije njihove izdelave in predelave, razvoj in pilotna proizvodnja posebnih materialov za elektroniko, fizikalno-metalurško in kemijsko-analitsko karakterizacijo materialov, matematično modeliranje in računalniško krmiljenje procesov ter racionalna uporaba energije in surovin v metalurški industriji. Skladno s programom dela ima laboratorije za mikrostrukturne, fizikalne, mehanske preiskave in za analitiko kovinskih materialov ter za pilotno proizvodnjo. Med raziskovalnimi aparaturami najdemo peči za taljenje vseh vrst kovin na zraku in v vakuumu, naprave za predelavo teh kovin v trak, palice in žico, napravo za atomizacijo kovin, optične mikroskope in vrstični (scanning) elektronski mikroskop za mikrostrukturne raziskave, elektronski mikroanalizator, dilatometer, naprave za preizkušanje kovin s statično in dinamično obremenitvijo pri visokih temperaturah, naprave za termično obdelavo, med njimi najsodobnejšo vakuumsko visokotemperaturno kalilno žarilno peč ter različne sodobne analitske naprave, na primer aparature za atomsko absorpcijsko spektrometrijo in emisijski spektrometer.



Pogled na vrstični elektronski mikroskop z napravo za elektronsko mikroanalizo in analizo slike

V teku je dobava naprave za vlivanje amorfnih trakov, ki bo skupaj z napravo za atomizacijo in izostatsko stiskanje, ki jo je inštitut nabavil skupno z inštitutom J. Stefan omogočila laboratorijsko sintezo najsodobnejših kovinskih materialov. Prav v tem letu se bo začel tudi uresničevati projekt pilotne proizvodnje usmerjen v izdelavo palic in žic iz posebnih materialov po tehnologiji računalniško vakuumskega taljenja in kontinuirnega litja.



Pogled na računalniško krmiljeno vakuumsko žarilno peč kalilno peč

Kaj prinaša nova tehnologija streljanja dodatnih materialov v jeklarsko prakso

Advance Technology in Steelmaking — Injection of Additions

B. Koroušič*, A. Šteblaj**

UDK: 669.18:669.891:669.046.521
ASM/SLA: D9r, D11r, EGf41, EGr

Opisana je nova metoda dodajanja različnih materialov v tekoče jeklo s streljanjem polne ali polnjene žice. Tehnika streljanja direktno v talino ima vrsto prednosti v primerjavi s klasičnimi načini, celo v primerjavi s tehniko vpihovanja materialov v talino. Predstavljena je metoda streljanja — žice v cilju izvajanja kontrolirane desoksidacije taline v ponvi in zagotavljanja ciljane vsebnosti aluminija, kar je danes osnovni pogoj za uspešno izvajanje ponovne metalurgije.

Modern method of adding different materials by wire injection into molten steel is described. The method has numerous advantages over classic method of addition as well as over the pneumatic injection of powdered materials. The wire injection method for controlled deoxidation in ladle and attainment of prescribed final Al content of steel which is the main condition for successful secondary metallurgy operations is described.

UVOD

Sodobna metoda streljanja ali injektiranja polne ali polnjene žice oziroma profila je naša široko področje aplikacij: od tehnike dezoksidacije, legiranja, razžveplanja in nažveplanja do specialnih tehnik mikrolegiranja s B, Ti, Zr in dr.

Njene osnovne prednosti v primerjavi s klasičnimi metodami so:

- visoka prilagodljivost različnim industrijskim napravam z neodvisnim spreminjanjem premera žice in hitrosti dodajanja,

- zelo zanesljiv način dodatka in visok izkoristek elementov,

- širok spekter dodatnih elementov in spojin,

- enostavna in relativno poceni naprava za dodajanje,

- idealna enota za avtomatizacijo procesov.

Čprav smo na Metalurškem inštitutu v Ljubljani pričeli akcijo uvajanja te sodobne metode v naše jeklarne že leta 1980, večjega uspeha nismo imeli, predvsem zaradi togosti in ustaljenih navad, katere je zelo težko spremeniti.

Prvi prototip polindustrijske naprave, ki je bila izdelana v Železarni Ravne v letu 1983, je dal vzpodbudne rezultate na področju streljanja Al-žice v talino¹⁾. Zaradi težav z avtomatiko v industrijskih pogojih so ustavili nadaljevanje začetih poizkusov. Čprav je bilo še nekaj akcij, da se začeto raziskovalno delo nadaljuje, večjih uspehov ni bilo.

INTRODUCTION

The modern wire or cored wire additions method has been widely applied for deoxidation, alloying, desulphurization or sulphur alloying, special microalloying with B, Ti, Zr, etc. Main advantages of the method as compared to classic methods are:

- high adaptability to different industrial devices with independent changes of wire diameter and feeding rate,

- high reliability and recovery of addition,

- wide spectra of added materials and compounds,

- simple and comparatively cheap device,

- ideal unit for process control and automation.

Although the work on introduction of the method into our steelworks started on Metallurgical Institute in 1980 there was no significant success mainly because of the well-known inertia of conservative-minded steelmakers. First prototype made on semiindustrial scale in Steelworks Ravne in 1983 showed encouraging results in the field of Al-wire addition¹⁾. The tests were stopped due to difficulties met during development of an automated industrial device. There were some initiatives to continue with the work however, no significant success has been achieved.

Only at the end of 1986 first industrial tests on calcium wire additions started in Ironworks Jesenice. At last the wire addition method has aroused enough interest in our steelworks so the tests with commercial devices have finally started.

1. DEVELOPMENT OF INJECTION TECHNIQUES FOR ADDITIONS INTO MOLTEN STEEL

Modern steelmaking technology is based on combined use of a number of processes which makes it possible to reach optimum results and a high production

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Šele konec 1986. leta je prišlo v železarni Jesenice do prvih industrijskih poskusov streljanja Ca-žice v talino. Kot kaže, je metoda streljanja žice dokončno postala zanimiva tudi za naše jeklarne, ker trenutno potekajo poskusi v vseh slovenskih železarnah s komercialno izdelanimi napravami.

1. RAZVOJ TEHNOLOGIJE STRELJANJA DODAJNIH MATERIALOV V TEKOČE JEKLO

Sodobna jeklarska tehnologija sloni na kombinaciji več postopkov, kar omogoča optimalno delo in visoko fleksibilnost proizvodnje.

Klasični postopki izdelave jekla v enem talilniškem agregatu so v razvitih državah večinoma že zgodovina.

Novi kombinirani postopki, kot je tehnološka linija:

EOP + VAD + CC ali IC*

oziroma

EOP + AOD + CC ali IC

so narekovali tudi delno zamenjavo konvencionalnih načinov dodajanja materialov, kot so: **manjši dodatki legur, dodatki dezoksidantov, posebni dodatki FeB, FeP, FeS itd., ki se pri standardni praksi dodajajo v talino ali curek ob prebodu.**

Zaradi vse večjih zahtev po večji točnosti zadevanja kemične analize in ožjih toleranc v predpisnih mejah, zlasti kar se tiče posebnih elementov, kot so: Ca, Ti, B, S, Al, N itd., so postale klasične metode dodatkov nezanesljive in neekonomične. Prišlo je do razvoja novih metod dodatka omenjenih materialov v talino, katere lahko razvrstimo v dve veliki skupini:

- vpihovanje drobnozrnatih materialov v talino,
- streljanje polnjene žice ali profilov direktno v talino (SPŽ — metoda)**.

Obe skupini postopkov sta našli hitro uporabo v jeklarski tehnologiji in tudi vsaka od omenjenih metod ima svoje pozitivne in negativne lastnosti. Za SPŽ — metodo kaže, da ima nekaj več prednosti in zato pridobiva številne zagovornike predvsem zaradi enostavnejše in cenejše aparature tehnike in nekaterih drugih ugodnosti, o katerih bo govor v naslednjih poglavjih.

2. OSNOVNE ZNAČILNOSTI METODE DIREKTNEGA STRELJAJA ŽICE V TEKOČE JEKLO

Naprave za direktno streljanje žice v tekoče jeklo sestojijo v glavnem iz dveh delov:

- gonilni mehanizem z več valjčnicami in enosmernim ali izmeničnim regulacijskim motorjem ter elektronsko regulacijo,
- odvijalna naprava, ki ima več variant — boben ali prosto odvijanje žice.

Na **sliki 1** vidimo tipično izvedbo postavitve naprave v bližini livne jame, s katero se izvaja obdelava taline s SPŽ-napravo.

Sodobne naprave za streljanje žice imajo poleg standardne opreme, tj. elektronske nastavitve hitrosti poda-

flexibility. Classic steelmaking in single metallurgical furnace in developed countries mainly belong to the history. New combined process such as the technological lines

*EAF + VAD + CC or IC**

EAF + AOD + CC or IC

required also a partial change in the addition method in low alloying, deoxidation, special additions of FeB, FeP, FeS, etc. which were usually carried out at tapping.

Due to ever increasing demands for higher reliability of achieving prescribed specifications and continuously closing tolerances especially for Ca, Ti, B, S, Al and N the standard method of additions into the stream or ladle became unsuccessful and unreliable. Newly developed addition methods can be divided into the two groups:

- *pneumatic injection of powdered material into the melt*
- *direct feeding of wire or cored wire into the melt (SPŽ)**.*

Both the groups have soon find wide application in steelmaking. Each of the methods mentioned has its own advantages and shortcomings. SPŽ method seems to appear more convincing mainly because of a simple and cheap operation technique and certain other advantages yet to be mentioned.

2. MAIN CHARACTERISTICS OF WIRE INJECTION METHOD

Devices for direct wire injection into molten steel are mainly composed of the two parts:

- *driving mechanism with a number of rollers and DC or AC electromotor with electronic control and*
- *despooling device of drum type.*

A typical installation used for SPŽ injection is seen on fig. 1. Modern units for wire injection beside electronic control of feeding rate (0—400 m/min) make it possible to preset the required length of wire, to control the wire end and internal temperature of device.

Device operation is very simple and well adapted to the work conditions in smelting shop. The spool brake is flipped off (modern devices are equipped with remote controls) and unwind sufficient length of wire to reach driving mechanism. The roller adjustment in the beginning is set in dependence on wire diameter and the depth of melt in ladle. During the operation it automatically changes to fit eventual minor changes in wire or profile diameter.

All necessary preparation take only few minutes which is very helpful for convincing workers to accept the new technique as a routine method.

Recently advanced devices with two or three strand mechanism (ODERMATH STAHLWERSTECHNIK GmbH) which enable simultaneous injection of two different materials (e. g. Al wire and Ca-Si wire). Special devices can be made on buyers request to suit the user requirements, of course.

* EOP — električna obločna peč,
VAD — vakuumsko-obločno razogljčenje z možnostjo dogrevanja taline,

AOD — argonsko kisikovo razogljčenje,
CC — kontilitje jekla,
IC — litje jekla v ingote.

** S(P)Ž — streljanje (polnjene) žice ali profilov v talino (predlog)

* EAF — Electric Arc Furnace

VAD — Vacuum Arc Decarburisation (with additional heating)

AOD — Argon Oxygen Decarburisation

CC — Continuous Casting

IC — Ingot Casting

** SPŽ — Shooting of wire or cored wire into melt (proposition).

janja žice (0—400 m/min) tudi možnost nastavitve željene dolžine, kontrole konca žice po končani obdelavi, nadzor notranje temperature v napravi itd.

Posluževanje naprave je zelo enostavno in prilagojeno pogojem dela v topilnici:

Na odvijalnem bobnu sprostimo zavoro (novejše izvedbe npr. nudijo možnost delovanja zavore s komandnega pulta) in s koluta odvijemo zadostno količino žice, da premostimo razdaljo med odvijalnim bobnom in pogonskim delom naprave. Nastavitev valjev je pogojena s premerom žice in globino taline v ponovci, ki se potem avtomatsko prilagaja eventualnim manjšim spremembam profila žice.

Pripravo naprave za streljanje žice izvedemo v nekaj minutah, kar je zelo pomembno za **pripravljenost ljudi, da uporabljajo tovrstne naprave kot rutinske metode.**

V zadnjem času se razvijajo tudi naprave z dvo- in večžilnim krmilnim mehanizmom (ODERMATH STAHL-WERKSTECHNIK GmbH), ki omogočajo istočasno dodajanje dveh različnih materialov (npr. Al-žice in CaSi-žice). Možne so seveda tudi posebne izvedbe, ki se prilagajajo zahtevam kupcev.

3. SPLOŠNO O MATERIALIH ZA STRELJANJE V TEKOČE JEKLO

Prvotna ideja o streljanju dodatnih materialov v tekoče jeklo se je porodila iz naravnih omejitev, da imajo številni materiali, katere želimo dodati v talino, neprimerne fizikalne lastnosti za pogoje jeklarskih temperatur:

- gostota materiala je ponavadi znatno nižja od jekla,
- velika reaktivnost s kisikom in žveplom v talini in žilindri,
- visok parni tlak in zato dokaj slab izkoristek dodanega elementa,
- cena tovrstnih materialov je zelo visoka in vezana na uvoz,
- skladiščenje in manipuliranje ni enostavno in zahteva posebno skrb.

Kasneje je na razvoj vplivala tudi potreba po avtomatizaciji procesov in izboljšanju delovnih pogojev v jeklarnah. Vse skupaj pa je vplivalo na večjo zanesljivost zavedanja ciljanih načrtovanih želenih vrednosti, kot je končna vsebnost Al, uspešnost mikrolegiranja z B, S, Ti, V, uspešnost modifikacije nekovinskih vključkov in dr.

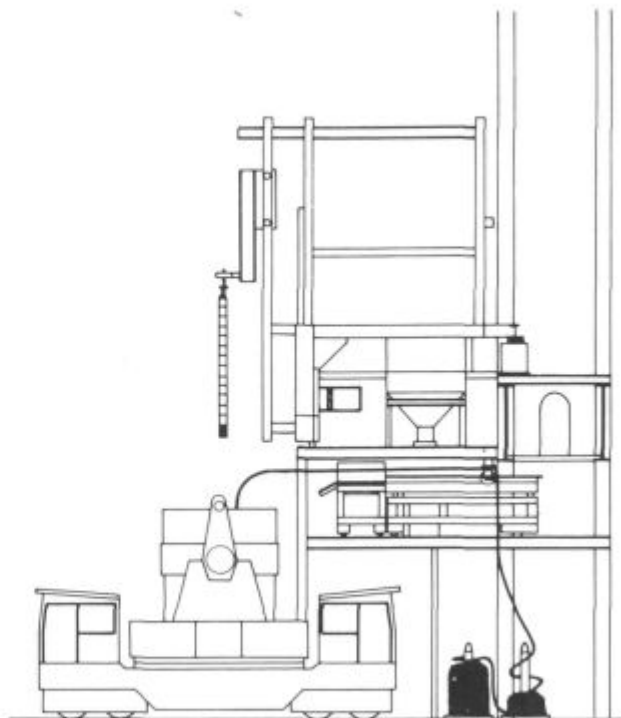
4. DODAJANJE Al-ŽICE V TEKOČE JEKLO (deoksidacija + legiranje)

Osnovni cilj uporabe metode streljanja ali injektiranja aluminijeve žice je transport Al na čim večjo globino v tekoče jeklo, in sicer preden se začne njegova reakcija s kisikom v talini. S tem smo dosegli ključni pogoj, da tekoči Al reagira s kisikom v talini, pri čemer ferostatični tlak in mešanje taline s argonom skrbita, da reakcija poteka v celoti do meje topnosti.

Za doseg teh idealnih pogojev moramo zagotoviti nekaj pogojev:

- hitrost podajanja žice mora biti prilagojena debelini žice in globini taline v jeklarski ponovci,
- ob dodatku Al v talino moramo zagotoviti zadostno mešanje taline s plinskimi mediji, ker na ta način povečujemo homogenost taline in omogočimo lažjo porazdelitev dodanega aluminija.

Raziskave hitrega dodajanja Al-žice v tekoče jeklo so pokazale, da se Al-žica, npr. $\varnothing 12$ mm, prvih 50—100 ns prevleče z jeklenim plaščem, nato se v naslednjem ča-



Slika 1

Postavitev naprave za streljanje žice v bližini livne jame

Fig. 1

Typical installment of wire injection unit in the vicinity of casting pit

3. MATERIALS FOR INJECTION INTO MOLTEN STEEL

The new injection methods have been developed due to the fact that physical properties of numerous materials used for addition are not suitable for the classic addition method:

- density is usually considerably lower than that of steel,
- high affinity to oxygen and sulphur in steel and slag
- high partial vapor pressure which means low yield of added element,
- materials are imported and prices are usually quit high and
- storing and manipulation is not simple and require special care.

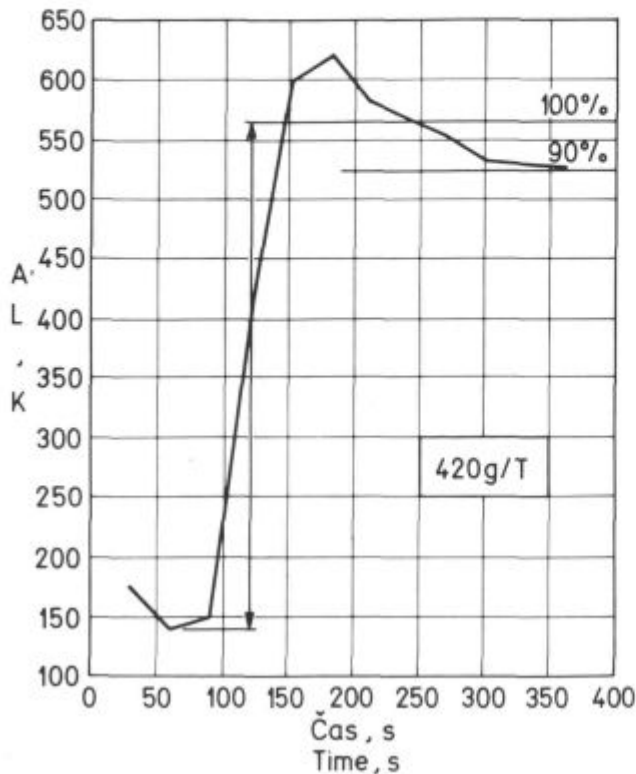
Later on the trend for process automation and improvement of working conditions have also contributed to the overall drive for change.

The general results obtained are mainly a higher reliability of achieving prescribed specifications such as final Al content, successful microalloying with B, S, Ti, V and modification of non-metallic inclusions, etc.

4. INJECTION OF Al WIRE (Deoxidation + alloying)

The main aim of Al wire injection is to transport Al to the higher possible depth of melt as quickly as possible to prevent it from reacting with oxygen in melt. This is of decisive influence to obtain the reaction of molten Al with oxygen dissolved in steel which supported by ferostatic pressure and argon mixing proceeds completely i. e. to the solubility limit. This ideal result can be obtained by satisfying the following conditions:

STRELJANJE AL - ŽICE INJECTION OF AL - WIRE



Slika 2

Izvajanje dezoksidacije v 190-tonski ponovci s streljanjem Al-žice v količini okoli 420 g/t

Fig. 2

Deoxidation of a 190 ton heat by 420 g/t Al-wire injection

sovnem obdobju 100–800 ns Al topi, pri čemer je debelina jeklenega plašča še vedno debela okrog 2 mm. Šele nato se začne taljenje jeklenega plašča in burna reakcija Al z kisikom³⁾.

Na sliki 2 vidimo profil naraščanja Al v talini pri streljanju 420 g Al/t v 190-tonsko ponovco.

Ob uporabi kisikove sonde za točno ugotovitev vsebnosti kisika v talini pred pričetkom streljanja Al lahko dosežemo točnost zadevanja Al:

$$0.05 \pm 0.009 \% \text{ Al}_k,$$

kar je odvisno tudi od vsebnosti oksidov, zlasti (FeO + MnO) v žilindri, in vsebnosti kisika v talini pred streljanjem aluminija. Tipična porazdelitev Al pri izdelavi večjega števila šarž s metodo streljanja Al-žice kaže slika 3.

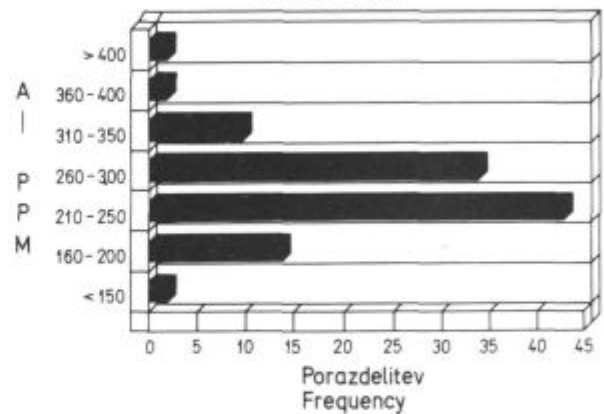
5. ZAKLJUČKI

V članku smo predstavili sodobno metodo, tako imenovano »streljanje« ali »injektiranje« polne ali polnjene žice v tekoče jeklo (SPŽ — metoda). Opisana metoda se uporablja v sodobnih jekelnah več kot 10 let in je danes nenadomestljiva tehnika za izvajanje kontrolirane dezoksidacije in modifikacije oksidnih nekovinskih vključkov v ponovci pred litjem ali celo v medponovci pri kontolitju jekla. V zadnjih letih se uspešno uporablja tudi za mikrolegiranje jekel, kot so dodatki Ti, B, V, C, N in dr.

Naprave za avtomatsko dodajanje polne ali polnjene žice so danes komercialne izvedbe in ločimo dva tipa:

STRELJANJE AL - ŽICE INJECTION OF AL - WIRE

Porazdelitev Al
Distribution Al



Slika 3

Porazdelitev aluminijev talini pri uporabi streljanja žice v talino

Fig. 3

Al distribution obtained by Al wire injection method

— appropriate feeding rate must be used depending on wire diameter and the depth of melt,

— sufficient argon flow for efficient mixing must be applied during wire injection in order to ensure the homogeneity and easier distribution of added aluminium.

Investigation of aluminium wire injection at high feeding rate revealed that Al wire of 12 mm diameter is covered with solidified steel during first 50–100 ns. Aluminium melts during the next 100–800 ns period, however the thickness of solidified steel layer is about 2 mm³⁾

Only afterwards steel layer starts to melt and vigorous reaction of Al and oxygen dissolved in steel takes place.

Increase in Al content of 190 ton steel melt during 420 g/t Al wire injection can be seen in fig. 2.

By the use of an oxygen probe for the measurement of active oxygen in steel immediately before the injection it is possible to attain the accuracy of final Al content:

$$0.05 \pm 0.009 \% \text{ Al}_k,$$

which depends also on the content of oxides especially (FeO + MnO) in slag and the oxygen content of steel before the injection. Typical Al distribution obtained by Al wire injection in a high number of heats can be seen in fig. 3.

5. CONCLUSIONS

Modern (SPŽ-method) method of Al-wire or cored wire injection into molten steel is described. The method has been used in steelworks for more than 10 years. To day it is the standard method for controlled deoxidation and modification of non-metallic inclusions in carried out in ladle before casting or even in tundish before continuous casting. Recently it has been successfully used for microalloying of steel with Ti, B, V, C, N etc also.

Commercial injection devices for addition of common or cored wire can be divided into the two groups: a) Devices with driven drum which serves as a spool for wire and b) devices with free unwinding of wire from the spool interior.

a) naprave s pogonom odvijalnega bobna, na katerem je navita žica in b) naprave s prostim odvijanjem žice iz notranjosti koluta.

Dosedanje praktične izkušnje z metodo SPŽ so pokazale, da pri kombinaciji s kisikovo sondo, ki določi vsebnost aktivnega kisika, pred dodatkom žice dosežemo učinkovito in reproduktivno dezoksidacijo taline.

Točnost zaževanja Al je izredno visoka in znaša standardna napaka na nivoju $Al = 0.05 \pm 0.009\%$. SPŽ — metoda je pokazala izredne rezultate tudi pri modifikaciji nekovinskih vključkov s streljanjem žice, polnjene s Ca-zlitinami, zlasti če predhodno uspešno izvedena dezoksidacija taline in vsebnost žvepla v talini ne presega 100 PPM.

Operational experience obtained with the injection method has shown that combined with the use of oxygen probe which determines the active oxygen content of steel before the Al wire injection the efficient and reproducible deoxidation of steel can be achieved.

The accuracy of attaining prescribed final Al content is very high. The standard error at the level of $Al = 0.05 \pm 0.009\%$. SPŽ method has shown extraordinary results in modification of nonmetallic inclusions also by the injection of Ca alloy cored-wire especially in cases where previous deoxidation and desulfuration depressed the sulfur content under 100 ppm level.

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**Lastno znanje, dobro
delo in več kot stoletna
tradicija zagotavljajo
kakovost naših
izdelkov.**



**SLOVENSKE
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Obdelava jekla s streljanjem oplaščene žice v štorski in ravnski železarni

Treatment of Steel in Štore and Ravne Steelworks by Injection of Cored Wire

V. Prešern*, D. Kmetič*, A. Rozman**, P. Bračun***

UDK: 669.18:669.891
ASM/SLA: D9r, ADr, EGI41, EGr

Postopek streljanja oplaščene žice, polnjene s CaSi, borom, titanom, žveplom, ogljikom itd. predstavlja nov način izredno natančnega dolegiranja in obdelave jekla s kalcijem v ponovci. Novo tehnologijo smo v začetku 1988 pričeli uvajati v štorsko in ravnsko železarno, danes pa že predstavlja standardno prakso obdelave jekla v ponvi. Prikazali smo rezultate uvajanja tega postopka v pogledu vsebnosti žvepla, kisika in kalcija, sestave žilindre, čistosti jekla, modifikacije in livnosti.

Injection of cored wire with CaSi, boron, titanium, sulphur, carbon, . . . is a new method of a very accurate additional alloying and of treatment of steel in ladle with calcium. The new technology was introduced in Štore and Ravne Steelworks in the beginning of 1988, and today it is the standard practice of steel treatment in ladle. The results of the introduction period from the point of view of sulphur, oxygen, and calcium contents, of slag composition, of steel purity, of modification, and of castability are presented.

1. UVOD

V slovenskih železarnah imamo že večletne izkušnje pri obdelavi jekla v ponvi z vpihovanjem CaSi. Z uvedbo tega postopka v redno proizvodnjo smo dobili čistejše jeklo z modificiranimi vključki, kar omogoča odlivanje jekla tudi z več kot 0,025 % aluminija na kontinuirni livni napravi za gredice manjših presekov. Pomemben učinek vpihovanja CaSi je tudi odlično razžveplanje, kajti brez posebnih težav dosegamo vsebnosti žvepla, manjše od 0,010 %.

Najvažnejši razlogi in glavne prednosti uvedbe postopka vpihovanja CaSi so bili^{1, 2, 3}:

— Obdelava jekla s CaSi omogoča kompletno modifikacijo aluminatnih vključkov v aluminijem pomirjenih jeklih. S tem je odstranjena nevarnost mašenja izlivičkov med litjem na kontinuirnih livnih napravah za gredice z majhnimi preseki.

— Kot posledico odličnega razžveplanja, dodatne dezoksidacije, modifikacije vključkov in močnega premešavanja jekla v ponvi, dobimo čistejše jeklo z dobro površino gredic.

— Nekatere mehanske lastnosti, kot n. pr. žilavost v prečni in vzdolžni smeri, trdnost in elongacija, se lahko povečajo do 30 %.

Ker pa ima postopek vpihovanja CaSi poleg naštetih prednosti tudi nekatere pomanjkljivosti, so v svetu v zadnjih nekaj letih razvili in zelo hitro uvedli v redno proizvodnjo obdelavo jekla s streljanjem CaSi v obliki polnjene žice.

1. INTRODUCTION

Slovene Ironworks have a many-year experience with steel treatment in ladle by injection of CaSi. Introduction of this method into regular manufacturing enabled to obtain purer steel with modified inclusions, thus steel with even more than 0.025 % aluminium could be continuously cast into billets of smaller cross sections. Essential effect of CaSi injection is also excellent desulphurisation since sulphur contents below 0.010 % are achieved without special difficulties.

The most important reasons and the basic advantages for the introduction of CaSi injection were^{1, 2, 3}:

— Treatment of steel with CaSi enables practically complete modification of aluminate inclusions in aluminium-killed steel. Thus the danger of stoppage of nozzles in the continuous casting equipment for billets of smaller cross sections was removed.

— Purer steel with good surface of billets is obtained due to excellent desulphurisation, additional deoxidation, modification of inclusions, and good stirring of melt in the ladle.

— Some mechanical properties, e. g. toughness in lateral and transversal direction, strength, and elongation can be increased up to 30 %.

Since the CaSi injection method has also some disadvantages beside the mentioned advantages, the treatment of steel by the injection of CaSi in form of cored wire was developed in recent years in the world, and it was very rapidly introduced in standard steelmaking.

The main reasons for introduction of this method in our steelworks were:

— Treatment by the injection of cored wire is a simple method, and it demands no additional technical knowledge.

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Glavni razlogi za uvedbo tega postopka v naše jeklarne so bili:

— obdelava s streljanjem žice je enostaven postopek in ne zahteva skoraj nobenega dodatnega tehničnega znanja;

— velike količine argona (več kot 1000 l/min), ki jih potrebujemo pri vpihovanju CaSi pogosto povzročijo, da se žindra odpre, kar povzroča reoksidacijo taline in povečanje vsebnosti dušika;

— postopek vpihovanja CaSi je občasno povzročil, da ni bilo mogoče pravilno zadeti vsebnosti aluminija, imeli smo težave s kontrolo temperature, prihajalo pa je tudi do prekinitev procesa vpihovanja zaradi mašenja kopja za vpihovanje;

— postopek obdelave jekla s streljanjem oplaščenih žic je mnogo bolj fleksibilen in omogoča tudi zelo natančno dolegiranje oz. dodajanje elementov, kot titana, bora, ogljika, žvepla.

2. OPIS POSKUSOV

Tako v Štorah kot na Ravnah so nabavili dvožilno napravo za streljanje oplaščene žice.

Polnjena žica je v obliki samonavijalnih kolutov. Preizkusili smo s CaSi polnjeno žico, premera 13 mm in 9 mm. Vsebnost kalcija v CaSi je vedno 30 %.

Žico s premerom 9 mm smo streljali v ponev s hitrostjo ca 150 m/min, 13 mm žico pa s hitrostjo ca 75 m/min.

V ravnski jeklarni smo postopek streljanja uvedli pri VAD tehnologiji, ki zagotavlja vsaj 20-minutno premešavanje z argonom po zadnjem dodatku aluminija.

V štorski jeklarni pa smo istočasno s procesom streljanja žice uvedli tudi premešavanje z argonom skozi kamen na dnu ponve, kar nam bo omogočilo zadostno premešavanje.

V naši standardni tehnološki praksi bi morali za uspešen potek postopka obdelave jekla s streljanjem oplaščene žice v ponvi zagotoviti naslednje pogoje⁴:

- dolomitno bazično oblogo,
- uspešno dezoksidacijo z aluminijem,
- dobro dezoksidirano, bazično, dobro tekočo žindro z majhno vsebnostjo FeO + MnO (tipične analize žlinder pred streljanjem in po njem so prikazane v tabeli 1).

— zadostno količino žlindre v ponvi (v svetu uporabljajo med 6 in 12 kg žlindre na tono jekla).

Vsekakor pa je potrebno zagotoviti pravilno sestavo in količino žlindre v ponvi tudi zaradi naslednjih razlogov^{5,6}:

— Great amount of argon (over 1000 l/min) needed in injection of CaSi powder often causes the slag "opening", and thus the melt is reoxidized and nitrogen content is increased.

— Injection of CaSi powder sometimes caused that the correct aluminium content could not be achieved, there were difficulties in temperature control, and the injection was periodically interrupted due to stoppage of the injection lance.

— Steel treatment by injection of cored wire is much more flexible process which also enables a very accurate additional alloying or adding titanium, boron, carbon, sulphur.

2. DESCRIPTION OF EXPERIMENTS

In Štore and in Ravne steelworks twin-wire feeder was purchased.

The cored wire is in form of self-winding coils, and CaSi cored wire, 9 and 13 mm in diameter, was tested. Calcium content in CaSi was always 30 %.

9 mm thick wire was injected into ladle with around 150 m/min, and 13 mm wire with around 75 m/min.

In Ravne steelworks the injection process was introduced in the VAD technology which enables at least a 20 minute stirring with argon after final addition of aluminium.

In Štore steelworks the cored wire injection was introduced together with the argon stirring through a porous plate on bottom of ladle which will enable sufficient stirring.

In our standard technological practice the following conditions must be achieved for a successful treatment of steel with the injection of cored wire into ladle¹:

- dolomitic basic lining,
- successful deoxidation by aluminium,
- well deoxidized, basic, easily flowable slag with low FeO-MnO contents (typical slag analyses before and after the injection are given in Table 1),
- sufficient amount of slag in ladle (6 to 12 kg slag per ton steel are applied in the world).

Anyhow, the correct composition and the amount of slag in ladle must be achieved also due to the following reasons^{5,6}:

- to create the possibility of binding the products of deoxidation and desulphurisation reactions,
- to avoid the reoxidation of steel with atmosphere air,
- to avoid uncontrolled reactions between slag and steel.

Tabela 1: Tipična sestava žlinder pred in po streljanju oplaščene žice s CaSi

		CaO %	MgO %	SiO ₂ %	Al ₂ O ₃ %	FeO %	MnO %	CaF ₂ %
Jeklarna Štore	pred	46	16	16	12	2	1	7
	po	50	16	15	12,5	1	0,5	5
Jeklarna Ravne	pred	52,5	10	15	12	1,5	1	8
	po	53	10	14,5	13	1	0,5	8

Table 1: Typical composition of slags before and after the injection of CaSi cored wire

		CaO %	MgO %	SiO ₂ %	Al ₂ O ₃ %	FeO %	MnO %	CaF ₂ %
Štore Steelworks	Before	46	16	16	12	2	1	7
	After	50	16	15	12,5	1	0,5	5
Ravne Steelworks	Before	52,5	10	15	12	1,5	1	8
	After	53	10	14,5	13	1	0,5	8

- da ustvarimo možnost vezave produktov reakcij dezoksidacije in razžveplanja,
- da preprečimo reoksidacijo jekla iz atmosfere,
- da preprečimo nekontrolirane reakcije med žlindro in jeklom.

3. METALURŠKI REZULTATI

3.1. Kalcij

Osnovna naloga kalcija pri obdelavi jekel, pomirjenih z aluminijem, je modifikacija čistih trdnih aluminatnih vključkov v tekoče kompleksne vključke, vrste $\text{CaO-Al}_2\text{O}_3$.

Vsebnost kalcija v jeklu mora biti tolikšna, da je razmerje kalcij:aluminij večje kot $0,14^{7,8}$, ko pride do modifikacije v željeno obliko kompleksnih vključkov s tališčem pod temperaturami litja jekel.

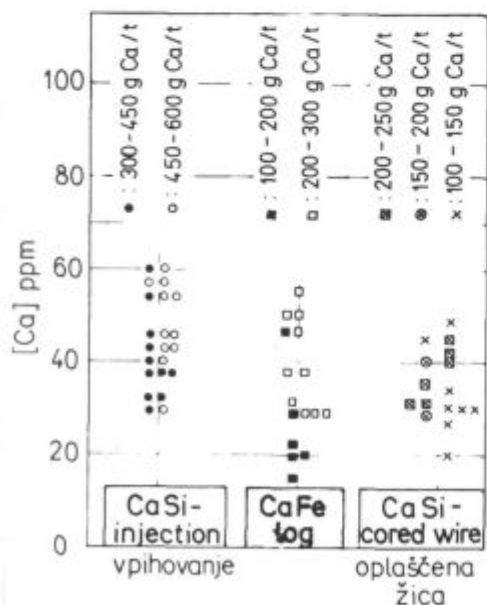
Da pa v glavnem dobimo takšno razmerje, je potreben poznati izkoristek kalcija pri streljanju oplasčene žice. Ugotovili smo, da je bil izkoristek pri opazovanih talinah med 15 in 25 % in je večji in v ožjih mejah trosenja, kot je pri obdelavi jekla z vpihovanjem drobnostnega CaSi . Primerjava izkoristkov kalcija pri treh različnih metodah, ki smo jih uporabljali v slovenskih železarnah, je razvidna s **slike 1**; razmerje med kalcijem in aluminijem pri opazovanih talinah pa prikazuje **slika 2**.

Izkoristki kalcija se zelo dobro ujemajo tudi s podatki iz drugih jeklarn po svetu^{7,9,10,11}.

Količina kalcija je v osnovi odvisna od količine dodane žice in dokazali smo, da lahko v naših pogojih pričakujemo optimalne rezultate pri naslednjih količinah dodane žice polnjene s CaSi :

- ogljik < 0,25 % : 0,7 do 0,9 kg CaSi/t
- 0,25 % < ogljik < 0,40 % : 0,7 kg CaSi/t
- ogljik < 0,40 % : 0,4 do 0,6 kg CaSi/t

Razdelitev vsebnosti aluminija in kalcija za nekatere poskusne taline prikazuje **sliki 3 in 4**.



Slika 1

Primerjava izkoristkov kalcija pri vpihovanju CaSi , uporabi CaFe -logov in streljanju oplasčene žice s CaSi

Fig. 1

Comparison of calcium yields in injection of powdered CaSi , in applying CaFe logs, and in injection of CaSi cored wire

3. METALLURGICAL RESULTS

3. 1. Calcium

Basic task of calcium in the treatment of aluminium-killed steel is the modification of pure solid aluminate inclusions into liquid complex inclusions of $\text{CaO-Al}_2\text{O}_3$ type.

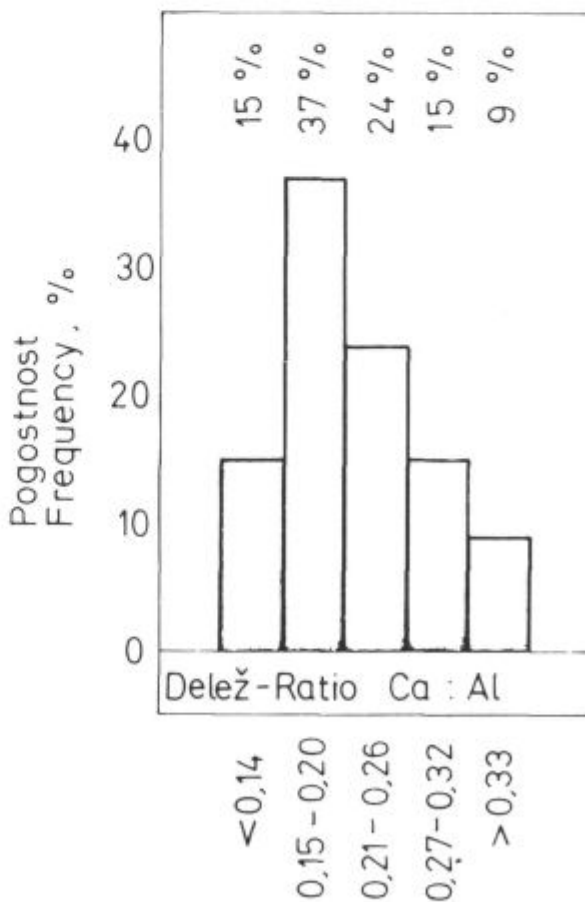
Calcium content in steel must be such that Ca/Si ratio is greater than $0,14^{7,8}$ when modification into desired form of complex inclusions with melting points below the casting temperature of steel is achieved.

In order to achieve such a ratio, it is necessary to know the yield of calcium in the injection of cored wire. It was found that the yield in tested melts varied between 15 and 25 %, and it is higher and in narrower limits than in the treatment of steel by the injection of fine grained CaSi . Comparison of calcium yields by three different methods being applied in Slovene Ironworks is shown in **Fig. 1**, and Ca/Si ratio in the investigated melts in **Fig. 2**.

Calcium yields are in a very good agreement with the data of some other steel plants in the world^{7,9,10,11}

The amount of calcium itself depends on the amount of added wire, and it was proved that the optimal results can be expected for our conditions at the following amounts of added CaSi cored wire:

- carbon < 0,25 % : 0,7 to 0,9 kg CaSi/t
- 0,25 % < carbon < 0,40 % : 0,7 kg CaSi/t
- carbon > 0,40 % : 0,4 to 0,6 kg CaSi/t .

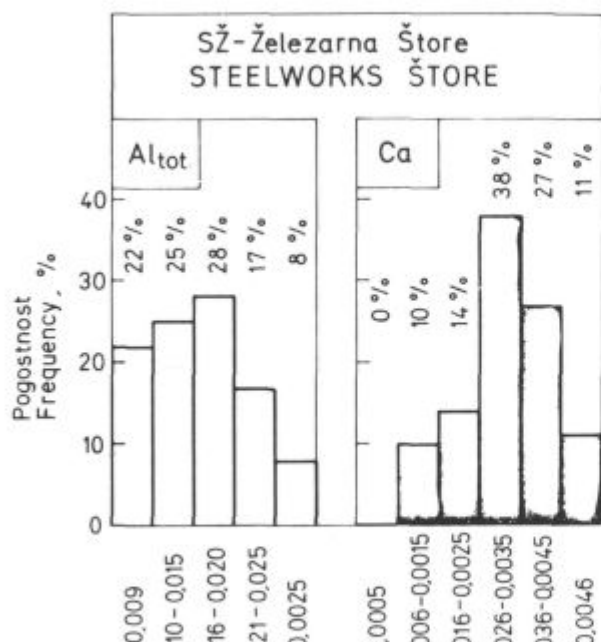


Slika 2

Razmerje med kalcijem in aluminijem v poskusnih talinah

Fig. 2

Calcium/aluminium ratio in tested melts



Slika 3:

Vsebnosti aluminija in kalcija v poskusnih talinah v štorski jeklarni

Fig. 3

Aluminium and calcium contents in tested melts in Štore steelworks

3.2 Kisik

Ker je končna vsebnost kisika v jeklu eden od najvažnejših kazalcev kvalitete jekla, smo analizirali spreminjanje vsebnosti kisika od streljanja žice s CaSi do končne vsebnosti v izvaljanem jeklu.

Že kar v uvodu lahko postavimo važno ugotovitev, da so rezultati poskusov jasno pokazali, da je bolj kot sam vpliv kalcija in aluminija za vsebnost kisika v jeklu odločilno premešavanje z argonom in sestava žilindre v ponvi. Taline, ki naj bi po termodinamičnih zakonitostih imele več kisika, pa so bile dovolj preprihane z argonom pod ustrezno žilindro, so imele bistveno manjše končne vsebnosti kisika od nepreprihane talin.

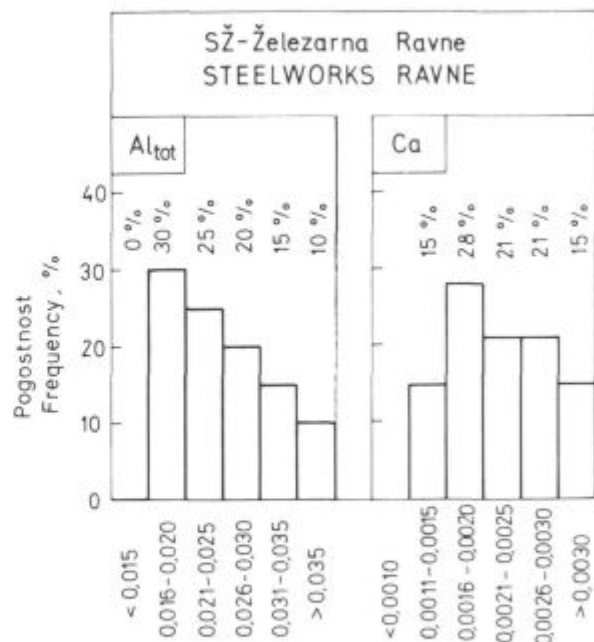
Razdelitev skupnega končnega kisika v poskusnih talinah prikazuje v tabeli 2.

Tabela 2: Razdelitev skupnega končnega kisika v poskusnih talinah obdelanih s streljanjem oplaščene žice s CaSi

Otot, %		< 0,0030	0,0031—0,0050	0,0051—0,0070	> 0,0071
Ravne (20 talin)	Delež	30	65	5	0
Štore (50 talin)	Delež	10	46	40	4

Table 2: Distribution of total final oxygen in tested melts treated by the injection of CaSi cored wire

Otot, %		< 0,0030	0,0031—0,0050	0,0051—0,0070	> 0,0071
Ravne (20 melts)	Portion	30	65	5	0
Štore (50 melts)	Portion	10	46	40	4



Slika 4

Vsebnosti aluminija in kalcija v poskusnih talinah v ravnski jeklarni

Fig. 4

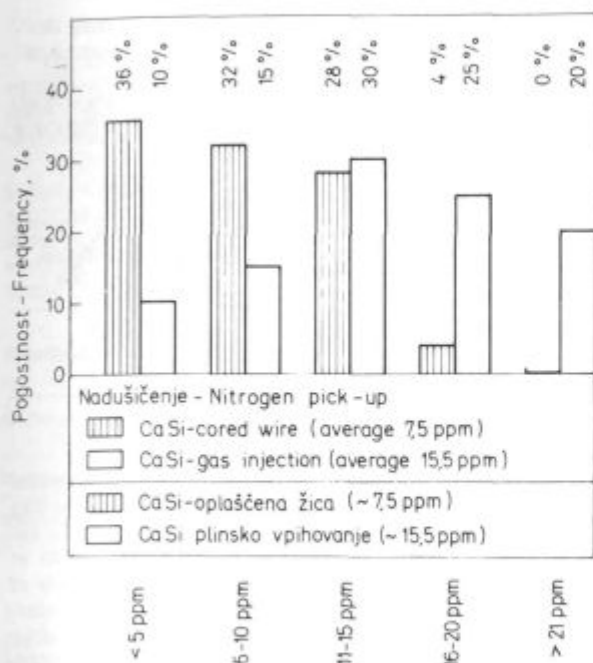
Aluminium and calcium contents in tested melts in Ravne steelworks

Distribution of aluminium and calcium in some tested melts is shown in Figs. 3 and 4.

3.2. Oxygen

Since the final oxygen content in steel is one of the most important parameters of the steel quality, the variation of oxygen content from the injection of CaSi cored wire to its final content in rolled steel was followed and analyzed.

The results clearly showed that the oxygen content in steel is more influenced by argon stirring and slag composition in ladle than by calcium and aluminium, which is an important finding. The melts which should contain more oxygen according to thermodynamic rules but they were well stirred with argon under a suitable slag contained essentially less oxygen than those which were not stirred.



Slika 5

Primerjava nadušičenja zaradi vpihovanja CaSi in streljanja oplasčene žice s CaSi

Fig. 5

Comparison of nitrogen pick-up in injection of powdery CaSi and CaSi cored wire

Ustvarjanje pogojev za dovolj majhne končne vsebnosti kisika je nujna naloga, saj trdijo^{12, 13}, da lahko zadostno čistost jekla pričakujemo le, ko je skupna vsebnost kisika manjša od 0.0050 ali celo 0.0040 %.

3.3 Dušik

Povprečne vsebnosti dušika v jeklu iz naših elektroobločnih peči so 70 do 100 ppm. Pri obdelavi jekla v ponvi pa pride do povečanja vsebnosti dušika v jeklu. Z meritvami v različnih fazah tehnološkega postopka smo potrdili, da se vsebnosti dušika povečajo.

Izdelali smo primerjavo povečanja vsebnosti dušika med talinami, obdelanimi s streljanjem žice, polnjene s CaSi, in z vpihovanjem CaSi, kar prikazuje slika 5.

Pri vpihovanju CaSi pogosto prihaja do povečanja vsebnosti dušika za 20 in več ppm, povprečno povečanje večjega števila talin pa je bilo 15,5 ppm. Rezultati obdelave s streljanjem žice pa kažejo, da je povečanje vsebnosti dušika za polovico manjše.

Razlog je, da prihaja pri streljanju žice le poredko do odpiranja površine žilindre oz. jekla v ponvi, ker uporabljamo bistveno manjše količine argona kot pri vpihovanju in je reakcija mnogo mirnejša.

3.4 Žveplo

Znano je, da postopka streljanja žice s CaSi ne uporabljamo za razžvepljanje. Pri poskusnih talinah z optimalnimi količinami uporabljene žice so bile stopnje razžvepljanja med streljanjem dejansko majhne (do 15 %).

Že v uvodu smo omenili, da lahko pride pri obdelavi jekla z večjo vsebnostjo žvepla (nad 0.020 %) do tvorbe čistih vključkov, vrste CaS, ki imajo visoko tališče in lahko povzročajo mašenje izlivkov, podobno kot čisti aluminatni vključki. Eden od pogojev za uspešno obdelavo s

Distribution of total final oxygen in tested melts is shown in Table 2.

Creating the conditions to achieve sufficiently low final oxygen contents is an urgent task, since it is claimed^{12, 13} that a sufficient purity of steel can be expected when total oxygen content is below 0.0050 or even 0.0040 %.

3.3. Nitrogen

Average nitrogen contents in steel from our electric arc furnaces vary between 70 and 100 ppm. During steel treatment in ladle nitrogen content in steel is increased. Measurements of nitrogen content in various stages of technological process confirmed this.

A comparison of the increase of nitrogen content between the melts which were treated by the injection of CaSi core wire and by the injection of powdered CaSi was made, and it is presented in Fig. 5.

When powdery CaSi is injected the nitrogen contents often increase for 20 or more ppm. The mean value for a greater number of tested melts was 15.5 ppm. The results of treatment by the injection of cored wire show that the nitrogen content is increased for half of previous values.

The reason is that injection of wire only seldom causes "the opening" of slag layer in ladle since smaller amounts of argon are applied than in the injection of powder, and the reaction is much more smooth.

3.4. Sulphur

It is known that the injection of CaSi cored wire is not applied as a desulphurisation method. In tested melts with the optimal amounts of applied wire, the desulphurisation during injection was virtually low (up to 15 %).

It was mentioned already in the introduction that pure CaS inclusions with high melting point can be formed in treatment of steel with higher sulphur content (over 0.020 %), and they can cause stoppage of nozzles like pure aluminate inclusions. One of the conditions for successful treatment by the injection of cored wire is sufficient preceding desulphurisation.

Also steel with sulphur contents over 0.020 % was treated by the injection of CaSi cored wire, but accurate metallographic investigations did not reveal pure CaS inclusions. Thus we are of opinion that the obtained results confirm (also in agreement with some references^{7, 18}) that the permitted interval of sulphur content at a suitable amount of aluminium and calcium is wider than theoretically supposed^{9, 20}.

3.5. Yield of Elements in Cored Wire

The yield of calcium which was added in form of CaSi cored wire, and the yield in the injection of fine grained CaSi was already discussed. Thus some data on yields of boron and titanium which were added in form of cored wire in Štore and in Ravne Steelwork will be explained here.

FeTi and FeB cored wires were tested. FeTi wire had 13 mm diameter and it contained 72 % titanium and 4.5 % aluminium, while FeB wire had 9 mm diameter and it contained 12 % boron.

Both wires were tested in combination with the injection of CaSi cored wire and just here the extraordinary flexibility and suitability of the injection equipment with two drives and guides was proved. As mentioned, the

streljanjem žice zato je, da zagotovimo zadostno predhodno razžveplanje.

S streljanjem oplasčene žice s CaSi smo obdelali tudi jekla z vsebnostmi žvepla nad 0,020 %, vendar kljub natančnim metalografskim preiskavam čistih CaS vključkov nismo zasledili. Zato menimo, da dobljeni rezultati potrjujejo (tudi v soglasju z delom literature^{7, 16}), da je dovoljeno območje vsebnosti žvepla pri primerni količini aluminija in kalcija širše, kot ga navajajo teoretične predpostavke^{9, 20}.

3.5 Izkoristki elementov v oplasčeni žici

O izkoristku kalcija, dodanega v obliki CaSi v žici, in o primerjavi z izkoristkom pri vpihovanju drobnozrnatega CaSi smo že govorili, na tem mestu pa bomo podali nekatere podatke o izkoristkih bora in titana, ki smo ju v obliki polnjene žice preizkusili tako v štorski kot ravenski železarni.

Preizkusili smo s FeTi in FeB polnjene žice (FeTi z 72 % titana in 4,5 % aluminija ter premerom 13 mm, FeB z 12 % bora in premerom žice 9 mm).

Obe vrsti žice smo preizkušali v kombinaciji s streljanjem žice s CaSi in prav tu se je pokazala izredna fleksibilnost in pripravnost naprave za streljanje z dvema pogonom in vodiloma. Kot že rečeno, je namen titana predvsem v vezavi dušika, bor v obliki karbida pa pomaga doseči željeno območje zanesljive prekaljivosti.

Izračunani izkoristki tako titana kot bora so odlični in v zelo ozkih mejah trosenja in jih prikazujemo v tabeli 3.

Tabela 3: Izplen elementov pri dodajanju v oplasčeni žici

Element	Analično območje določevanja, (%)	Poprečen izplen, (%)	δ	Dezoksidacijska praksa
titan	0.010 — 0.050	90	5	Si + Al
bor	0.0015 — 0.0030	85	5	Si + Al + Ti
kalcij	0.0010 — 0.0060	15—25		Si + Al

3.6 Livnost

Že dolgo vemo, da je livnost večine jekel, pomirjenih z aluminijem (posebno pri postopku kontinuirnega ulivanja gredic manjših dimenzij), največkrat močno zmanjšana zaradi trdnih aluminatnih vključkov, ki se nabirajo na izlivkih¹⁴. Do hitrega mašenja manjših izlivkov pride že pri vsebnostih aluminija nad 0,010 %. Velika notranja medfazna energija aluminatnih vključkov v jeklu je tista pogonska sila, da se aluminatni delci lepijo na stene iz ognjevarnega materiala in med seboj.

Takšne težave pri odlivanju jekel smo uspešno rešili z uvedbo postopka vpihovanja drobnozrnatega CaSi z argonom. Vendar pa je od časa do časa še prihajalo do težav pri odlivanju, predvsem zaradi večkrat nezanesljivega zadevanja vsebnosti aluminija in pa, kot že omenjeno, zaradi prekinitev postopka vpihovanja zaradi zamašitve kopja za vpihovanje.

Z uvedbo postopka streljanja oplasčene žice s CaSi smo gotovo naredili tehnološki korak naprej. Ne samo, da pri vseh dosedanjih poskusih nismo imeli tehničnih problemov in smo dejansko vedno lahko v jeklo dodali željeno količino CaSi, mnogo lažji in enostavnejši ter veliko bolj kontroliran je celotni postopek. Poleg tega pa imamo še novo možnost izredno natančnega dodajanja poljubnih količin ostalih materialov.

aim of titanium addition is binding of nitrogen, while boron in form of carbide enables to achieve the desired region of hardenability band.

Calculated yields of titanium and of boron are excellent and in very narrow limits of dissipation, and they are shown in Table 3.

Table 3: Yield of elements added with cored wire

Element	Analytical region of determination (%)	Mean yield (%)	δ	Deoxidation practice
Titanium	0.010 — 0.050	90	5	Si + Al
Boron	0.0015 — 0.0030	85	5	Si + Al + Ti
Calcium	0.0010 — 0.0060	15—25		Si + Al

3.6. Castability

It is known for a long time that the castability of most aluminium killed steel (especially for continuous casting of billets with small cross section) is often highly reduced due to solid aluminate inclusions which pile in nozzles¹⁴. Smaller nozzles are rapidly stopped already at aluminium contents over 0.010 %. High internal interphase energy of aluminate inclusions in steel is the driving force for sticking of aluminate particles on the refractory walls and to each other.

Such problems in steel casting were successfully solved by the introduction of the injection of fine grained CaSi with argon. But difficulties in casting appear from time to time mainly due to uncertainty in achieving the aluminium content or, as also mentioned before, due to interruption of the process when the injection lance is stopped.

Introduction of the injection of CaSi cored wire means certainly a technological step forward. Not only that in all tests so far no technical problems appeared and that always the desired amount of CaSi could be added into steel, the overall method is much easier and more simple and much more easily controllable. Besides, there is still a new possibility for a very accurate adding of optional amount of other materials.

4. METALLOGRAPHIC INVESTIGATIONS

The basic finding of metallographic investigations of steel melts being treated by the injection of cored wire was that a suitable amount of wire assures the modification of aluminate inclusions and thus sufficiently pure steel.

Typical composition of an oxide inclusion can be represented by $x\text{CaO}-y\text{Al}_2\text{O}_3-\text{CaS}$ and examples of such inclusions in some melts are given in Figs. 6 and 7. The inclusion contained 25 % calcium and 35 % aluminium. Steel purity determined by the K4 method is presented in Fig. 4. It is evident that suitable shape of inclusions^{5, 16, 17} enabled to obtain purer steel.

Table 4: Steel purity determined by the K4 method

Way of treatment	Portion of melts, %		
	K 4 < 5	K 4 < 15	K 4 < 30
Untreated	0	50	85
Treated by injection of CaSi cored wire	25	70	100

At a certain aluminium content in steel, there exists theoretically a critical sulphur content above which for-

4. METALOGRAFSKE PREISKAVE

Osnovna ugotovitev metalografskih raziskav jekel, obdelanih s streljanjem oplaščene žice, je, da smo s primerno količino žice zagotovili modifikacijo aluminatnih vključkov in dovolj čisto jeklo.

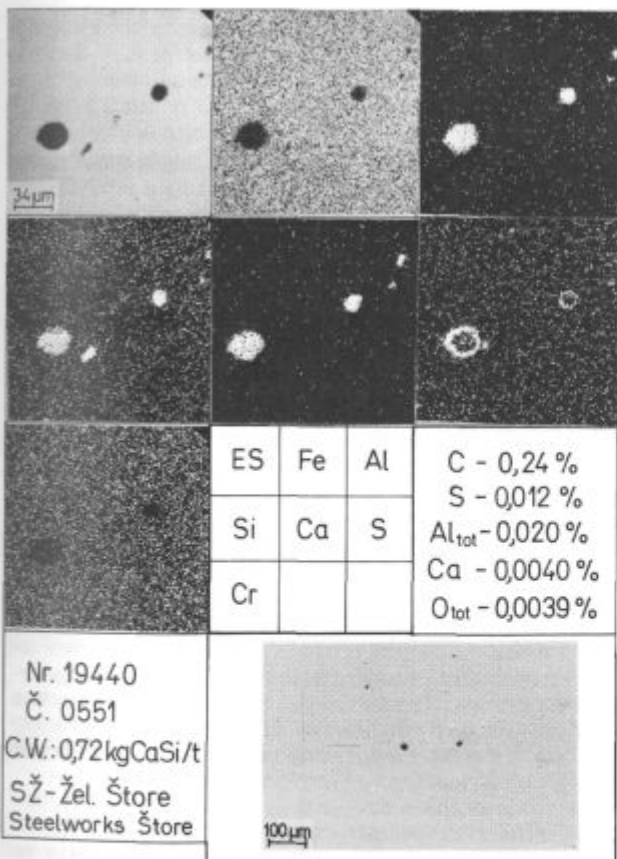
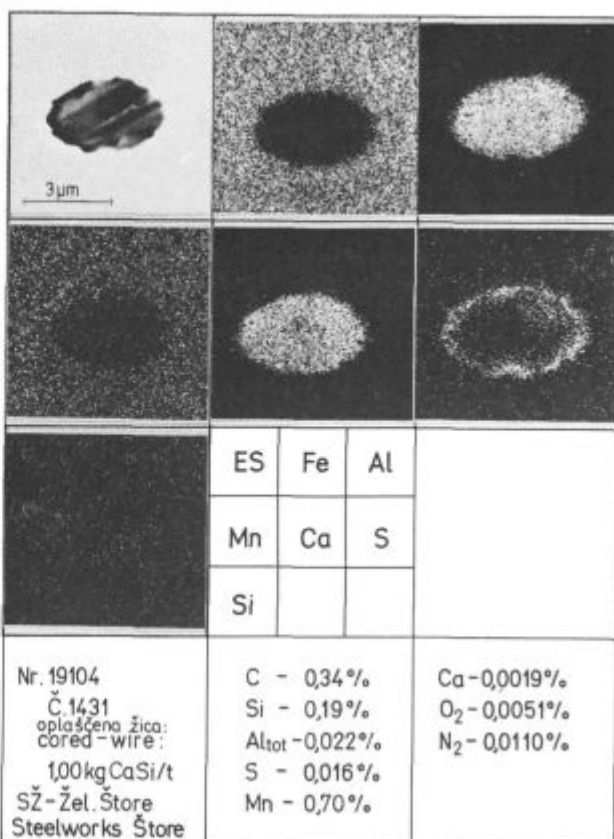
Tipična sestava oksidnega vključka je $x\text{CaO} \cdot y\text{Al}_2\text{O}_3 \cdot \text{CaS}$ in primeri takih vključkov v nekaterih talinah so prikazani na slikah 6, 7 a in 7 b, kjer smo v vključku določili 25 % kalcija in 35 % aluminija. Čistost jekla po metodi K4 prikazujemo v tabeli 4. Ravidno je, da smo dobili čistejše jeklo s primerno obliko vključkov^{15, 16, 17}.

Tabela 4: Čistost jekla po metodi K 4

Način obdelave	Delež talin, %		
	K 4 < 5	K 4 < 15	K 4 < 30
Neobdelane	0	50	85
Streljanje žice s CaSi	25	70	100

Pri določenih vsebnosti aluminija v jeklu obstaja teoretično neka kritična vsebnost žvepla, nad katero lahko pričakujemo tvorbo CaS. Istočasno pa je v jeklu potrebna določena količina kalcija za zagotovitev popolne modifikacije čistih trdnih aluminatnih vključkov.

Kot pa že rečeno, so naše raziskave potrdile, da gre za širše dovoljeno območje vsebnosti aluminija, žvepla in kalcija. Čistih vključkov vrste CaS nismo zasledili, do-

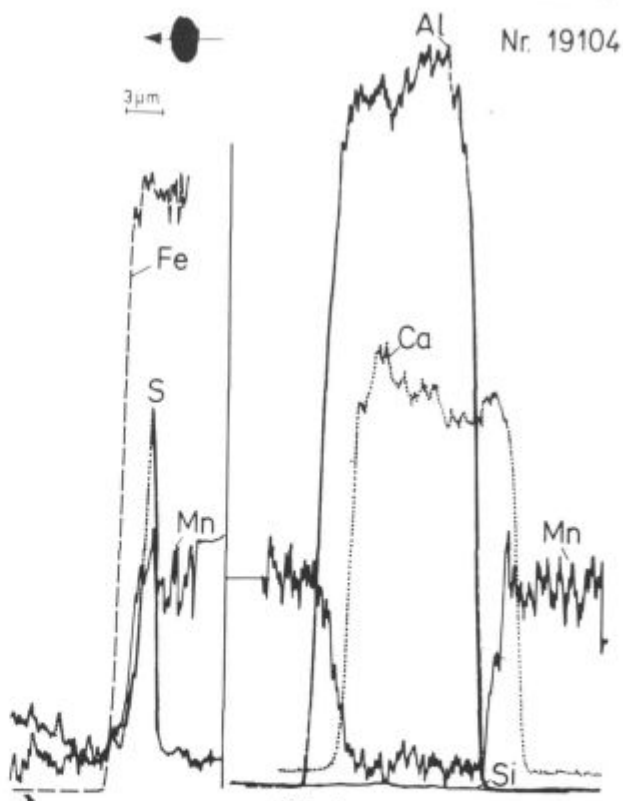


Slika 6

Tipičen izgled in sestava modificiranega vključka

Fig. 6

Typical appearance and composition of modified inclusion

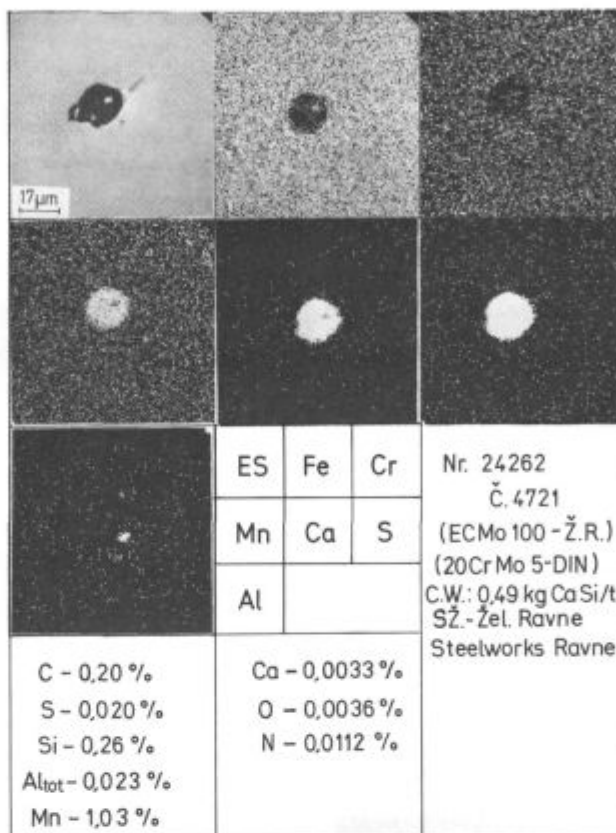


Slika 7

a) Izgled modificiranega vključka
b) Kvantitativna analiza tega vključka

Fig. 7

a) Appearance of modified inclusion
b) Quantitative analysis of this inclusion



Slika 8

Izgled in sestava modificiranega vključka vrste CaO-CaS-MnS

Fig. 8

Appearance and composition of CaO-CaS-MnS modified inclusion

kazali pa smo prisotnost kompleksnih vključkov vrste CaS-MnS (slika 8), ki pa verjetno ne povzročajo težav pri litju.

5. OCENA STROŠKOV

Za ocenitev tehnologije streljanja oplasčene žice je potrebna tudi groba ocenitev stroškov takega postopka in primerjava postopka streljanja oplasčene žice s postopki vpihovanja drobnostnega CaSi.

Moderna naprava za vpihovanje stane danes približno 10-krat toliko kot naprava za streljanje žice z dvema žilama.

Seštevek in pregled nekaterih najpomembnejših operativnih stroškov in primerjavo teh stroškov med obema postopkoma dodajanja CaSi podajamo v tabeli 5.

Podatke v razpredelnici smo dobili na osnovi naslednjih ocen stroškov:

- CaSi prah za vpihovanje : ca 3 DM/tono
- CaSi v oplasčeni žici : ca 9 DM/tono
- Električna energija : 0,08 DM/kWh
- Argon : 4 DM/m³

Računali smo, da je povprečna poraba CaSi pri oplasčeni žici 0,7 kg/tono, pri vpihovanju CaSi pa 2,0 kg/tono.

Ocenjeni stroški pri uporabi CaSi v obliki polnjene žice so 10,4 DM/tono in 15,0 DM/tono pri vpihovanju CaSi. Ugotovimo lahko, da je minimalno zmanjšanje stroškov pri prehodu na obdelavo jekla s streljanjem oplasčene žice 4,6 DM/tono jekla, kar se dobro ujema tudi s podatki iz tujih jeklarn^{7,21}.

Simultaneously steel must contain a certain amount of calcium in order to achieve complete modification of pure solid aluminate inclusions.

As already mentioned, our investigations confirmed that permitted intervals of aluminium, sulphur, and calcium contents are wider. Pure CaS inclusions were not found, but presence of complex CaS-MnS inclusions (Fig. 8) was confirmed, though they probably do not cause difficulties in casting.

5. ESTIMATION OF COSTS

In order to evaluate completely the technology of injection of cored wire, also a rough estimate of costs of such a method and a comparison of costs between the injection of cored wire and the injection of fine grained CaSi are needed.

Modern injection equipment for gas injection costs ten times more than a twin-wire feeder equipment for cored wire.

The sum and review of some most important operational costs and comparison of these costs for the two methods are given in Table 5.

Data in the table were obtained from the estimates of the following costs:

- CaSi powder for injection : around 3 DEM/t
- CaSi in cored wire : around 9 DEM/t
- electric power : 0.08 DEM/kWh
- argon : 4 DEM/m³

We have assumed that mean CaSi consumption for cored wire is 0.7 kg/t steel while in injection of powdery CaSi it is 2.0 kg/t.

Tabela 5: Primerjava stroškov med vpihovanjem CaSi in streljanjem oplaščene žice s CaSi
(Oceñeni stroški v aprilu 1988 v DM na tono jekla pri letni obdelavi 50.000 ton jekla s CaSi)

Vrsta stroška	Vpihovanje CaSi	Oplaščena žica
Investicija v opremo	2	0.2
Vzdrževanje	1.5	0.5
Ognjevdružna obzidava	3	3
Kopje (monolitno)	2	0
Argon	0.1 (500 l/min)	0
Energija za toplotne izgube	0.4 (+ 10 K)	(prihranek 5 kWh/t)
Delo	0.4	0.4
CaSi potreben za obdelavo (kg/t)	(2.0)	(0.7)
Cena CaSi	5.6	6.3
Skupno	15.0	10.4
Obdelava z oplaščeno žico		10.4 DM/t
Obdelava z vpihovanjem		15.0 DM/t

Estimated costs in applying CaSi in form of cored wire are 10.4 DEM/t, while in injection of powdery CaSi they are 15.0 DEM/t. It can be stated that minimal reduction of costs is 4.6 DEM/t steel if injection of cored wire is applied, which is in a good agreement with the data of foreign steel plants^{7, 21}.

Table 5: Comparison of costs between the injection of powdered CaSi and the injection of CaSi cored wire
(Estimated costs in April 1988 in DEM/ton steel for annual treatment of 50,000 t steel with CaSi)

Cost	Powdered CaSi	Cored wire
Investment into equipment	2	0.2
Maintenance	1.5	0.5
Refractory lining	3	3
Lance (monolithic)	2	0
Argon	0.1(500 l/min)	0
Energy for heat losses	0.4 (+ 10 K)	(Savings 5 kWh/t)
Labour	0.4	0.4
CaSi for treatment (kg/t)	(2.0)	(0.7)
Cost of powder	5.6	6.3
Total	15.0	10.4
Treatment with cored wire		10.4 DM/t
Treatment by powdered CaSi		15.0 DM/t

6. ZAKLJUČKI

Po nekajmesečnem delovanju novega postopka streljanja oplaščene žice s CaSi (pa tudi borom, titanom) v štorski in ravnski jeklarni lahko ugotovimo, da s tem postopkom uspešno nadomestimo postopek vpihovanja drobnozrnatega CaSi pri izdelavi in odlivanju z aluminijem pomirjenih jekel.

S primerno tehnologijo lahko izdelamo in na kontinuirni napravi za gredice manjših dimenzij odlijemo dovolj čisto jeklo z majhno vsebnostjo kisika in primerno sestavo ter obliko nekovinskih vključkov.

Najvažnejše in najbolj pomembne prednosti postopka streljanja oplaščene žice s CaSi in prednosti tega postopka v primerjavi z vpihovanjem CaSi so:

- zaradi mnogo mirnejše reakcije je manjše povečanje vsebnosti dušika, vodika in tudi kisika, mnogo manjša je emisija plinov med reakcijo,
- izkoristek kalcija je pri streljanju žice bistveno boljši in v primerjavi z vpihovanjem je poraba CaSi skoraj 3-krat manjša;
- v primerjavi s klasično tehnologijo je neprimerno boljši in v ožjih mejah trosenja tudi izkoristek ostalih elementov, ki jih dodajamo v polnjeni žici;
- manjše so toplotne izgube: običajno pade temperatura jekla med obdelavo s streljanjem žice le ca 10 K, kar je bistveno manj od skoraj 30 K pri postopku vpihovanja;
- dana je možnost skoraj idealnega dolegiranja oziroma natančnega zadevanja vsebnosti nekaterih elementov, kot n. pr. aluminija, bora, titana, ogljika, žvepla, ...;
- z upoštevanjem optimalne tehnologije dosežemo kompletno modifikacijo aluminatnih vključkov v okrogle, kompleksne vključke z nizkimi temperaturami tališč, ki ne povzročajo težav pri odlivanju z aluminijem pomirjenih jekel;
- investicijski in operativni stroški so pri postopku streljanja oplaščene žice manjši v primerjavi s postopkom vpihovanja.

6. CONCLUSIONS

A few-months operation of the injection of CaSi (and also boron, and titanium) cored wire in Štore and Ravne Steelworks confirmed that his method can successfully substitute the injection of fine grained CaSi in manufacturing and casting aluminium killed steel.

Applying a suitable technology enables to make and continuously cast into billets of smaller cross section a sufficiently pure steel with low oxygen content, and suitable composition and shape of non-metallic inclusions.

The most important advantages of the injection of CaSi cored wire, also in comparison with the injection of powdered CaSi are:

- *due to much smoother reaction the increase of nitrogen, hydrogen, and also oxygen contents is smaller, and much smaller is also the emission of gases during the reaction,*
- *calcium yield is in injection of cored wire essentially better, and compared with the injection of powdered CaSi the CaSi consumption is nearly 3 times lower,*
- *compared with the standard technology this method is essentially better since yield of other elements added with cored wire is in narrower limits of dispersion,*
- *heat losses are lower: usually temperature drop of steel melt in treatment by the injection of cored wire is only about 10 K, which is essentially less than 30 K in the injection of powdered CaSi,*
- *the possibility of nearly ideal additional alloying or achieving accurate contents of some elements as aluminium, boron, titanium, carbon, sulphur, etc. is given,*
- *applying the optimal technology gives the complete modification of aluminate inclusions into spheroidal, complex inclusions with low melting points which do not cause difficulties in casting aluminium killed steel,*
- *investment and operational costs for the injection of cored wire are lower than those for the injection of powdered CaSi.*

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Platiranje orodnih jekel na konstrukcijska jekla

Plating Tool Steel on Structural Steel

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V Železarni Ravne uspešno platirajo z vročim valjanjem orodna jekla na nosilno konstrukcijsko jeklo. Za nekatere pare jekel je postopek platiranja osvojen in poteka z ustreznim izkoristkom.

O poteku ogrevanja in valjanja je bilo na voljo pre malo podatkov, da bi se lahko projektirala tehnologija izdelave različnih parov orodno jeklo — nosilno konstrukcijsko jeklo. Raziskave naj bi omogočile boljše poznavanje fizikalno-metalurških procesov vročega preoblikovanja compound jekel.

In Ravne Ironworks the process of plating tool steel on bearing structural steel by hot rolling is successfully applied. For some steel pairs the plating process is mastered and it is carried out with a suitable yield.

There was not sufficient data on heating and rolling conditions to prepare the technology of manufacturing various tool steel/bearing structural steel pairs. The investigation should enable a better knowledge of physico-metallurgical processes during the hot working of compound steel.

UVOD

Vedno več industrijskih nožev in drugih orodij se izdeluje po postopku vročega platiranja. Tako izdelana orodja imajo pri ustreznih mehanskih lastnostih precejšnje ekonomske prednosti zaradi prihranka dragih legiranih jekel, saj je iz orodnega jekla izdelan le koristen del orodja. Prednost je tudi v lažji mehanski obdelavi in v veliko lažjem doseganju dimenzijskih toleranc.

Program preiskav je bil obširen in je potekal v več fazah:

- priprava parov orodno jeklo-konstrukcijsko jeklo iz različnih jekel, ki pridejo v poštev za program platiranih orodij, pri čemer smo veliko pozornost posvetili pravi stični površini in varjenju paketov;
- ogrevanje vzorcev;
- valjanje vzorcev pri različnih termomehanskih pogojih (temperatura, parcialna in skupna redukcija);
- metalografske preiskave vzorcev s ciljem, da opredelimo mikrostrukturne značilnosti na stiku orodno jeklo-konstrukcijsko jeklo po žarjenju, po valjanju in po toplotni obdelavi. Opredelili smo porazdelitev legiranih elementov v prehodni coni med obema jekloma;

Osikro spec.:	0,8 % C, 0,4 % Si, 0,4 % Mn, 1 % Cr, 2 % W, 0,3 % V
BRM 2:	0,9 % C, 4 % Cr, 6,5 % W, 5 % Mo, 1,9 % V
OSV 1:	1,5 % C, 4,5 % Cr, 6,5 % W, 3,5 % Mo, 5 % V, 5 % Co
OCR 12 spec.:	2,1 % C, 0,3 % Si, 0,3 % Mn, 12 % Cr, 0,7 % W
OCR 12 extra:	1,65 % C, 0,3 % Si, 0,3 % Mn, 12 % Cr, 0,5 % W, 0,6 % Mo, 0,1 % V
OCR 12 VM:	1,55 % C, 0,3 % Si, 0,3 % Mn, 12 % Cr, 0,9 % Mo, 1 % V
Utop Mo 4:	0,5 % C, 1 % Si, 0,3 % Mn, 5 % Cr, 1,5 % Mo, 1 % V

INTRODUCTION

Various cutting and other tools in industry are manufactured by hot plating. So made tool saves expensive tool steel which is used only for the working part of the tool which does not lose its original mechanical properties. Further advantage is easier machining and easier achieving dimensional tolerances.

Program of investigations was extensive and they were made in several steps:

- preparation of tool steel/structural steel pairs, applying steels suitable for plating tools. Great attention was given to the preparation of contact surfaces, and to welding the packs,
- heating of samples,
- rolling of samples at various thermomechanical conditions (temperature, partial and overall reduction),
- microstructural investigations of samples in order to determine microstructural characteristics on the contact tool steel — structural steel after annealing, after rolling, and after heat treatment. The distribution of alloying elements in the transition zone between the two steel was determined,

Osikro spec.:	0,8 % C, 0,4 % Si, 0,4 % Mn, 1 % Cr, 2 % W, 0,3 % V
BRM 2:	0,9 % C, 4 % Cr, 6,5 % W, 5 % Mo, 1,9 % V
OSV 1:	1,5 % C, 4,5 % Cr, 6,5 % W, 3,5 % Mo, 5 % V, 5 % Co
OCR 12 spec.:	2,1 % C, 0,3 % Si, 0,3 % Mn, 12 % Cr, 0,7 % W
OCR 12 extra:	1,65 % C, 0,3 % Si, 0,3 % Mn, 12 % Cr, 0,5 % W, 0,6 % Mo, 0,1 % V
OCR 12 VM:	1,55 % C, 0,3 % Si, 0,3 % Mn, 12 % Cr, 0,9 % Mo, 1 % V
Utop Mo 4:	0,5 % C, 1 % Si, 0,3 % Mn, 5 % Cr, 1,5 % Mo, 1 % V
OH 49:	0,6 % C, 3,3 % Cr, 1,1 % Mo, 0,15 % V
145 V 33:	1,45 % C, 0,3 % Si, 0,4 % Mn, 3,2 % V
Ck 15:	0,12—0,18 % C, 0,15—0,35 % Si, 0,30—0,60 % Mn
EC 80:	0,14—0,19 % C, 0,15—0,40 % Si, 1—1,3 % Mn, 0,8—1,1 % Cr
EC 100:	0,17—0,22 % C, 0,15—0,40 % Si, 1,1—1,4 % Mn, 1—1,3 % Cr

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OH 49:	0,6 % C, 3,3 % Cr, 1,1 % Mo, 0,15 % V
145 V 33:	1,45 % C, 0,3 % Si, 0,4 % Mn, 3,2 % V
Ck 15:	0,12—0,18 % C, 0,15—0,35 % Si, 0,30—0,60 % Mn
EC 80:	0,14—0,19 % C, 0,15—0,40 % Si, 1—1,3 % Mn, 0,8—1,1 % Cr
EC 100:	0,17—0,22 % C, 0,15—0,40 % Si, 1,1—1,4 % Mn, 1—1,3 % Cr

— mehanske preiskave z opredelitvijo trdnosti vezi med orodnim in konstrukcijskim jeklom.

Navedene preiskave smo naredili na parih iz orodnih jekel, kvalitete Osikro spec. (Č.6445), BRM 2 (Č.7680), OSV 1 (Č.9880), OCR 12 spec. (Č.4650), OCR 12 extra (Č.4750), OCR 12 VM (Č.4850), Utop Mo 4 (Č.4757), OH 49 (Č.7440), 145 V 33 (Č.8140), in konstrukcijskih jekel Ck 15 (Č.1221), EC 80 (Č.4320) in EC 100 (Č.4321). Preiskave smo naredili tudi na nekaterih parih iz konstrukcijskih jekel in na vzrocih, platiranih iz štirih vrst različnih jekel. Približna kemična sestava navedenih jekel je naslednja:

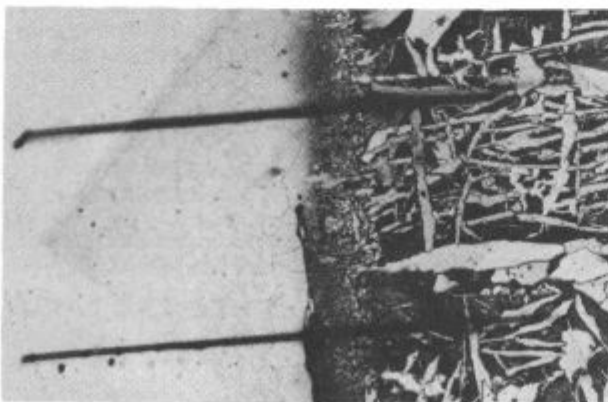
EKSPERIMENTALNO DELO

Žarjeni vzorci

Vzorci paketov, zvarjenih iz orodnega in konstrukcijskega jekla, na katerih smo naredili preiskave po žarjenju, smo ogrevali skupno z vzorci, ki smo jih valjali. Vzorce smo po predgrevanju žarili 1, 3 in 6 ur v temperaturnem intervalu od 900 do 1300 °C.

V mikrostrukturi stičnih površin orodnega in konstrukcijskega jekla se vidi, da so med ogrevanjem potekali difuzijski procesi. Koncentracijske profile legirnih elementov Cr, V, Mo, W, Si in Mn v prehodni coni smo naredili v elektronskem mikroanalizatorju. Analizo C smo naredili le na nekaterih vzorcih s kvantometrom, tako da smo na stični površini jekel postopno odbrusili tanke plasti. Meritve sicer niso tako točne kot meritve v elektronskem mikroanalizatorju, se pa dobro ujemajo s koncentracijskimi profili ostalih legirnih elementov in z mikrostrukturnimi značilnostmi prehodne plasti.

Stične površine jekel so bile različno obdelane, skoblane, brušene in polirane. V nobenem primeru pa obdelava površin in zavaritev paketa ni bila tako popolna, da bi stični površini popolnoma nalegali, pač pa se stikata le na določenih mestih. Preko teh stičnih mest pričnejo potekati difuzijski procesi (sl. 1). Potek difuzije je odvisen



Slika 1

Mikrostruktura prehodne plasti na vzorcu BRM 2/Ck 15 žarjenjem 6 ur na 1200 °C (pov. 200 ×)

Fig. 1

Microstructure of the transition zone in sample BRM 2/Ck 15, annealed 6 hours at 1200 °C (magn. 200 ×)

— mechanical investigations in order to determine the strength of bond between tool and structural steel.

The mentioned investigations were made with the following tool steels: Osikro spec. (Č.6445), BRM 2 (Č.7680), OSV 1 (Č.9880), OCR 12 spec. (Č.4650), OCR 12 extra (Č.4750), OCR 12 VM (Č.4850), Utop Mo 4 (Č.4757), OH 49 (Č.7440), 145 V 33 (Č.8140), and the following structural steel: Ck 15 (Č.1221), EC 80 (Č.4320), and EC 100 (Č.4321). Investigations were made also with some pairs of structural steels, and with plated samples made of four various steels. Approximate chemical composition of mentioned steels is the following:

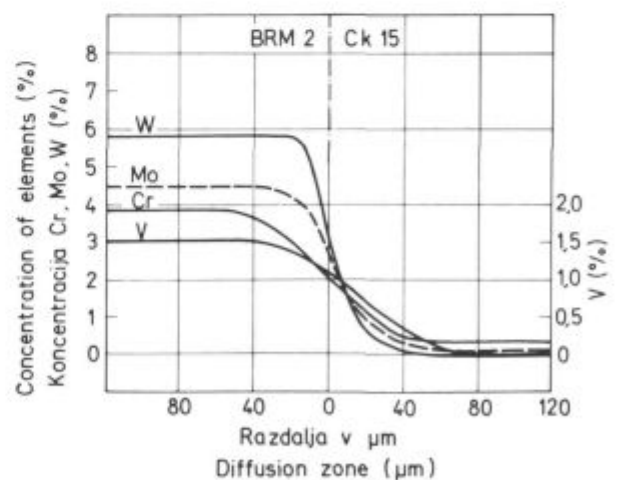
EXPERIMENTAL WORK

Annealed samples

Samples of packs where tool and structural steel were welded, and which were investigated after annealing, were heated together with the samples for rolling. After preheating the samples were annealed 1, 3, and 6 hours in the interval between 900 and 1300 °C.

The microstructure of contact surfaces between tool and structural steel revealed that diffusion occurred during the heating. Concentration profiles of alloying elements (Cr, V, Mo, W, Si, and Mn) in the transition zone were made by electron microprobe analyzer. Carbon was analyzed only in some samples by quantometer. The analysis was made so that gradually thin layers on contact surface were ground off. These measurements are not as accurate as those by electron microanalyzer but they are in a good agreement with the concentration profiles of other alloying elements, and with the microstructural characteristics of the transition layer.

Contact surfaces of steels were machined in various ways, they were planed, ground, and polished. In no case the machining of surface and the welding of pack was so perfect that the contact surfaces would fit to one to another, but contacts were achieved only on some spots. The diffusion commences through these contact areas (Fig. 1). Diffusion course depends on the temperature and the annealing times. The higher temperature



Slika 2

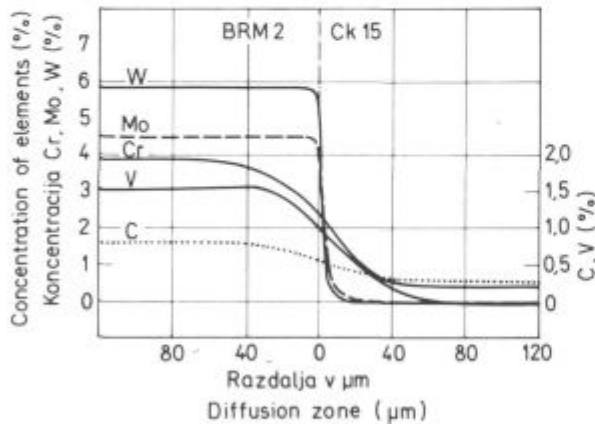
Koncentracijski profili legirnih elementov na vzorcu BRM 2/Ck 15 (1200 °C, 6 ur) na mestu kjer se jekli stikata (mikroskopisnetek na sl. 1)

Fig. 2

Concentration profiles of alloying elements in sample BRM 2/Ck 15 (1200 °C, 6 hours) on the contact between the two steels (microscopic picture in Fig. 1)

od temperature in časa žarjenja. Čim višja je temperatura in daljši so časi žarjenja, širša je cona, v kateri poteka difuzijski procesi. Sicer pa poteka difuzija dovolj hitro, da lahko govorimo o difuzijskem spoju, pri temperaturah $T > 0,5T_m$, pri čemer je T_m absolutna temperatura tališča kovine (1).

Iz diagramov na sliki 2 in 3 se vidi, da poteka difuzija zelo hitro preko stičnih točk in na teh mestih je nastal



Slika 3

Koncentracijski profili legirnih elementov na vzorcu BRM 2/Ck 15 (1200 °C, 6 ur) na mestu kjer je med jekloma reza (mikroskopisnetek na sl. 1)

Fig. 2

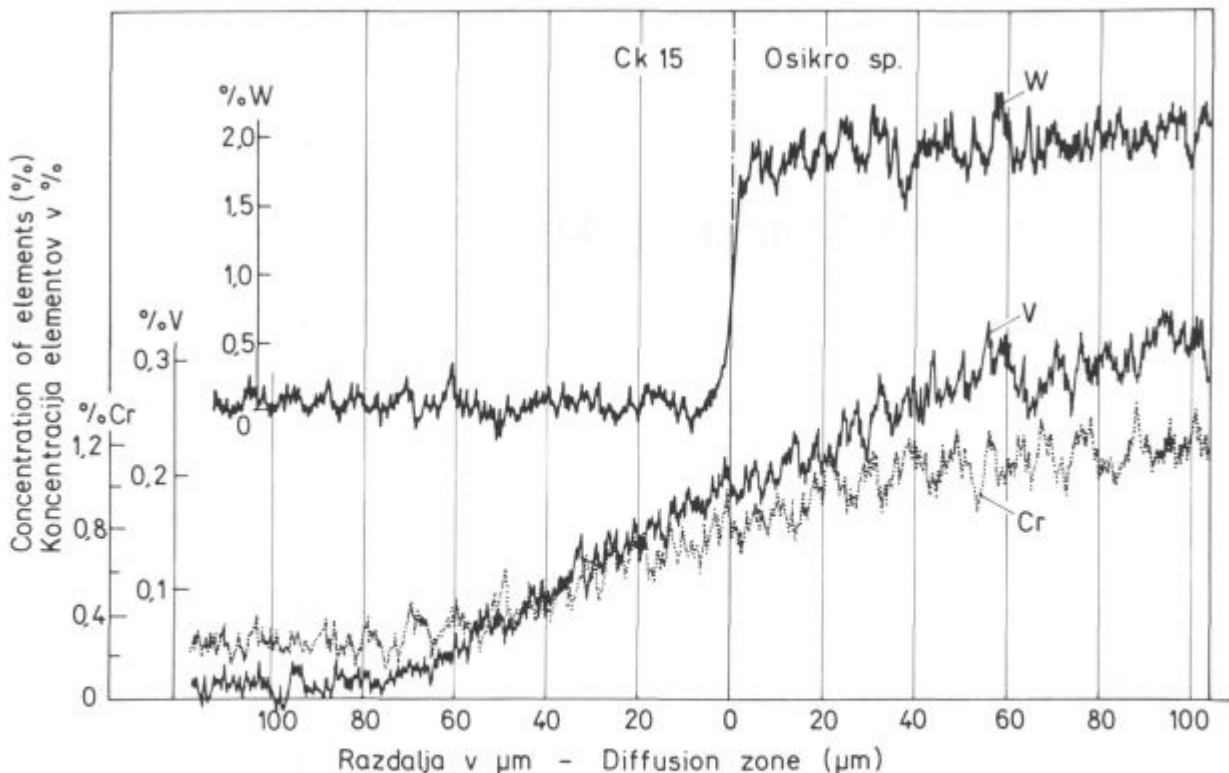
Concentration profiles of alloying elements in sample BRM 2/Ck 15 (1200 °C, 6 hours) around the gap between the two steels (microscopic picture in Fig. 1)

and the longer annealing times the deeper is the zone into which the action of diffusion was felt. Anyhow, the diffusion is fast enough that we can speak about diffusion bond at temperatures $T > 0,5T_m$, where T_m is the melting point of metal in absolute temperature (1).

Plots in Fig. 2 and 3 show that diffusion through contact points is very fast, and on these spots a solid bond was formed between the tool and the structural steel. Diffusion of Cr, V, Si, Mn, and C from tool into structural steel is very fast while the diffusion of Mo and W is rather slow. Also surface diffusion of Cr, V, Si, Mn, and C from contact points is very fast. Thus the course of concentration curves for those elements is continuous also on the areas where a gap exists between the tool and the structural steel. Depth of diffusion is greater on the contact areas. Diffusion of Mo and W is slower to such an extent that the concentration curves are continuous on the contact areas and in the samples which were annealed for a longer time (3 and 6 hours) at temperatures 1200 °C or more. On the areas where a gap exists a stepwise concentration variation of the two elements was found.

Figs. 4 and 5 present the actual course of concentration curves for Osikro spec. and OCR 12 VM tool steels in combination with Ck 15 structural steel. The curves reveal the influence of inhomogeneities, and of carbide grains.

Diffusion processes took place under isothermal conditions in austenite, but in cooling a new microstructure was formed, thus it is not possible to find how the diffusion acted on grain boundaries. Diffusion of carbon is the fastest since it is dissolved in iron interstitially. In the couples where Osikro spec. is the tool steel, the diffusion of carbon was the fastest. Though steel OCR 12



Slika 4

Dejanski potek koncentracijskih krivulj legirnih elementov na vzorcu Osikro sp./Ck 15 (1200 °C, 6 ur)

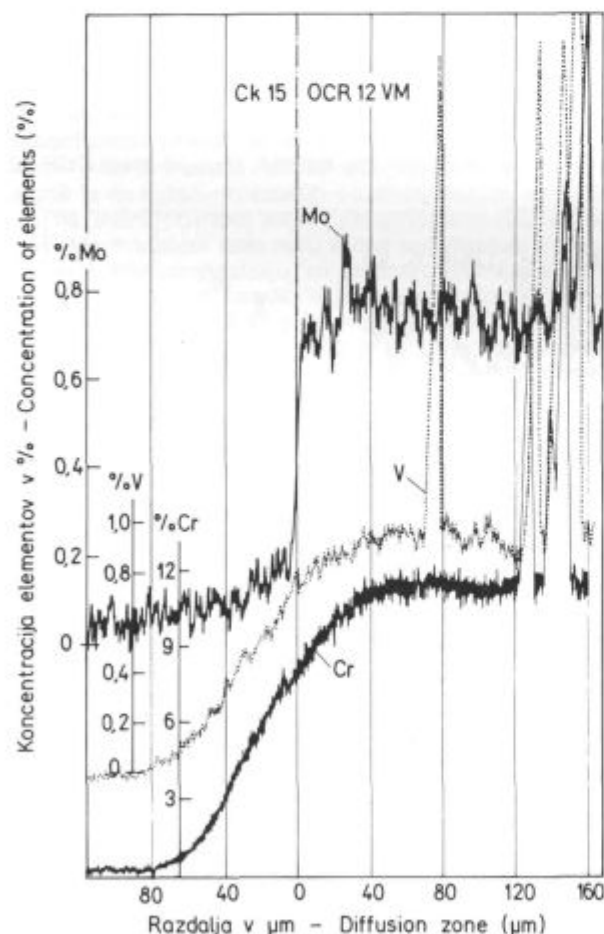
Fig. 4

Actual course of concentration curves of alloying elements in the sample Osikro sp./Ck 15 (1200 °C, 6 hours)

med orodnim in konstrukcijskim jeklom trden spoj. Difuzija Cr, V, Si, Mn in C poteka iz orodnega v konstrukcijsko jeklo zelo hitro, difuzija Mo in W pa je precej počasnejša. Tudi površinska difuzija Cr, V, Si, Mn in C s stičnih točk poteka zelo hitro. Potek koncentracijskih krivulj je zato za te elemente zvezen tudi na mestih, kjer je med orodnim in konstrukcijskim jeklom sicer reža. Globina, do katere je potekala difuzija, pa je večja na stičnih mestih. Difuzija Mo in W je toliko počasnejša, da so koncentracijske krivulje zvezne na stičnih mestih in na vzorcih, žarjenih dalj časa (3 in 6 ur) pri temperaturah 1200 °C ali več. Na mestih, kjer je med jeklom reža, je koncentracijski prehod za ta dva elementa sicer skokovit.

Na slikah 4 in 5 je prikazan dejanski potek koncentracijskih krivulj za orodni jekli Osikro spec. in OCR 12 VM v paru s konstrukcijskim jeklom Ck 15. Na krivuljah se vidi vpliv nehomogenosti in karbidnih zrn.

Difuzijski procesi so potekali pri izotermnih pogojih v avstenitu in pri ohlajanju je nastala nova mikrostruktura, zato ne moremo opredeliti, kako je potekala difuzija po kristalnih mejah. Difuzija ogljika je najhitrejša, ker je ta v železu raztopljen intersticijsko. Pri parih, pri katerih je kot orodno jeklo Osikro spec., je difuzija ogljika najhitrejša. Jekla, vrste OCR 12, imajo sicer višjo vsebnost C, vendar pa poteka difuzija C v teh jeklih počasneje. Verjetno je vzrok to, da se veliki ledeburitni karbidi



Slika 5

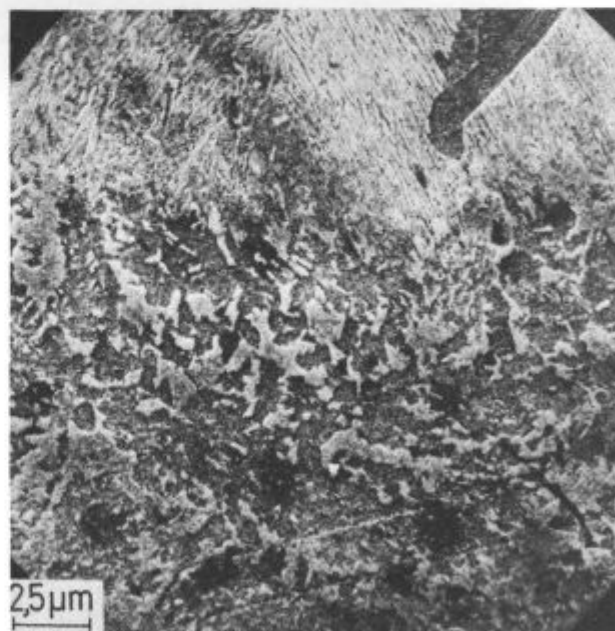
Dejanski potek koncentracijskih krivulj legirnih elementov na vzorcu OCR 12 VM/Ck 15 (1200 °C, 6 ur)

Fig. 5

Actual course of concentration curves of alloying elements in the sample OCR 12 VM/Ck 15 (1200 °C, 6 hours)

has higher carbon content, the diffusion of carbon in this steel was slower. The explanation could be, that big ledeburite carbides dissolve less easily in annealing, but the other possibility is that higher concentration of Cr retards the diffusion of carbon. Diffusion of carbon is the slowest in pairs Utop Mo 4—Ck 15 (EC 80) where the difference in C content between the tool and the structural steel is the smallest. The other elements form a substitutional solution with iron, and the diffusion processes take place through vacancies, by rotational mechanism, or by exchange of two atoms (5). Diffusion of Si, and Mn due to small concentration differences between the tool and the structural steel is not essential for formation of transition zone between the two steels. Formation of transition zone is the most influenced by C, Cr, and V. Diffusion of alloying elements on the contact surface is fast also because the surface is thermodynamically less stable due to numerous defects (vacancies, dislocations). A relatively low diffusion of Mo and W corresponds to the fact that the activation energy of diffusion is proportional to the melting point of metal.

The size of crystal grains in tool and structural steel depends on the conditions of annealing. Tool steel has martensitic micro structure, while structural steel has ferritic pearlitic bainitic microstructure. Due to concentration variations a transition layer is formed at the contact of tool and structural steel, and its microstructural characteristics depend on the steels used in couples and thus also on the concentration of alloying elements and the conditions of cooling. In pairs Osikro spec. — Ck 15 (EC 80) a fine lamellar pearlite was found in the transition zone, in some cases there was bainite. In other pairs we have found that the intermediate layer was composed of two phases and it well differs from that of structural steel. Transition into tool steel is not distinct. Microscopic pictures of the transition layer made by SEM (Fig. 6) reveal precipitated carbides in the matrix. As already mentioned, the transition layer is the

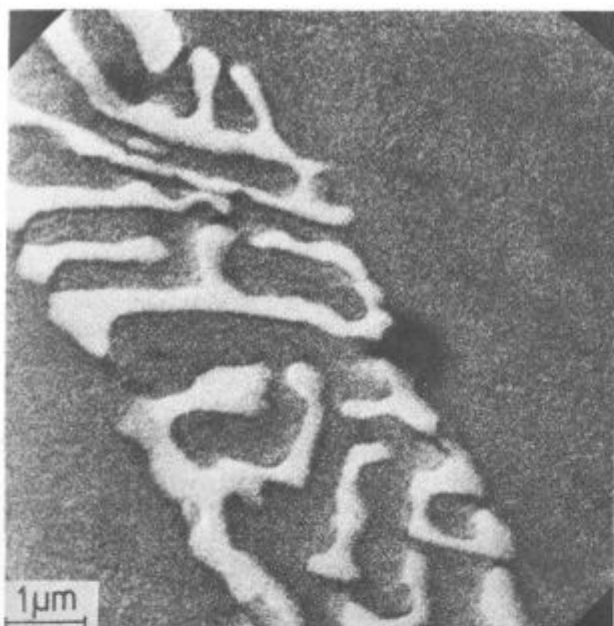


Slika 6

Mikrostruktura prehodne plasti na vzorcu OCR 12 VM/Ck 15 (1200 °C, 6 ur)

Fig. 6

Microstructure of the transition layer in the sample OCR 12 VM/Ck 15 (1200 °C, 6 hours)

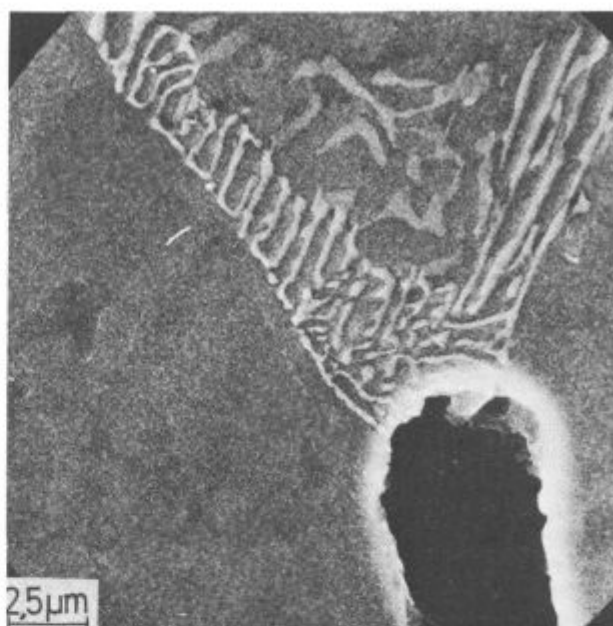


Slika 7

Začetna faza nastajanja mikropor med eutektičnimi karbidi po kristalnih mejah na vzorcu BRM 2/Ck 15 (1200 °C, 3 ure)

Fig. 7

Initial phase of formation of micropores between eutectic carbides on the crystal boundaries in the sample BRM 2/Ck 15 (1200 °C, 3 hours)



Slika 8

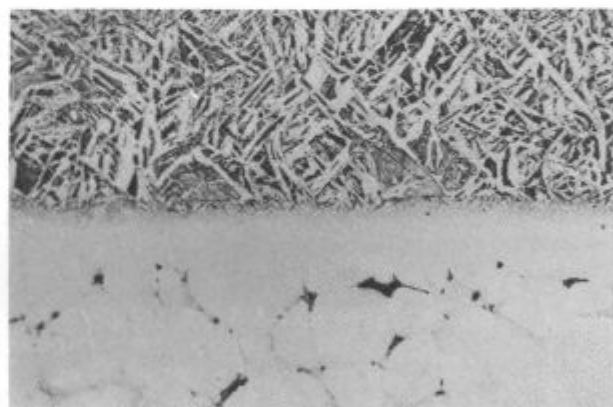
Mikroporozno mesto na kristalni meji po kateri so izločeni eutektični karbidi na vzorcu OCR 12 VM/Ck 15 (1200 °C, 6 ur)

Fig. 8

Microporous area on the crystal boundary where eutectic carbides in the sample OCR 12 VM/Ck 15 are formed (1200 °C, 6 hours)

pri žarjenju težje razstaplajo, možno pa je tudi, da visoka koncentracija Cr zavira difuzijo C. Difuzija C je najpočasnejša pri parihih Utop Mo 4/Ck 15 (EC 80), kjer je razlika med vsebnostjo C v orodnem in konstrukcijskem jeklu najmanjša. Ostali elementi so raztopljeni v železu substitucijsko in difuzijski procesi potekajo preko praznin, po rotacijskem mehanizmu ali z menjavo dveh atomov (5). Difuzija Si in Mn zaradi majhnih koncentracijskih razlik med orodnim in konstrukcijskim jeklom za nastanek prehodne cone med jekloma ni pomembna. Na izoblikovanje prehodne plasti imajo tako največji vpliv C, Cr in V. Difuzija legirnih elementov je na stični površini hitra tudi zaradi tega, ker je površina zaradi številnih napak (praznine, dislokacije) termodinamično manj stabilna. Sorazmerno počasna difuzija Mo in W se ujema z dejstvom, da je aktivacijska energija, potrebna za difuzijo, sorazmerna temperaturi tališča kovine.

Velikost kristalnih zrn v orodnem in konstrukcijskem jeklu je odvisna od pogojev žarjenja. Orodna jekla imajo martenzitno mikrostrukturo, konstrukcijska pa feritno-perlitno-bainitno mikrostrukturo. Zaradi koncentracijskih sprememb nastane na stiku orodnega jekla s konstrukcijskim prehodna plast, katere mikrostrukturne značilnosti so odvisne od vrste jekel v paru in s tem od koncentracij legirnih elementov in pogojev ohlajanja. Pri parihih Osikro spec./Ck 15 (EC 80) smo v prehodni coni opazili drobno lamelaren perlit, v nekaterih primerih pa tudi bainit. Pri ostalih parihih pa smo opazili, da je vmesni sloj dvofazen in se dobro loči od konstrukcijskega jekla. Prehod v orodno jeklo je zabrisan. Na mikroposnetku prehodne plasti, narejene v SEM, se na **sliki 6** vidijo v matici izločeni karbidi. Kot smo že omenili, je prehodna plast širša, čim višja je temperatura in daljši je čas žarjenja; s tem je tudi večja gostota in velikost karbidnih delcev. Najbolj je izrazita ta plast pri parihih, kjer je orodno jeklo iz vrste OCR 12.



Slika 9

Mikroposnetek pozornosti po kristalnih mejah zaradi difuzije legirnih elementov na vzorcu BRM 2/Ck 15—1300 °C, 1 ura (pov. 100 ×)

Fig. 9

Microscopic picture of the porosity on crystal boundaries due to diffusion of alloying elements in the sample BRM 2/Ck 15—1300 °C, 1 hour (magn. 100 ×)

wider the higher is the temperature and the longer is the time of annealing, and thus also the density and the size of carbide inclusions is increased. The most pronounced is this layer in pairs where tool steel is of OCR 12 type.

At annealing temperatures 1200 °C or higher a very fast diffusion was found with OCR 12 and BRM 2 steels. The concentration of alloying elements on the grain boundaries is increased to such an extent that boundaries start to melt (4) which accelerates the diffusion of alloying elements into structural steel, and it becomes faster than the flow of new atoms. During the solidifica-

Pri temperaturah žarjenja 1200 °C in več smo pri jeklih, vrste OCR 12 in BRM 2, opazili zelo hitro difuzijo. Po kristalnih mejah pride do take koncentracije legirnih elementov, da se te natalijo (4), kar pospeši difuzijo legirnih elementov v konstrukcijsko jeklo v taki meri, da je ta hitrejša od dotoka novih atomov na njihova mesta. Med strjevanjem nataljenih mej, po katerih nastanejo evtektični karbidi, se zato pojavijo zaradi praznin mikroporozna mesta. Linija cone, v kateri nastanejo mikropore, se s časom žarjenja oddaljuje od mejne površine orodno jeklo/konstrukcijsko jeklo (sl. 7, 8 in 9).

Valjanje klinastih vzorcev

Orodna in konstrukcijska jekla imajo različne fizikalne lastnosti (modul elastičnosti, toplotna prevodnost, temperaturni razteznostni koeficient) in različno deformacijsko trdnost (meja tečenja, utrjanje). Tudi fazne preme, ki potekajo pri različnih temperaturah, so povezane z volumskimi spremembami. Zaradi tega nastanejo med jekloma pri ogrevanju, med valjanjem in pri ohlajanju precejšnje notranje napetosti. Zvar med ogrevanjem ne sme popustiti, sicer se zaradi oksidacije stičnih površin jekli med valjanjem ne zavarita. To lahko prepreči tudi prisotnost varilne žilindre. Zaradi različnih lastnosti jekel se med valjanjem ustvarijo med jekloma take napetosti, da se valjanci krivijo. Krivljenje se nadlajuje tudi med ohlajanjem. S padajočo temperaturo valjanja se razlike v lastnostih jekel večajo, zato je krivljenje intenzivnejše pri

tion of partially melted boundaries where eutectic carbides are formed microporous areas are formed due to vacancies. Line of zone where micropores are formed moves away from the tool steel/structural steel boundary surface with the time of annealing (Figs. 7, 8, and 9).

Rolling of Wedge Samples

Tool and structural steel have different physical properties (modulus of elasticity, thermal conductivity, expansion coefficient), and different deformation strength (yield strength, hardening). Also phase transformations occurring at various temperatures are connected with the volume changes. Thus rather high internal stresses appear between the two steel during heating, in rolling, and during cooling. The weld during heating must not break, since the contact surfaces do not weld again in rolling because the surfaces are oxidized. The same effect can have the presence of welding slag. Due to different properties of steel such stresses appear between the two steel in rolling that the rollings are buckled. Further buckling occurs in cooling. Reduced rolling temperature increases the differences in steel properties, and buckling is more intensive at lower rolling temperatures. By a certain shape of welded packs the buckling can be avoided to a considerable extent.

By wedge samples rolled in the interval of specific reduction between 0 and 40 % the influence of the degree of deformation on the formation of transition diffusion layer and on the strength of bond between the two steel could be more accurately determined.

Tool and structural steel in all cases stuck well together at the 15 % degree of reduction. At lower reductions various defects are influential though the bond can also be good.

The transition zone is the narrower the higher is the degree of reduction. Temperature does not influence the adherence of steel if the degree of reduction is high enough, but it influences only the thickness of the layer in which the diffusion processes took place (Fig. 10).

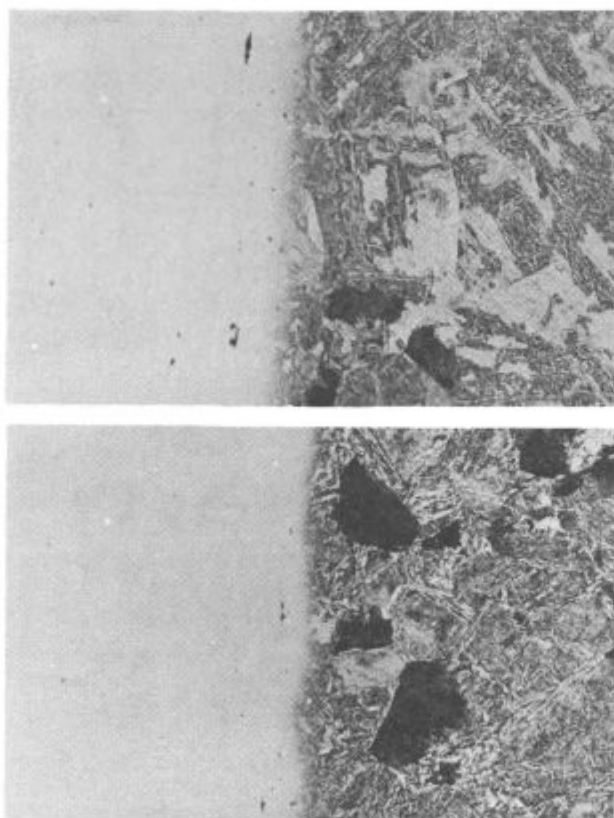
Measuring forces in rolling, the degree and the rate of deformation enables us to calculate the yield stresses. They are regardless to the temperature and the degree of reduction between 80 and 190 N/mm². These values correspond to the yield strengths of tool steel which shows that structural steel has small influence on the workability of compound steel. But rolling of such steel has specific demands.

Rolling with many passes

Test samples were rolled in six passes at most with 12, 20, and 25 % degree of partial deformation. Temperature of samples was measured at the beginning and at the end of rolling.

The same findings as given for the annealed samples are also valid for the diffusion of alloying elements. Alligatoring was observed only at the first pass, and the reasons for it could be exactly determined. If the two steels adhered in this step the alligatoring practically could not occur in further rolling. Thus we are of opinion that higher degree of reduction is needed in the first pass (at least 15 %) to prevent alligatoring. Recrystallization taking place in rolling and in the intervals between single passes contributes to the bond between the tool and the structural steel.

Comparison of the thicknesses of layers in which diffusion took place in annealed and in rolled samples revealed mainly by applying the concentration lines for Cr



Slika 10

Mikrostruktura valjanega vzorca OCR 12 VM/Ck 15, predhodno 30 min. žarjenega na 1160 °C, pri 15 (zgoraj) in 40 % (spodaj) redukciji (pov. 200 ×)

Fig. 10

Microstructure of rolled sample OCR 12 VM/Ck 15, initially annealed 30 mins at 1160 °C at 15 % (above) and 40 % (below) reduction (magn. 200 ×)

nižjih temperaturah valjanja. Z določeno obliko zavarjenih paketov se krivljenju lahko v precejšnji meri izognemo.

Na klinastih vzorcih, zvaljanih v področju specifične redukcije od 0 do 40 %, smo želeli natančneje ugotoviti vpliv stopnje deformacije na izoblikovanje prehodne difuzijske plasti in trdnost spoja med jekloma.

Orodno in konstrukcijsko jeklo sta se v vseh primerih pri 15 % stopnji redukcije že dobro sprijeli. Pri manjših stopnjah redukcij pridejo do izraza različne napake, čeprav je lahko spoj že dober. Prehodna difuzijska plast je ožja, čim večja je stopnja redukcije. Temperatura pri zadostni stopnji redukcije ne vpliva na sprijetost jekel, pač pa le na debelino plasti, v kateri so potekali difuzijski procesi (sl. 10).

Iz meritev sile valjanja, stopnje deformacije in hitrosti deformacije smo izračunali preoblikovalno trdnost. Ta je glede na temperaturo in stopnjo redukcije od 80 do 190 N/mm². Te vrednosti ustrezajo poreoblikovalnim trdnostim orodnih jekel, kar kaže, da konstrukcijsko jeklo le malo vpliva na preoblikovalnost compound jekel. Vendar pa veljajo za valjanje teh jekel določene specifičnosti.

Valjanje z več redukcijami

Preizkusne vzorce smo zvaljali v največ šestih redukcijah z 12, 20 in 25 % stopnjami parcialnih deformacij. Na vzorcih smo merili temperaturo na začetku in na koncu valjanja.

Za difuzijo legirnih elementov veljajo iste ugotovitve, kot smo jih podali za žarjene vzorce. Odpiranje vzorcev smo opazili le pri prvi redukciji, vzroke za to pa smo lahko točno opredelili. Če sta se jekli v tej fazi sprijeli, med nadaljnjim valjanjem praktično ne more priti do razslojevanja. Zato menimo, da je ustrežnejša višja stopnja prve redukcije (vsaj 15 %), da se tako izognemo razslojevanju. Rekristalizacija, ki poteka med valjanjem in v času med redukcijami, pospešuje vezavo med orodnim in konstrukcijskim jeklom.

Iz primerjave debelin plasti, v kateri so potekali difuzijski procesi v žarjenih in valjanih vzorcih, smo predvsem na osnovi koncentracijskih krivulj za Cr in V ugotovili, da se je prehodna plast med valjanjem zožila za specifično stopnjo deformacije. Kristalna zrna so zaradi rekristalizacije drobnejša, opazi pa se, da so zrna v konstrukcijskem jeklu v coni, kjer so potekali difuzijski procesi, večja kot sicer po preseku. Sicer pa je velikost zrn odvisna tudi od končne temperature valjanja.

Po literarnih podatkih (1, 2) se difuzija med deformacijo močno poveča. Smer difuzije je paralelna s silo valjanja. Pri naših meritvah smo sicer skušali ločiti difuzijo, ki je potekala med ogrevanjem, od difuzije med valjanjem, vendar nam to ni uspelo. Verjetno je temu vzrok v premalo natančni pripravi vzorcev (popolno naleganje površin) in tudi v možnostih naše raziskovalne opreme. Upoštevati pa moramo tudi to, da so časi delovanja deformacijskih napetosti v primerjavi s časi žarjenja izredno kratki. Sicer pa tudi v literaturi nismo zasledili nobenih konkretnih podatkov.

Toplotno obdelani vzorci

Analize koncentracij Si, Mn, Cr, V, Mo in W, narejene v prehodni coni toplotno obdelanih valjanih vzorcev (mehko žarjenje, normalizacija, kaljenje, poboljšanje), niso pokazale, da bi ta bistveno vplivala na difuzijo teh elementov. Mikrostrukturne preiskave pa so pokazale, da normalizacija in deloma mehko žarjenje oz. počasno ohlajanje vplivata na difuzijo ogljika. To smo opazili tudi pri nekaterih valjanih vzorcih, ki so bili počasi ohlajeni.

and V that the transition layer was thinned during the rolling for the specific degree of deformation. Crystal grains are finer due to recrystallization, but it was observed that the grains in the diffusion zone of structural steel were greater than those outside it. Further, the grain size depends also on the final temperature of rolling.

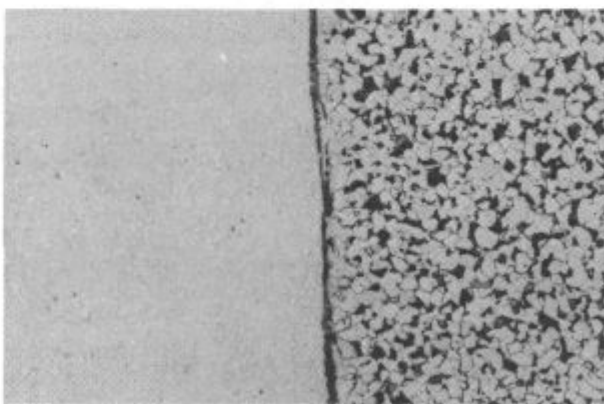
According to references (1, 2) diffusion is highly increased during the deformation. Direction of diffusion is parallel to the rolling force. Our trial to determine the difference between the diffusion during annealing and during rolling was not successful. The reason maybe in a not enough accurate preparation of samples (perfect fit of surfaces) or in the capacity of our research equipment. But it must be taken in account that the duration of deformation stresses is much shorter in comparison with the annealing times. Anyhow, also in references no concrete data could be found.

Heat treated samples

Analyses of concentrations of Si, Mn, Cr, V, Mo, and W in the transition zone of heat treated rolled samples (soft annealing, normalizing, quench hardening, hardening and tempering) did not show any special influence of heat treatment on the diffusion of those elements. But microstructural investigations showed that normalising and partially soft annealing, or slow cooling have influence on the diffusion of carbon. This was observed also in some rolled samples which were slowly cooled. During heating, or annealing and rolling carbon diffuses into structural steel. Under certain conditions, especially in slow cooling between A_{r3} and A_{r1} , the activity of carbon is changed and the direction of diffusion is reversed. The activity of carbon is influenced also by other alloying elements. In structural steel a layer of pearlite is formed on the boundary with the tool steel, followed by a layer of ferrite. Such microstructure is shown in Fig. 11. In hardened and tempered samples such rearrangement of carbon does not occur (Fig. 12).

Strength of bond

Mechanical properties, especially tensile strength of plated steel is given by the strength of structural steel, but to a great extent it depends also on the preparation of packs, and on the microstructural characteristics of the transition zone.



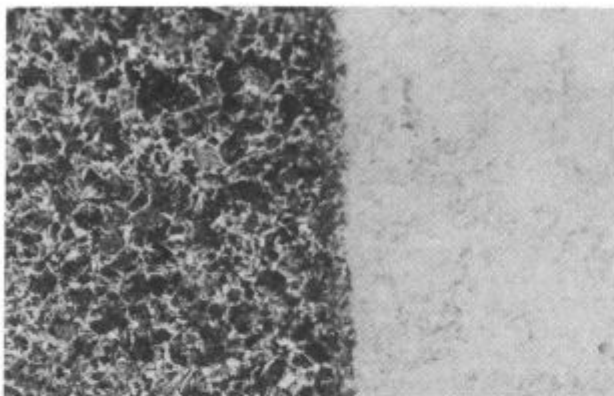
Slika 11

Mikrostruktura prehodne plasti vzorca OCR 12 VM/Ck 15 (1000 °C, 6 ur, 3 × 20 % redukcija) po normalizaciji (pov. 100 ×)

Fig. 11

Microstructure of the transition layer of the sample OCR 12 VM/Ck 15 (1000 °C, 6 hours, 3 × 20 % reduction) after normalising (magn. 100 ×)

Med ogrevanjem, oz. žarjenjem in valjanjem difundira C v konstrukcijsko jeklo. V določenih pogojih, predvsem pri počasnem ohlajanju med A_{r3} in A_{r1} , se aktivnost C spremeni in difuzija poteka v obratni smeri. Aktivnost C je odvisna tudi od ostalih legirnih elementov. V konstrukcijskem jeklu nastane na meji z orodnim jeklom plast perlita, ki ji sledi plast ferita. Taka mikrostruktura je prikazana na **sliki 11**. Na poboljšanih vzorcih ne pride do take prerazporeditve C (**sl. 12**).



Slika 12

Mikrostruktura prehodne plasti poboljšane vzorca Osikro sp./Ck 15—1200 °C, 1 ura, 4 × 20 % redukcija, 880 °C olje, popuščanje 200 °C, 60 HRC, raztržna trdnost spoja 640 N/mm² (pov. 200 ×)

Fig. 12

Microstructure of the transition zone of hardened and tempered sample Osikro sp./Ck 15—1200 °C, 1 hour, 4 × 20 % reduction, 880 °C oil, tempering 200 °C, 60 HRC, tensile strength of bond 640 N/mm² (magn. 200 ×)

Trdnost spoja

Mehanske lastnosti, predvsem raztržna trdnost platiranih jekel je podana s trdnostjo konstrukcijskega jekla, precej pa je odvisna tudi od priprave paketov in mikrostrukturnih značilnosti prehodne plasti.

Oksidacijski film, ki lahko nastane med ogrevanjem za valjanje, je krhek in se med plastično predelavo trga in drobi, vendar kljub temu bistveno zmanjša trdnost spoja. Če je ta film debelejši, pa prepreči spojitev konstrukcijskega jekla z orodnim jeklom. Enak učinek ima tudi varilna žilindra, če med varjenjem paketov zalije rezo med jekloma.

Na raztržno trdnost platiranih jekel vplivajo tudi pogoji ogrevanja (temperatura, čas) in valjanja (začetna in končna temperatura valjanja, redukcija). Mikropore v orodnem jeklu, intermetalne faze in karbidi, ki nastanejo v prehodni plasti pri neustreznih pogojih ogrevanja in valjanja, zmanjšajo trdnost spoja. Mikrostrukturne nehomogenosti so v prehodni plasti največje pri platiranih jeklih, kjer je v paru s konstrukcijskim jeklom ledeburitno orodno jeklo, vrste OCR 12. Že zelo tanek oksidni film, bogat s Cr, močno ovira spojitev jekel. Zato je pri platiranju teh jekel, bolj kot pri ostalih, pomembno, da poteka ogrevanje in valjanje pri optimalnih pogojih.

Dodatnim napetostim, nastalim med platiranjem in toplotno obdelavo, zaradi različnih fizikalno-metalurških lastnosti jekel, se ne moremo izogniti.

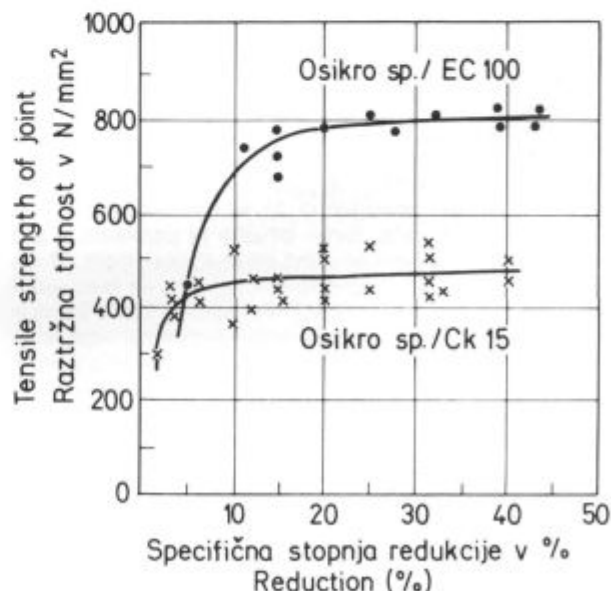
Na diagramih na **slikah 13 in 14** je prikazana odvisnost raztržne trdnosti, od specifične stopnje redukcije v poboljšanem stanju za vzorce, platirane iz orodnih jekel Osikro spec. in OCR 12 VM s konstrukcijskimi jekli Ck 15, EC 80 in EC 100. Raztržna trdnost je le malo odvi-

Oxide film which can be formed in heating before rolling is brittle and it is broken during plastic working, but nevertheless it essentially reduces the strength of the bond. If this film is thicker, it can even prevent the adherence of tool and structural steel. The same effect has welding slag if it in welding the packs fills the gap between the two steels.

The tensile strength of plated steel is influenced also by the conditions of heating (temperature, time) and of rolling (initial and final temperature of rolling, reduction). Micropores in tool steel, intermetallic phases and carbides which are formed in the transition zone under unsuitable conditions of heating and rolling reduce the strength of bond too. Microstructural inhomogeneities in the transition zone are the highest in plated steel if a ledeburitic tool steel of OCR 12 type is in combination with a structural steel. Already a very thin oxide film rich with Cr hinders the adherence of steel to a great extent. Therefore it is especially in plating these steels important that heating and rolling is done under the optimal conditions.

Additional stresses which appear in plating and in heat treatment cannot be avoided due to different physico-metallurgical properties of steels.

Plots in Figs. 13 and 14 show the relation between the tensile strength and the specific degree of reduction in as hardened and tempered samples where tool steels Osikro spec. and OCR 12 VM were combined with Ck 15, EC 80, and EC 100 structural steels. Tensile strength varies with the reduction only to a small extent if it is higher than 15 %. Bond between the two steels is better and tensile strength is higher if samples were rolled in more passes. Due to recrystallization the microstructural inhomogeneities in the transition zone are smaller. Fracture of tensile test pieces occurs on the boundary of the two steels chiefly in the areas of any kind of structural inhomogeneities, and in structural steel, but only partially in tool steel.

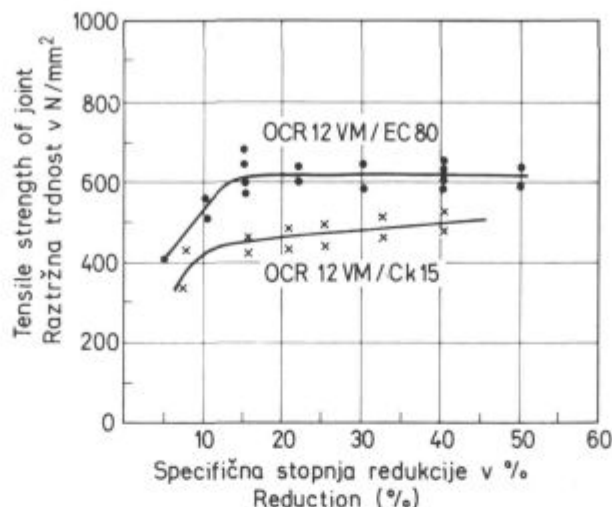


Slika 13

Raztržna trdnost spoja platiranih jekel Osikro sp./Ck 15 in Osikro sp./EC 100 v odvisnosti od stopnje redukcije

Fig. 13

Tensile strength of bond of plated Osikro sp./Ck 15 and Osikro sp./EC 100 steel related to the degree of reduction



Slika 14

Raztržna trdnost spoja platiranih jekel OCR 12 VM/Ck 15 in OCR 12 VM/EC 80 v odvisnosti od stopnje redukcije

Fig. 14

Tensile strength of bond of plated OCR 12 VM/Ck 15 and OCR 12 VM/EC 80 steels related to the degree of reduction

sna od redukcije, ko je ta večja od 15 %. Spoj med jekloma pa je boljši in je raztržna trdnost višja pri vzorcih, valjanih v več redukcijah. Zaradi procesov rekristalizacije so mikrostrukturalne nehomogenosti v prehodni plasti manjše. Prelom nateznih preizkušancev poteka po meji med jekloma, predvsem tam, kjer so kakršnekoli mikrostrukturalne nehomogenosti, in po konstrukcijskem jeklu, deloma pa lahko tudi po orodnem jeklu.

ZAKLJUČEK

Pri platiranju orodnih jekel na konstrukcijska jekla z vročim valjanjem nastane trden spoj med jekloma zaradi difuzijskih procesov. Difuzija legirnih elementov poteka med ogrevanjem za valjanje in med valjanjem. Difuzija začne potekati preko stičnih mest in se hitro nadaljuje kot površinska difuzija in nato kot volumska difuzija. Difuzija C, Cr in V je hitra in ti elementi imajo največji vpliv na izoblikovanje prehodne cone. Difuzija Mo in W je zelo počasna. Si in Mn sicer hitro difundirata, vendar zaradi majhnih koncentracijskih razlik med orodnim in konstrukcijskim jeklom ne vplivata bistveno na mikrostrukturo prehodne plasti.

Orodna in konstrukcijska jekla imajo različne fizikalno-metalurške lastnosti in pri platiranju nastanejo med njimi precejšnje napetosti. Z ustrezno pripravo paketov za valjanje moramo zagotoviti, da sta stični površini čisti in da preprečimo oksidacijo stičnih površin med ogrevanjem za valjanje.

Širina in mikrostrukturalne značilnosti prehodne difuzijske plasti so odvisne od temperature in časa ogrevanja ter od termomehanskih parametrov vročega valjanja. Jekli se na stičnih mestih spojita že med ogrevanjem, trden spoj pa dobimo, če je redukcija med valjanjem večja od 15 %. Stopnja redukcije vpliva le v manjši meri na trdnost spoja, pač pa imajo višjo raztržno trdnost jekla, platirana v več redukcijah, kjer je prehodna plast zaradi procesov rekristalizacije homogenejša. Tudi s toplotno obdelavo (poboljšanje) se trdnost vezi izboljša. Pri mehkem žarjenju, normalizaciji, in predvsem pri počasnem ohlajanju v področju med A_{r3} in A_{r1} poteka difuzija ogljika v obratni smeri, to je iz konstrukcijskega jekla na mejo z orodnim jeklom. Difuzija ostalih legirnih elementov med

Conclusions

In plating tool steel on structural steel by hot rolling a firm bond is formed between the two steels due to diffusion processes. Diffusion of alloying elements occurs during heating before rolling and during rolling. Diffusion commences on contact spots and it is rapidly continued as a surface diffusion and later as a volume diffusion. Diffusion of C, Cr, and V is fast and these elements have the highest influence on the formation of the transition zone. Diffusion of Mo and W is very slow. Si and Mn diffuse namely fast but due to small concentration differences between the tool and the structural steel they do not have any essential influence on the microstructure of the transition zone.

Tool and structural steel have different physico-metallurgical properties and in plating considerable stresses appear between them. By a suitable preparation of rolling packs it is necessary to ensure that contact surfaces are pure and that oxidation of these surfaces is prevented during heating before rolling.

Width and microstructural characteristics of the transition diffusion layer depend on the temperature and the time of annealing and on thermomechanical parameters of hot rolling. The steels adhere on contact points already in annealing, strong bond is obtained if the reduction in rolling is more than 15 %. Degree of reduction has a minor influence on the strength of bond, but higher tensile strength was obtained with plated steels being rolled in more passes since recrystallization enables the formation of more homogeneous transition layer. Also heat treatment (hardening and tempering) improves the strength of bond. In soft annealing, normalising, and chiefly in slow cooling in the interval between A_{r3} and A_{r1} the diffusion of carbon has reverse direction, i. e. from structural steel to the boundary with tool steel. Diffusion of the other alloying elements during heat treatment has no perceptible influence on the transition zone.

Under unsuitable conditions of annealing and rolling the transition diffusion zone is wide and unhomogeneous. Micropores, carbides, and intermetallic phases reduce the strength of bond. Oxide film is broken during working, but it nevertheless reduces the strength of bond. Microstructural inhomogeneities are the highest

toplotno obdelavo nima zaznavnega vpliva na prehodno plast.

Pri neustreznih pogojih ogrevanja in valjanja je prehodna difuzijska plast široka in nehomogena. Mikropore, karbidi in intermetalne faze zmanjšajo trdnost spoja. Oksidni film se med preoblikovanjem sicer drobi, vendar zmanjša trdnost vezi. Mikrostrukturne nehomogenosti so največje pri platiranih jeklih, kjer je v paru s konstrukcijskim jeklom ledeburitno orodno jeklo, vrste OCR 12. Že zelo tanek oksidni film, bogat s Cr, močno ovira spojitev jekel. Sicer pa je raztržna trdnost spoja med orodnim in konstrukcijskim jeklom poleg od omenjenih lastnosti odvisna predvsem od trdnosti šibkejšega gradnika.

in plated steel where a ledeburitic tool steel of OCR 12 type is in combination with a structural steel. Already a very thin oxide film rich with Cr hinders the adherence of steels to a great extent. Further, the ultimate tensile strenght of bond between the tool and the structural steel depends mainly on the strength of weaker material beside the previously mentioned properties.

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J-integral in morfologija preloma mikrolegiranih drobnozrnatih jekel Nionical 70 ter Niomol 490

J-Integral and Fracture Morphology of Micro-Alloyed Fine-Grained Steels Nionical 70 and Niomol 490

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UDK: 620.178.2:539.211:669.15
ASM/SLA: Q26r, M23p,AY

Opisano je merjenje lomne žilavosti mikrolegiranih drobnozrnatih jekel z metodo J-integrala. Rezultati kažejo, da je poleg standardnih kriterijev, nanašajočih se na zahtevano velikost preizkušancev, potrebno zaradi močne strižne deformacije na bokih preizkušancev upoštevati tudi še nekatere druge empirične kriterije.

Frakturne površine preizkušancev so v vseh primerih jamičaste, duktilne, velikost jamic pa je v dobri soodvisnosti z izmerjenimi J_{IC} vrednostmi.

Measuring of fracture toughness by J-integral method is described for micro alloyed fine-grained steels. The results show that it is not enough to consider only some standard criteria related to the demanded specimen size but that some other empirical criteria must be taken into account because of a severe shear strain on the sides of the specimen.

The fracture surfaces on the specimens are in all cases of ductile type with dimples and the size of dimples are in a good correlation with the measured J_{IC} values.

1. UVOD

Dolga leta so bila edina variva konstrukcijska jekla le normalizirana C-Mn jekla s feritno-perlitno mikrostrukturom. Zaradi zahtev po izboljšanju meje plastičnosti, varivosti ter žilavosti so bila pred desetletji razvita prva mikrolegirana drobnozrnata jekla. Tovrstna jekla so legirana s Ti, Nb, V, Zr oz. Mo, bodisi posamič bodisi v kombinacijah, pri čemer je povečanje meje plastičnosti doseženo deloma z izločevalnim utrjevanjem ferita, predvsem pa — in to velja še posebej za termomehansko predelana jekla — z zmanjšanjem velikosti feritnih zrn. Slednje vpliva ugodno tudi na žilavost, ker pomakne temperaturo prehoda v krhko stanje k nižjim vrednostim.

Danes od mikrolegiranih drobnozrnatih jekel zahtevamo mejo plastičnosti vsaj 500 MPa, ob tem pa mora biti Charpy-V žilavost visoka še tudi pri temperaturi -60°C . Vsebnost ogljika v novih vrstah mikrolegiranih jekel je zato nekoliko nižja, običajno med 0,03 in 0,12 %, pri čemer veljajo nižje vrednosti za termomehansko predelana jekla.

Lom konstrukcijskih jekel s povišano mejo plastičnosti je praviloma žilav in le redko polkrhek. Ker pa se takšna jekla uporabljajo za varjene konstrukcije, moramo upoštevati tudi možnost pojavljanja mikrorazpok v toplotno vplivanih conah varov, zato postane še kako pomembna izbira primerne porušitvenega kriterija. Pri kvazistatično obremenjenih konstrukcijah s planarnimi

1. INTRODUCTION

For many years the only weldable structure steels have been the normalized C-Mn steels with a ferritic-pearlitic microstructure. Some ten years ago the first micro-alloyed fine-grained steels were developed because of demands for better yield point, weldability and toughness. These steels are alloyed, separately or in combinations, with Ti, Nb, V, Zr and Mo. The better yield strength is partly obtained by precipitation hardening of ferrite but primarily by the reduction of ferrite grain size what is specially true for thermomechanically treated steels. Smaller grain size shows a favourable influence on toughness too, shifting the transition temperature towards lower values.

Nowadays it is required that the yield strength of micro-alloyed fine-grained steels should be at least 500 MPa and the V-notch Charpy toughness high even at the temperature of -60°C .

The carbon content in these new micro-alloyed steels is therefore somewhat lower, commonly between 0.03 and 0.12 %, the lower values are valid for thermomechanically treated steels.

The fracture of structural steels with the increased yield strength is nearly always tough and very seldom semi-brittle. Since such steels are used for welded structures, the possibility of microcracks in the heat-affected weld zones must be considered, too. Therefore the selection of an appropriate fracture criterion appears even more important.

In quasi-statically loaded structures with planer discontinuities, i. e. with cracks in the bearing cross-sections,

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diskontinuitetami, t. j. razpokami v nosilnem preseku, lahko načeloma izbiramo med dvema skupinama porušitvenih kriterijev¹. Prva skupina teh kriterijev (koncepti K, COD, J-integral, Tearing Modulus) temelji na elasto-ozroma elasto-plastomehaniki loma ter predpostavlja napredovanje nestabilne razpoke vse do loma konstrukcije. Druga skupina pa vključuje le kriterij plastičnega kolapsa², ki privzema, da do porušitve pride po plastični deformaciji neto preseka kot celote še pred napredovanjem razpoke.

Za naše raziskave smo tokrat izbrali dve različni mikrolegirani drobnozrnati jekli, namreč jeklo Nionical 70 ter jeklo Niomol 490. Obe jekli sta proizvod železarne Jesenice, v pogojih eksploatacije pa se, vse do nizkih temperatur, obnašata izrazito elasto-plastično. Za študij njihovih lastnosti smo zato izbrali metodo J-integrala, ki je na Inštitutu za metalne konstrukcije v Ljubljani osvojena do praktične rabe.

2. TEORETIČNI DEL

Pri nizkih temperaturah, velikih hitrostih deformacije ter v pogojih ravninskega deformacijskega stanja, t. j. pri zadostni debelini preizkušanca, je lom jekla praviloma krhek. V takšnih primerih je velikost plastične cone ob korenu planarne diskontinuitete, namreč inicialne mikro-razpoke na preizkušancu, zanemarljivo majhna, napredovanje razpoke do loma pa lahko popišemo z linearno elastomehaniko. Pri polkrhkem ali pa pri žilavem lomu pa je velikost plastične cone znatna ter je nikakor ne smemo zanemariti. Lom moramo v takšnem primeru obravnavati z nelinearno, takoimenovano elastoplastomehaniko.

Merilo za žilavost, in s tem tudi merilo za porušitev materiala s planarnimi diskontinuitetami v nosilnem preseku je v primeru, ko pri lomu ni potrebno upoštevati vpliva velikosti plastične cone, kar kritični faktor intenzitete napetosti ali loma žilavost materiala K_{IC} , kot se tudi imenuje. Merjenje lomne žilavosti K_{IC} je že dlje časa standardizirano^{3,4}.

Pri elastoplastičnem obnašanju materiala ob planarni diskontinuiteti pa zaradi učinkovanja znatne plastične cone koren diskontinuitete najprej nekoliko otopi ob sočasnem odpiranju ustja diskontinuitete. Kritična velikost odpiranja ustja neposredno pred lomom je — ob znani geometriji problema — izključno lastnost samega materiala.

Na merjenju kritičnega razmika površin razpoke je zato osnovana metoda merjenja žilavosti materiala (metoda COD). Gliha⁵ v svojem preglednem članku navaja, da je kritična velikost odpiranja ustja razpoke parameter, ki se nanaša samo na plastično cono ob korenu le-te. Lastnosti znotraj plastične cone pa se spreminjajo, zato pri merjenju kritične velikosti razmika površin razpoke prihaja do znatnega razsipanja rezultatov.

Parameter, ki ne zajema le vpliva plastične cone, je kritična vrednost krivuljnega integrala J vzdolž poljubne poti, ki objame konico razpoke. Za ravninski primer, ko ima preizkušaneč edinično debelino, velja:

$$J = -\frac{dU_p}{da} = \int_{\Gamma} W dy - \int_{\Gamma} \mathbf{T} \frac{\partial \mathbf{u}}{\partial x} ds, \quad (1)$$

pri čemer smo z dU_p/da označili spremembo potencialne energije na enoto podaljšanja razpoke, W je deformacijska energija na enoto volumna, \mathbf{u} je vektor pomika v smeri delovanja zunanje sile \mathbf{T} na konturo Γ . Člen $\mathbf{T}(\partial \mathbf{u}/\partial x) ds$ daje torej delež vložene dela iz napetostnega

grupa, it is principally possible to choose between two groups of fracture criteria¹. The first group (concepts K, COD, J-Integral, Tearing Modulus) is based on elasto- or elasto-plastomechanics of the fracture and presumes an unstable crack propagation to the final fracture of a structure. The second group includes merely the criterion of plastic collapse², supposing that fracture occurs after the netto cross-section has been plastically deformed as a whole immediately before the crack propagation commenced.

Two different micro alloyed fine-grained steels, i. e. Nionical 70 and Niomol 490 were chosen for our investigation. Both are manufactured by Jesenice Ironworks and they both exhibit pronounced elasto-plastic behaviour down to low temperatures during exploitation. To study their properties we therefore decided for the J-integral method which is practically applied in the Institute of metallic structures in Ljubljana.

2. THEORY

At low temperatures, at high deformation rates, and in plane-strain conditions, i. e. with sufficiently thick specimens, the fracture of steel is regularly brittle. In such cases the size of plastic zone at the root of plane discontinuity, i. e. at the initial microcrack on the specimen, is negligibly small and the crack propagation to the fracture can be described by linear elastomechanics. With semi-brittle or even tough fracture the size of plastic zone is considerably greater and therefore it should not be neglected by any means. In such cases the fracture must be analyzed by the non-linear, so-called elasto-plastomechanics.

When the influence of the plastic zone size needs not be considered, the toughness criterion and thus the criterion for fracture of material containing plane discontinuities in the bearing cross-section is represented by the critical stress intensity factor, also called the material fracture toughness K_{IC} . The method of K_{IC} measurement has been standardized^{3,4} for quite a long time.

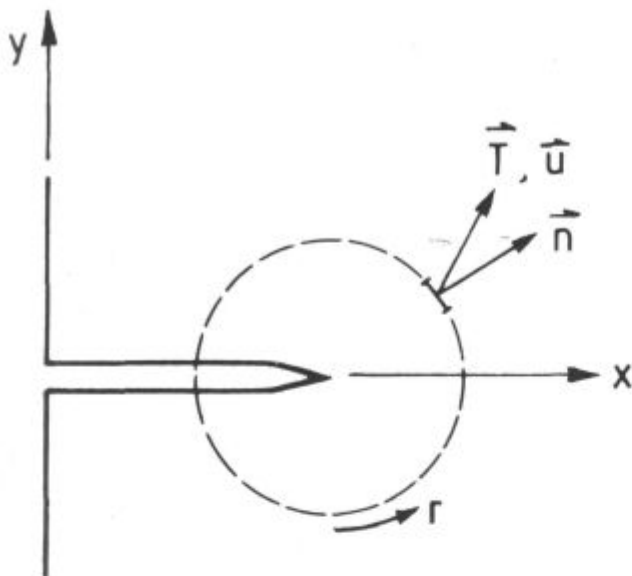
When material with plane discontinuities behaves elasto-plastically, the root of the discontinuity is initially blunted due to the influence of a considerable plastic zone and the crack starts simultaneously to open. The critical size of the crack opening displacement immediately before fracture occurs is — at the known geometry of problem — exclusively a material property.

Material toughness measurement (COD method) is therefore based on the method of measuring the critical displacement of the crack surface. Gliha⁵ quotes in his review paper that the critical size of a crack opening displacement is a parameter related only to the plastic zone at its root. The properties within the plastic zone are changing and thus we have to do with a considerable scatter of results when the critical size of the crack surface displacement is measured.

The parameter which does not include only the influence of plastic zone is the critical value of the curved J-integral along any arbitrary path, enclosing the crack tip. For the case that the specimen has unit thickness, it can be written as:

$$J = -\frac{dU_p}{da} = \int_{\Gamma} W dy - \int_{\Gamma} \mathbf{T} \frac{\partial \mathbf{u}}{\partial x} ds, \quad (1)$$

dU_p/da stands for the change of potential energy per unit crack propagation, W is deformation energy per unit volume, \mathbf{u} is the displacement vector in the direction of external force action \mathbf{T} on the contour Γ . The term $\mathbf{T}(\partial \mathbf{u}/\partial x) ds$ represents the rate of work input from the stress



Slika 1

Integracijska pot krivuljnega integrala J je kontura Γ , ki objema plastično cono ob korenu razpoke

Fig. 1

Integrating path of the curve J-integral is the contour Γ , surrounding the plastic zone at the crack root.

polja v področje, obdano s konturo Γ . Več o J-integralu najde bralec v zelo razširjeni tozadevni literaturi^{6,7}, pomen simbolov v enačbi (1) pa je sicer razviden tudi s sliko 1.

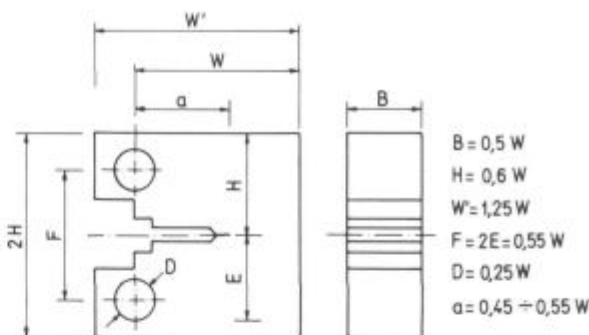
Metoda J-integrala je torej zasnovana na energijskem modelu loma, pri čemer je kritična vrednost J_C definirana kot vrednost J integrala tik pred lomom. Rice⁸ je dokazal, da je J-integral od poti neodvisen, zato lahko za njegovo izračunavanje, t. j. za vrednotenje elasto-plastičnega sproščanja energije namenoma izberemo takšno konturo, ki vključuje le bremena s pripadajočimi elastičnimi pomiki. Običajno je takšna kontura kar obris preizkušanca, za katerega so bremena in pomiki poznani, namreč izmerjeni.

Kako pa eksperimentalno določimo kritično vrednost J-integrala? V ta namen izdelamo večje število takojimenovanih CT preizkušancev, kakršen je prikazan na sliki 2. Ti preizkušanci imajo to posebnost — za razliko od podobnih CT preizkušancev za določevanje K_{IC} vrednosti — da lahko merilec hoda tzv. clip-gauge pozicioniramo natančno v linijo delovanja obremenitve. Zato, da dobimo dovolj oster koren razpoke, preizkušance predhodno pulzirajoče obremenjujemo z določeno, ne preveliko obremenitvijo.

Določevanje J_C vrednosti nato izpeljemo v pogojih kontroliranega pomika, t. j. pogojih kontroliranega odpiranja ustja razpoke, kar daje stabilno napredovanje razpoke. S sočasnim beleženjem obremenitve P ter odpiranja ustja razpoke δ dobimo opravljeno delo U enostavno s planimetričnim zapisom P- δ . Ob tem merimo še dolžino razpoke a, kot tudi njeno napredovanje Δa , kar predstavlja določen eksperimentalni problem. Vsakokratnemu napredovanju razpoke Δa ustreza odgovarjajoče opravljeno delo oz. energija U, s pomočjo katere izračunamo pripadajočo J vrednost v skladu z enačbo:

$$J = \frac{2U}{B(w-a)} f(a/w), \quad (2)$$

pri čemer je funkcija $f(a/w)$ odvisna od neto preseka preizkušanca. Najdemo jo v ustreznem standardu⁹.



Slika 2

Compact Tension (CT) preizkušavec za določevanje J integrala

Fig. 2

A compact tension (CT) specimen for determination of J-integral.

field into the area enclosed by the contour Γ . Detailed information about J-integral can be found in references^{6,7} and while the meaning of symbols used in equation (1) evident from Fig. 1.

This J-integral method is based on the fracture-energy model, the critical value J_C being defined as the value of J-integral immediately before the fracture sets in. Rice⁸ proved that J-integral is independent of the path. For its calculation, i. e. for the evaluation of elasto-plastic release of energy it is therefore possible to choose intentionally a contour including only loads with corresponding elastic displacements. Such a contour is usually represented by the very outline of the specimen for which loads and displacements are known, that is measured.

How can the critical J-integral value experimentally be defined?

In order to define it experimentally a great number of the so-called CT specimens (Fig. 2) was prepared. The peculiarity of these specimens is that the clip gauge can be positioned exactly in the line of load action in which they differ from the CT specimens used to determine K_{IC} values. In order to get a sufficiently sharp crack root the specimens are cycle loaded with a certain but not too heavy load.

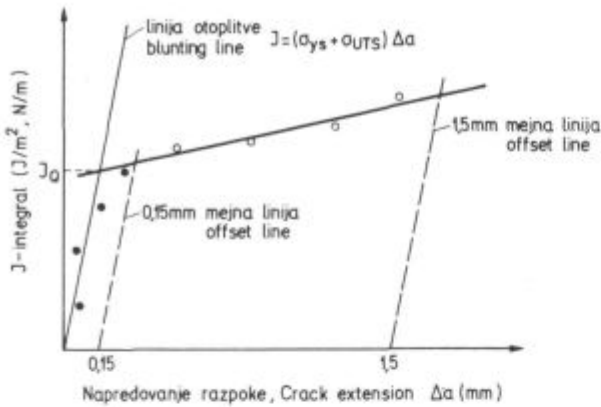
The J_C values are then determined under conditions of controlled displacement, i. e. under the conditions of controlled crack opening displacement, providing a stable crack propagation. By recording in the load P and the crack opening displacement δ , the work done U is obtained by planimetric treatment of the record P- δ plot. Simultaneously the crack length a and its propagation Δa are measured, which represents some experimental problem. Each crack propagation step Δa corresponds to an adequate work done or energy U. With the help of U it is possible to calculate the corresponding J-value according to equation:

$$J = \frac{2U}{B(w-a)} f(a/w), \quad (2)$$

The function $f(a/w)$ depends on the netto cross-section of a specimen and can be found in an adequate standard⁹.

The first measured J value is applied to determine the conditional J_0 value which must meet the following conditions:

$$B \text{ and also } (w-a) > \frac{25J}{\sigma_0}, \quad (3)$$



Slika 3

Odvisnost J integrala od napredovanja razpoke pri določanju J_{IC} vrednosti

Fig. 3

Relationship between the J-integral and the crack extension in determining the J_{IC} values.

Prva izmerjena vrednost J služi za določanje pogojne J_0 vrednosti, ki mora zadostiti zahtevam:

$$B, \text{ kot tudi } (w-a) > \frac{25 J}{\sigma_0}, \quad (3)$$

pri čemer smo s σ_0 označili napetost tečenja, ki je tu določena kot srednja vrednost med mejo plastičnosti σ_{ys} ter natezno trdnostjo σ_{uts} . S tako definirano napetostjo tečenja zajamemo namreč tudi deformacijsko utrjevanje materiala.

Minimalna debelina CT preizkušanca $B > 25 J/\sigma_0$ zagotavlja, da bo daljšanje razpoke Δa opravljeno pod pogoji ravninskega deformacijskega stanja, minimalna dolžina ligamenta $b = (w-a) > 25 J/\sigma_0$ pa preprečuje »tečenje« neto preseka preizkušanca.

Postopek določevanja veljavne J_{IC} vrednosti je prikazan na sliki 3. Postopek vključuje takoimenovano »blunting line procedure«, ki je uvedena za oceno navideznega napredovanja razpoke zaradi otopitve njenega korena. To navidezno napredovanje razpoke, merjeno z odpiranjem njenega ustja δ , bo manjše ali kvečjemu enako otopitvenemu radiusu korena, ki pa je enak polovici odpiranja, torej: $\Delta a \leq 0,5 \delta$. Upošteva se odvisnost $\delta = J/\sigma_0$, dobimo končno za enačbo linije otopitve naslednji izraz:

$$J = 2\sigma_0 \Delta a = (\sigma_{ys} + \sigma_{uts}) \Delta a \quad (4)$$

Omenimo naj še pomen obeh mejnih linij na sliki 3. Linija, označena kot 0,15 mm — mejna linija, zagotavlja, da bo napredovanje razpoke Δa vsaj 0,15 mm, da ga lahko dovolj natančno izmerimo. Linija, označena kot 1,5 mm — mejna linija, pa zagotavlja, da bo Δa v splošnem manjši od 6 % preostale dolžine ligamenta $(w-a)$, saj do te vrednosti ostane v veljavi enačba (2).

Veljavne vrednosti med obema linijama povežemo z regresijsko premico, katere presečišče z linijo otopitve daje J_0 vrednost. Tako določena pogojna J_0 vrednost je, ako sta izpolnjena pogoja (3), že tudi J_{IC} integral.

3. EKSPERIMENTALNI DEL Z REZULTATI

3.1 Določevanje J_{IC} -integrala

Za preiskave smo izbrali dva kosa jeklene pločevine, in sicer pločevino, debeline 40 mm, izdelano iz jekla Nionical 70, ter pločevino, debeline 25 mm, izdelano iz jekla Niomol 490.

σ_0 indicates the yield stress, defined as the mean value of the yield point σ_{ys} and the ultimate stress σ_{uts} . Yield stress defined in this way includes the strain hardening of the material, too.

The minimal thickness of a CT specimen $B > 25 J/\sigma_0$ guarantees that the crack propagation Δa will proceed under plane strain conditions and the minimal length of ligament $b = (w-a) > 25 J/\sigma_0$ prevents the yielding of the netto cross-section of the specimen.

The method to determine the valid J_{IC} value is shown in Fig. 3. It includes the so-called »blunting line procedure« which has been introduced in order to estimate the apparent crack propagation due blunting of its root. This apparent crack propagation measured by the crack opening displacement δ will be smaller or at least equal to the blunted root radius which itself is equal to one half of the opening: $\Delta a < 0,5 \delta$. Considering that $\delta = J/\sigma_0$, the following expression is obtained for the blunting line equation:

$$J = 2\sigma_0 \Delta a = (\sigma_{ys} + \sigma_{uts}) \Delta a \quad (4)$$

The meaning of both offset lines in Fig. 3 should specially be explained. The 0.15 mm offset line guarantees that the crack propagation Δa must be at least 0.15 mm in order to enable accurate measurement. The 1.5 mm offset line, on the other hand, guarantees that Δa will on the whole be less than 6 % of the remaining ligament length $(w-a)$ because equation (2) is only valid up to this value.

The valid values between both lines can be connected by a regression straight line. Its intersection with the blunting line represents the J_0 value. In a case that both conditions (3) are fulfilled, the J_0 represents the J_{IC} integral as well.

3. EXPERIMENTS AND RESULTS

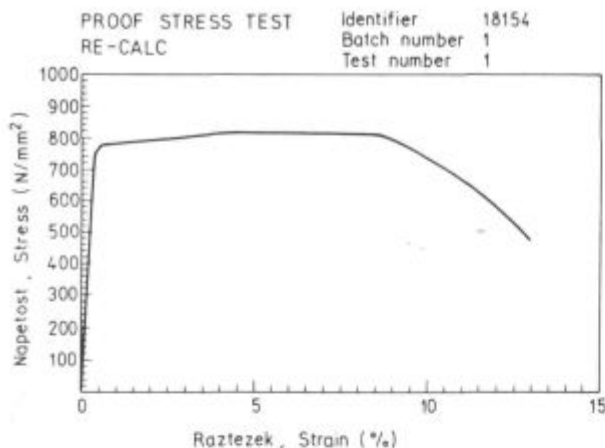
3.1 Determination of J_{IC} integral

For our investigation two pieces of steel sheet were chosen: a 40 mm thick sheet of Nionical 70 and a 25 mm thick sheet of Niomol 490.

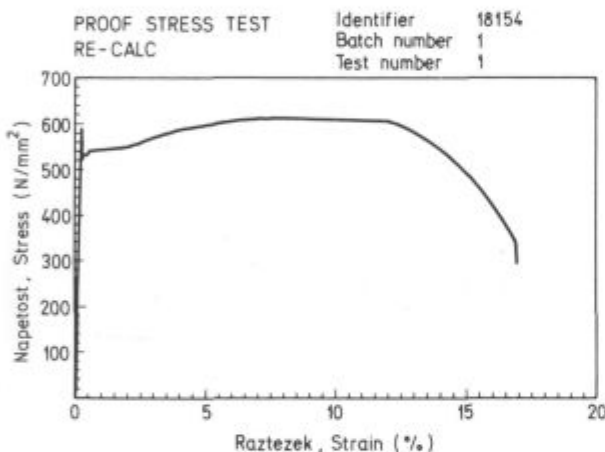
Nionical 70 is a micro-alloyed steel applicable for dynamically loaded structures on low temperatures, containing 0.15 % C, 1.2 % Cr, 2.6–2.8 % Ni, 0.3 % Mo and 0.07 % V. With an ultimate tensile strength of 740–940 MPa, the yield strength of this steel with tempered martensitic microstructure achieves the value of at least 690 MPa. At a temperature of -60°C the V-notch Charpy toughness in longitudinal direction is still 94 J and in transversal direction 47 J. In welding conventional thicknesses, this steel must be preheated to 120°C .

Niomol 490 is of more recent date and it belongs to the group of micro alloyed steels which needn't be preheated in welding. It contains up to 0.10 % C, 1.2 % Mn, 0.3 % Mo and 0.04 % Nb and has a bainitic microstructure with a yield strength of at least 490 MPa at an ultimate tensile strength of 560–740 MPa. The V-notch Charpy toughness measured at -60°C is somewhat lower than in Nionical, being at least 39 J in longitudinal and 31 J in transversal direction.

Of both steels a greater number of CT specimens was made with the characteristic dimension $w = 36,50$ or 100 mm in longitudinal as well as in transversal direction. Besides, some cylindrical specimens were made for determination of conventional mechanical properties. The results of tensile tests are shown in plots in Figures 4 and 5. In Nionical 70 the yield strength of 748 MPa and



Slika 4
Zapis nateznega preiskusa jekla Nionical 70
Fig. 4
Record of the tensile test for Nionical 70.

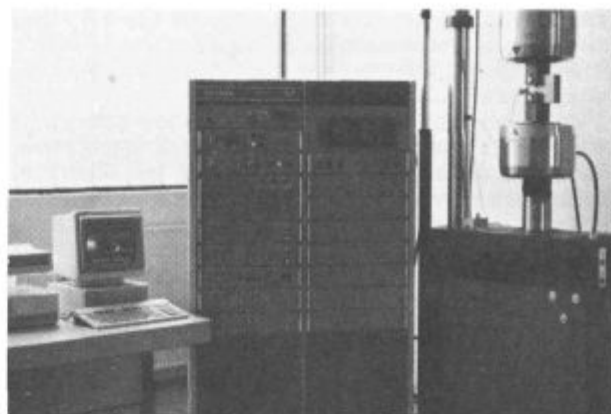


Slika 5
Zapis nateznega preiskusa jekla Niomol 490
Fig. 5
Record of the tensile test for Niomol 490.

Nionical 70 je mikrolegirano jeklo, uporabno za dinamično obremenjene konstrukcije pri nizkih temperaturah. Vsebuje od 0,15 % C, 1,2 % Cr, od 2,6 do 2,8 % Ni, 0,3 % Mo ter 0,07 % V. Pri trdnosti 740 do 940 Mpa dosega meja plastičnosti tega jekla z mikrostrukturo popuščene martenzita vsaj 690 MPa. Žilavost Charpy-V je pri temperaturi -60°C v vzdolžni smeri še vedno 94 J ter v prečni še vedno 47 J. Pri varjenju običajnih debelin moramo to jeklo predgrevati do temperature 120°C.

Jeklo Niomol 490 je novejšega izvora ter spada v skupino mikrolegiranih jekel, ki jih pri varjenju ni potrebno predgrevati. Vsebuje do 0,10 % C, do 1,2 % Mn, 0,3 % Mo ter 0,04 % Nb. Ima bainitno mikrostrukturo z mejo plastičnosti vsaj 490 MPa pri trdnosti od 560 do 740 MPa. Žilavost Charpy-V, merjena pri temperaturi -60°C, pa je nekoliko slabša kot pri Nionicalu. V vzdolžni smeri dosega vsaj 39 J, v prečni pa vsaj 31 J.

Iz obeh kosov pločevine smo izdelali večje število CT preizkušancev s karakteristično dimenzijo $w=36$, 50 oziroma 100 mm, in sicer tako v vzdolžni kot tudi v prečni smeri. Poleg teh smo izdelali še tudi nekaj cilindričnih preizkušancev za določevanje konvencionalnih mehanskih lastnosti. Rezultati nateznih preizkusov so prikazani



Slika 6
Preiskuševalni stroj INSTRON 1343
Fig. 6
"INSTRON 1343" testing machine.

the ultimate tensile strength of 823 MPa were measured. The corresponding values for Niomol 490 were 533 MPa and 618 MPa respectively.

J-integral was determined with the help of the static/dynamic testing machine INSTRON 1343 with the capacity of 500/250 kN, controlled by a HP 9000/310 computer. The testing machine shown in Fig. 6 is used at Inštitut za metalne konstrukcije in Ljubljana and is of a hydraulic type with a closed control system.

For specific testing requirements a series of clip gauges was made to measure the crack opening displacements. In Fig. 7 a 15 mm clip gauge is shown. Its accuracy is 0.5 %. It is mounted on a CT specimen in the line of load action.

The fatigue crack was initiated in all specimens by a dynamic load of a sine shape in the range of stress intensity factor $\Delta K=1000 \text{ Nmm}^{-3/2}$ by 850 cycles per mm of crack propagation increment. All measurements were made at 20°C.

J-integral was determined in two ways, either with several specimens or with a single one. In the case of several-specimens method the crack extension was marked by thermal etching. In the case of a single specimen, however, the crack length was determined from the deflection of the specimen at partial unloading. The deflection of the specimen determined from the unloading line slope is directly related to the length of the crack.

Not fulfilling the size criterion (3) CT specimens with characteristic dimension $w=36$ mm were found unsuitable. Results obtained on specimens with $w=50$ mm were much better. Specimens with $w=100$ mm are tested now.

Plot in Fig. 8 shows the results for Nionical 70 measured by the method of unloading of a single specimen in transversal direction.

After a series of repeated measurements the following values were obtained:

	J_{IC} (kJ/m ²)
Nionical 70 in longitudinal direction	810—1020
in transversal direction	290—460
Niomol 490 in longitudinal direction	1570—1680
in transversal direction	700—990

v diagramih na slikah 4 in 5. Pri jeklu Nionical 70 smo namerili mejo plastičnosti 784 MPa ter trdnost 823 MPa, pri jeklu Niomal 490 pa mejo plastičnosti 533 MPa ter trdnost 618 MPa.

Za določevanje J-integrala smo uporabili statični/dinamični preizkuševalni stroj INSTRON 1343, zmogljivosti 500/250 kN, upravljan preko računalnika HP 9000/310. Preizkuševalni stroj, prikazan na sliki 6, je montiran na Inštitutu za metalne konstrukcije v Ljubljani in je hidravličnega tipa z zaprtim kontrolnim sistemom.

Za specifične potrebe preizkušanja smo izdelali serijo merilcev hoda (clip gauge) za merjenje odpiranja ustja razpoke. Na sliki 7 je prikazan merilec hoda 15 mm točnosti 0,5 %, montiran na CT preizkušancu v liniji delovanja obremenitve.

Vnašanje utrujenostne razpoke je pri vseh preizkušancih potekalo z dinamično obremenitvijo sinusne oblike v območju faktorja intenzitete napetosti $\Delta K = 1000 \text{ Nmm}^{-3/2}$ z 850 cikli na mm prirastka razpoke. Vsa merjenja so bila opravljena pri temperaturi 20 °C.

J-integral smo določali na dva načina, bodisi z več preizkušanci, pri katerih smo nato napredovanje razpoke markirali s toplotnim jedkanjem, bodisi z enim samim preizkušancem, kjer smo dolžino razpoke določili iz podajanja preizkušanca pri delnem razbremenjevanju. Iz naklona razbremenilne linije določena podajanje preizkušanca je namreč v neposredni zvezi z dolžino razpoke.

CT preizkušanci karakteristične dimenzije $w = 36 \text{ mm}$ so se že po prvih testih izkazali za neuporabne, ker ne zadovoljujejo velikostnega kriterija (3). Boljši so bili rezultati, dobljeni na preizkušancih s karakteristično dimenzijo $w = 50 \text{ mm}$, v teku pa so preizkusi na preizkušancih s karakteristično dimenzijo $w = 100 \text{ mm}$.

V diagramu na sliki 8 so zbrani rezultati merjenja z metodo enega preizkušanca z razbremenjevanjem, veljajo pa za jeklo Nionical 70 v prečni smeri.

Po velikem številu ponovljenih merjenj imamo končno:

		J_{IC} (kJ/m ²)
Nionical 70	vzdolžno	810—1020
	prečno	290—460
Niomal 490	vzdolžno	1570—1680
	prečno	700—990

Na sliki 9 je prikazana serija uporabljenih CT preizkušancev različnih debelin. Za polkrožno utrujenostno razpoko je možno na vsakem preizkušancu opaziti s toplotnim jedkanjem obarvano temnejšo frakturno površino, ki označuje med preizkušanjem napredovalo razpoko. Preseneča pa močna lateralna kontrakcija bokov preizkušancev ter s tem povezana strižna ustnica na frakturnih površinah celo največjega od uporabljenih preizkušancev, kar govori v prid domnevi, da je velikost plastične cone znatna v primerjavi z dimenzijami preizkušancev. Literatura^{10, 11} navaja, da pri merjenju odvisnosti lomne žilavosti (določene preko J-integrala) od temperature preizkušanja dosežemo določeno žilavost, ki jo pri višjih temperaturah preizkušanja nič več ne presežemo, pač pa žilavost le še pada. Govorimo o takoimenovanem platu žilavosti, ki pa je odvisen od debeline CT preizkušanca. Plato se pojavi, ko postane velikost plastične cone ravninskega napetostnega stanja r_p primerljiva z debelino preizkušanca B . V teh pogojih pride do močne plastične deformacije pred korenem razpoke in merjenje žilavosti ni več veljavno.

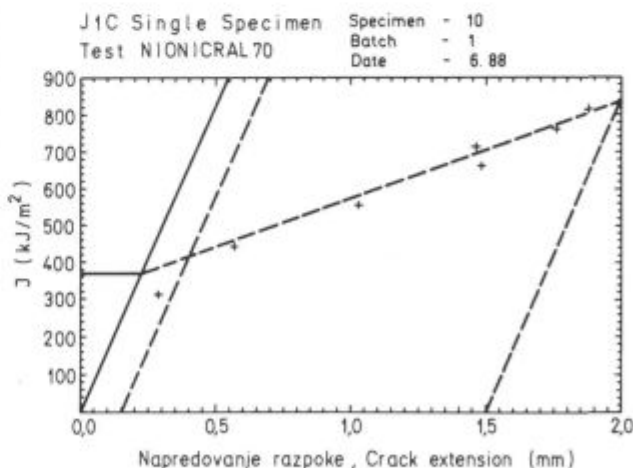


Slika 7

Obremenjen CT preizkušavec z montiranim merilcem hoda v liniji delovanja obremenitve

Fig. 7

Loaded CT specimen with a clip gauge mounted in the line of load action.

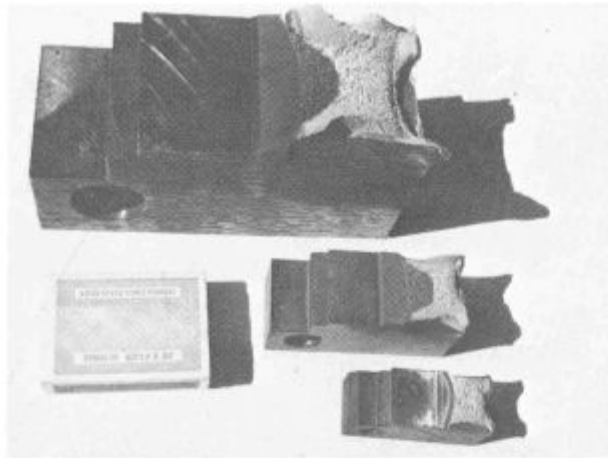


Slika 8

Diagramski prikaz določevanja J_{IC} vrednosti za jeklo Nionical 70 v prečni smeri

Fig. 8

Diagrammatical presentation of determining J_{IC} values in transverse direction for Nionical 70



Slika 9

Serijsa uporabljenih CT preiskušancev različnih debelin. Na sliki je za primerjavo še škatlica vžgalic.

Fig. 9

A series of used CT specimens of various thicknesses. For comparison's sake there is a box of matches.

Velikost plastične cone za ravninsko napetostno stanje določimo z enačbo:

$$r_p = \frac{1}{2\pi} \left(\frac{K_{IC}}{\sigma_{ys}} \right)^2 \quad (5)$$

Ker je med faktorjem intenzitete napetosti ter J-integralom naslednja zveza:

$$J = \frac{K_{IC}^2}{E'} \quad (6)$$

pri čemer je: $E' = E$ za ravninsko napetostno stanje ter $E' = E/(1 - \nu^2)$ za ravninsko deformacijsko stanje, dobimo končno rezultat, da pri meji plastičnosti 600 MPa, ki je na primer zgornja vrednost za Niomol 490, ter debelini preizkušanca 25 mm, lahko pravilno izmerimo le žilavost v območju do največ 240 MNm^{-3/2}, kar ustreza J_{IC} vrednosti največ 260 kJm⁻². Celo pri vzorcu dvojne debeline bi še vedno lahko pravilno merili le do 370 kJm⁻².

Milne in Chell^{12, 13} sta na primer pokazala, da testi s CT preizkušanci, ki sicer zadovoljujejo velikostne kriterije (3), lahko dajajo rezultate K_J (torej lomno žilavost izračunano preko J integrala), ki so tudi za faktor 2,5 večji od dejanske K_{IC} vrednosti.

Omenimo naj še empirično določen kriterij, ki so ga Bergerjeva in sodelavci¹⁴ našli za minimalno debelino CT preizkušancev za merjenje J-integrala. Kriterij v obliki:

$$B > 0,35 \left(\frac{K_J}{\sigma_{ys}} \right)^2 \quad (7)$$

predpisuje še dosti večje debeline preizkušancev, kot pa je to določeno s standardnim kriterijem (3).

Na osnovi povedanega lahko zaključimo, da so bile v okviru opravljenega eksperimentalnega dela izmerjene le okvirne vrednosti J_{IC} in da je pri korektnem merjenju J-integrala potrebno upoštevati poleg s standardom predpisanih kriterijev (3), nanašajočih se na debelino preizkušanca ter dolžino ligamenta, še tudi nekatere druge bolj ali manj empirične kriterije^{11, 14}.

3.2 Mikrofraktofske preiskave

Mikrofraktofske preiskave prelomnih površin CT preizkušancev so bile opravljene s scanning elektronskim mikroskopom na Metalurškem inštitutu v Ljubljani.

Fig. 9 shows several CT specimens of various thicknesses. For a semicircular fatigue crack it is possible to note a darker fracture surface coloured by thermal etching which denotes crack extension. Surprising is a severe lateral contraction of the sides and the shear lip on fracture surfaces even on the greatest specimens. It speaks in the favour of the hypothesis that the size of plastic zone is considerably great in comparison to the dimensions of specimens.

As cited in references^{10, 11}, a certain toughness is obtained when measuring the fracture toughness in relation (determined over a J-integral) to the testing temperature. At higher temperatures this toughness is not exceeded, it even tends to be reduced. We have to do with the so-called toughness plateau, depending on the thickness of the CT specimen. This plateau occurs when the size of plastic zone in the plane stress r_p becomes comparable to the thickness of the specimen B. Under these conditions a severe plastic deformation takes place in front of the crack root, making all subsequent toughness measurements non-valid.

The plane-strain plastic-zone-size-factor can be determined by the equation:

$$r_p = \frac{1}{2\pi} \left(\frac{K_{IC}}{\sigma_{ys}} \right)^2 \quad (5)$$

There is the following connection between the stress intensity factor and the J-integral:

$$J = \frac{K_{IC}^2}{E'} \quad (6)$$

where $E' = E$ for plane stress and

$E' = E/(1 - \nu^2)$ for plane strain

Thus it becomes evident that with the yield strength of 600 MPa, which is e. g. the peak value for Niomol 490, and with the sample thickness of 25 mm it is only possible to measure correctly the toughness values within the range up to 240 MNm^{-3/2}, which corresponds to a J_{IC} value of utmost 260 kJm⁻². Even with a specimen of a two-fold thickness it could be measured correctly only up to 370 kJm⁻².

Milne and Chell^{12, 13} have shown that tests with CT specimens which actually satisfy all size criteria (3) can give results for K_J (i. e. for fracture toughness calculated from J-integral being even 2.5 times higher than the actual K_{IC} values).

Let us mention here the empirically defined criterion for minimal thickness of CT specimens, found by Berger and his colleagues¹⁴, which is suitable for measuring the J-integral. According to the criterion in the form of:

$$B > 0,35 \left(\frac{K_J}{\sigma_{ys}} \right)^2 \quad (7)$$

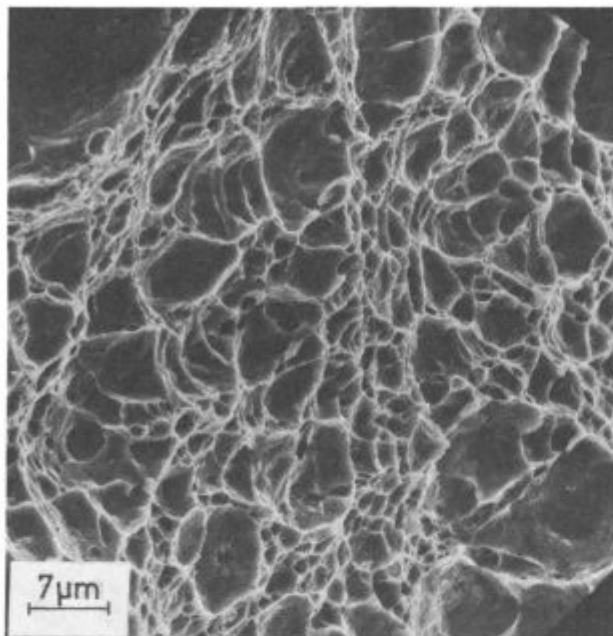
far greater thicknesses are demanded than those determined by the standard criterion (3).

It can be concluded that only approximate J_{IC} values were measured. For correct measuring of J-integral it is necessary to consider not only the standard criteria (3) referring to the thickness of a specimen and to the length of the ligament but also some other more or less empirical criteria^{11, 14}.

3.2 Microfractographic investigations

The fracture surfaces of CT specimens were investigated by a scanning electron microscope at the Institute of Metallurgy in Ljubljana.

In Fig. 10 there is a dimpled fracture surface (Niomol 490) which corresponds to a ductile type of fracture. The



Slika 10

Jamičasta frakturna površina CT preiskušanca iz jekla Niomol 490, sicer značilna za duktilno obliko loma.

Fig. 10

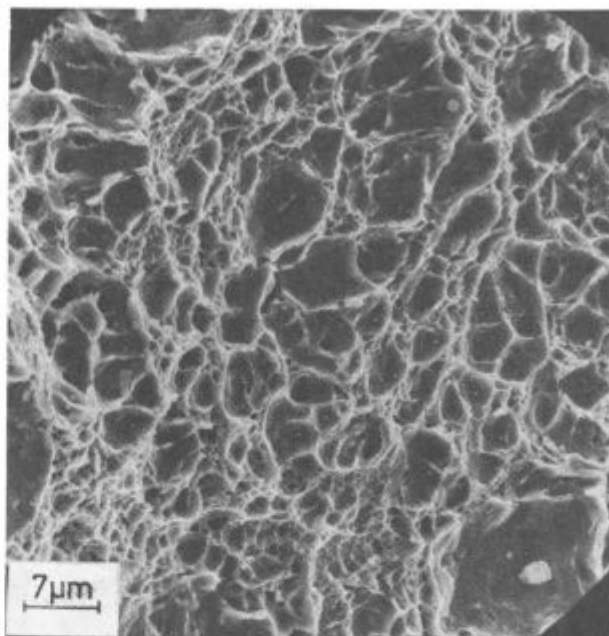
Dimpled fracture surface of a CT specimen of Niomol 490, normally characteristic for a ductile fracture.

Na sliki 10 je prikazana jamičasta prelomna površina pri jeklu Niomol 490, ustrežna duktilnemu tipu preloma. Premer jamic se giblje v mejah od 1,3 do 5 μm . Zelo podobna je prelomna površina pri jeklu Nionical 70, prikazana na sliki 11, čeprav je premer jamic v tem primeru nekoliko manjši, vsega 0,5 do 3,5 μm . Ti podatki se dobro ujemajo z rezultati merjenj J_{IC} vrednosti. Premer jamic na frakturni površini je namreč v določeni soodvisnosti z volumnom plastično deformiranega materiala neposredno ob frakturni površini, torej tudi v soodvisnosti z izmerjeno žilavostjo jekla. Vendar pa ta soodvisnost ni trdna, ker k žilavosti jekla, merjeni z metodo J-integrala, prispeva prvenstveno energija, nakopičena v plastični coni, in le v manjši meri energija, potrebna za neposredno formiranje novonastalih frakturnih površin. Vsekakor je velikost plastične cone pred korenem razpoke za več velikostnih redov večja od velikosti jamic na frakturnih površinah.

4. ZAKLJUČKI

Merjenja J_{IC} integrala drobnozrnatih mikrolegiranih jekel Nionical 70 ter Niomol 490 kažejo, da je žilavost Niomola, merjena pri temperaturi 20°C, znatno boljša od žilavosti Nionicala, čeprav so bile lahko izmerjene le orientacijske vrednosti. Močna lateralna kontrakcija bokov preizkušancev ter s tem povezana strižna ustnica na frakturnih površinah celo največjih CT preizkušancev namreč pomeni, da je velikost plastične cone primerljiva z debelino preizkušancev ter so zato izmerjene vrednosti vprašljive. Čeprav preizkušanci zadovoljujejo standardne velikostne kriterije (3), pa je pri korektnem merjenju potrebno upoštevati tudi še kriterij na osnovi velikosti plastične cone (5), kot je to opisano v članku, pa tudi empirični kriterij Bergerjeve¹⁴ (7), ki se zdi še ostrejši.

Mikrofraktografske preiskave potrjujejo rezultate merjenj žilavosti. Frakturne površine so v vseh primerih



Slika 11

Podobna kot na sliki 10 je tudi frakturna površina CT preiskušanca iz jekla Nionical 70

Fig. 11

The fracture surface of a CT specimen of Nionical 70, similar to that shown in Fig. 10.

diameter of dimples ranges within 1.3 and 5 μm . The fracture surface for Nionical 70 shown in Fig. 11 is very similar to the previous one although the diameter of dimples was slightly smaller — 0.5 to 3.5 μm . These results are in a good agreement with results obtained by J_{IC} measurements. The diameter of dimples on a fracture surface is namely to some extent related to the volume of plastically deformed material in the surrounding of the fracture surface and therefore also to the measured toughness of a steel too. But this relation is not fixed, as the energy accumulated in the plastic zone contributes much more to the steel toughness measured by J-integral method than to the energy needed for direct formation of newly initiated fracture surfaces. In any case the size of plastic zone in front of the crack root is for several orders of magnitude greater than the size of dimples on fracture surfaces.

4. CONCLUSIONS

Measurements of J-integral in fine-grained micro-alloyed steels Nionical 70 and Niomol 490 indicate that the toughness of Niomol 490 measured at 20°C is much better than that of Nionical, although only approximate values could be measured. A severe lateral contraction of the sides of specimens and the corresponding shear lip on the fracture surfaces of even the greatest CT specimens mean that the size of plastic zone is comparable to the thickness of a specimen, thus the measured values are questionable. Although the specimens satisfy the standard size criteria (3) it is necessary for obtaining correct results to consider the criterion based on the size of plastic zone (5) as described in the paper, as well as the empirical Berger's criterion¹⁴ (7) which seems even more rigid.

Microfractographic investigations confirm the results of toughness measurements. Fracture surfaces are in all

jamičaste, duktilne, vendar pa je volumen jamic pri Niomolu opazno večji od volumna jamic pri Nionicalu. Zveza med velikostjo jamic na frakturnih površinah ter izmerjeno žilavostjo pa ni preveč trdna zaradi dominantnega prispevka plastične cone — slednja je za več redov velikosti večja od velikosti jamic — k izmerjeni žilavosti jekla.

cases of ductile type with dimples, though the volume of dimples in Niomol is notably greater than that in Ninicral. The relation between the size of dimples on fracture surfaces and the measured toughness is no very reliable due to the dominating contribution of the plastic zone — the latter is for several orders of magnitude greater than the size of dimples — to the measured steel toughness.

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SLOVENSKE ŽELEZARNE

ŽELEZARNA

ŠTORE

ŠTORE

PROIZVODNI PROGRAM

Toplo valjani profili

- kvalitetno in plemenito ogljikovo jeklo ter
- kvalitetno in plemenito nizko legirano jeklo v okrogli, ploščati in kvadratni obliki,
- specialni profili po načrtih

Hladno oblikovani profili

- vlečeno in brušeno jeklo v vseh kvalitetah v okrogli, ploščati in specialni izvedbi

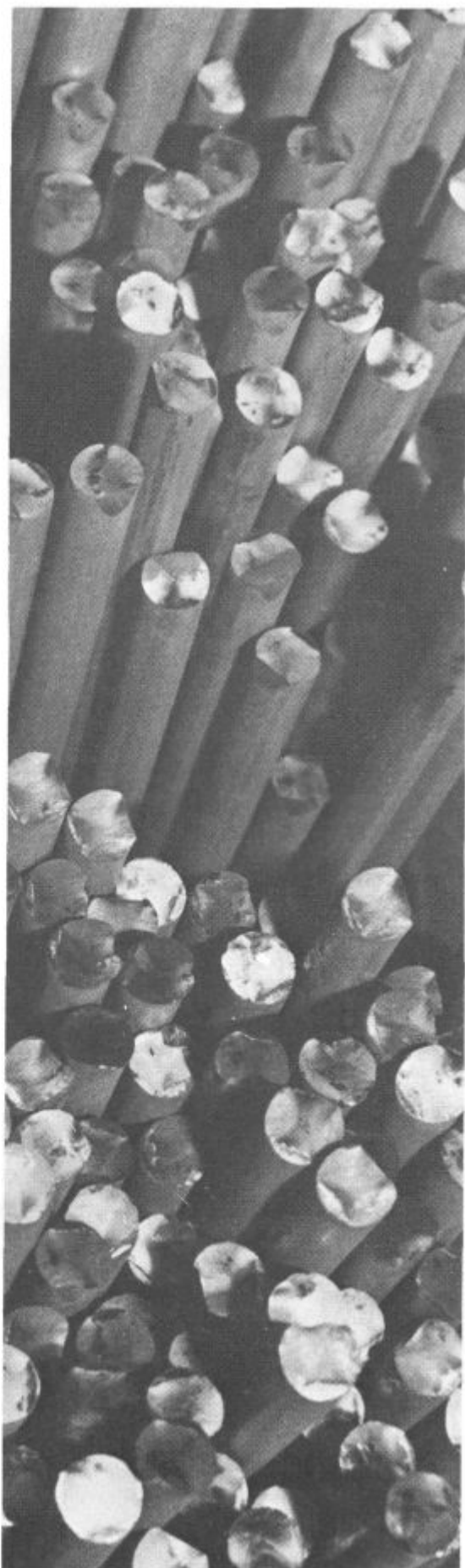
Livarski proizvodi

- ulitki iz sive litine,
- ulitki iz nodularne (KGR) litine,
- kontinuirno liti profili,
- litoželezni valji,
- jeklarske kokile,
- priklopna sedla,
- mehanski sklopi,
- strmoramenska platišča

Industrijska oprema

- industrijski gorilniki, industrijske peči za ogrevanje, žarenje itd.,
- indukcijske peči,
- rekuperativna toplotna tehnika,
- plinski oskrbovalni sistemi za ZP in zamenljive mešanice

*Vlečene
palice
kakovostnega
jekla*



Lomna žilavost ledeburitnega kromovega jekla

Fracture Toughness of Ledeburite Chromium Steel

S. Golubović*, L. Kosec**

UDK: 620.178:669.15—196.58
ASM/SLA: Q6, Q7, Q26q, T5h, 2 — 64

S poskusi smo ugotovili kritično vrednost faktorja intenzivnosti napetosti pri ravninski deformaciji za kromovi ledeburitni jekli Č.4150 in Č.4850. Jekli sta bili kaljeni in popuščeni pri temperaturah 180, 400 in 500 °C.

Kritično vrednost faktorja intenzivnosti napetosti K_{IC} smo določali s polempirijsko metodo. Uporabili smo CT epruvete, v katerih smo z utrujanjem ustvarili začetne razpoke. S temperaturo popuščenja se lomna žilavost obeh jekel zmanjšuje. Jeklo Č.4850 ima skozi ves interval temperatur popuščenja boljše lomno žilavost.

The magnitude of the critical stress intensity factor in plane strain state was found out experimentally for ledeburite chromium steels Č.4150 and Č.4850. The two steel qualities were hardened and subsequently tempered to temperatures 180, 400 and 500 °C. The critical stress intensity factor K_{IC} was determined by a semi-empirical method. In the experiments CT-specimens were used which were fatigued to create initial cracks. It was found out that with increasing temperature of tempering the fracture toughness of both steel qualities decreases.

1. UVOD

Visokoogljčna in mnogolegirana orodna jekla imajo praviloma mnogo slabšo udarno in lomno žilavost od konstrukcijskih jekel. Ta jekla, vgrajena v orodja, morajo imeti visoko trdoto in z njo povezano obrabno obstojnost, visoko tlačno trdnost in mnoge tehnološke lastnosti, tako, da ostanejo v jeklu zelo majhne rezerve oz. prostostne stopnje, ki naj poskrbe za žilavost.

Pri raznovrstnih orodjih, ki se izdelujejo iz teh jekel, pa so tudi odpornost proti udarcem, koncentracijam napetosti in krhkemu, nenadnemu prelomu pričakovane lastnosti. Pri tej vrsti jekel ni tako velikih absolutnih povečanj obeh vrst žilavosti, kot jih dosežejo npr. konstrukcijska jekla na račun spremenjene kemične sestave ali toplotne obdelave. Lahko pa se na podoben način dosežejo precejšnja relativna povečanja, kar znajo uporabniki teh jekel ceniti. Udarna žilavost je podatek, ki že v veliko primerih dopolnjuje tradicionalno opremo diagramov popuščenja, o lomni žilavosti pa pri tej vrsti jekel ni kaj posebej izmerjenega. Vzrok so težave pri meritvah.

Ledeburitna kromova jekla so dobro znana in uporabljena za orodja, ki delajo v hladnem. Poleg klasičnih primerov poškodb zaradi obrabe se mnogo teh orodij tudi poruši.

Podatki o žilavosti pomagajo pri načrtovanju, izbiri jekel in njihovi toplotni obdelavi. Namen tega prispevka je pokazati rezultate poskusa izmeriti lomno žilavost gradiva, ki je po svoji naravi krhko in zavoljo tega predstavlja veliko težavo pri preizkušanju.

Lomno žilavost dveh značilnih predstavnikov kromovih ledeburitnih jekel, Č.4150 in Č.4850, smo merili pri temperaturi okolice po treh temperaturah popuščenja (180, 400 in 500 °C).

1. INTRODUCTION

High carbon highalloyed tool steels are characterized by a much lower impact- and fracture toughness than structural steels. As tool components, these steels have to possess a high hardness and accompanying wear resistance, a high compressive strength and many other technological properties, so that there are very few reserves left in the steel to provide it with toughness.

The variety of tools which are manufactured of these steels requires the resistance to impact, stress concentrations and sudden brittle fracture which should also be counted among the expected properties. With this type of steel there are no absolute sharp increases in both types of toughness similar to those attained by structural steels due to their changed chemical composition or heat treatment. It is, however, possible by means of similar procedures to achieve considerable relative increases in toughness, which is much appreciated by the users of these steels. Impact toughness is an item of data which has in many cases entered the traditional tempering diagrams whereas fracture toughness is not especially mentioned with this type of steel. The reason for this lies in experimental difficulties.

Ledeburite chromium steels are well known and frequently used for cold work tools. Besides the classical types of damage due to wear, many of these tools also experience fracture.

The data about toughness contribute to better planning, and selection of steels and their heat treatment. The aim of this paper is to present the results of the experiments and the measured values of fracture toughness of a material which is characterized by nature as brittle and therefore difficult to test.

The fracture toughness of two representative chromium ledeburite steel qualities Č.4150 and Č.4850 was measured at the ambient temperature after three different temperatures of tempering (180, 400 and 500 °C).

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** Originalno objavljeno: ZEB 22 (1988) 4

*** Rokopis prejet: avgust 1988

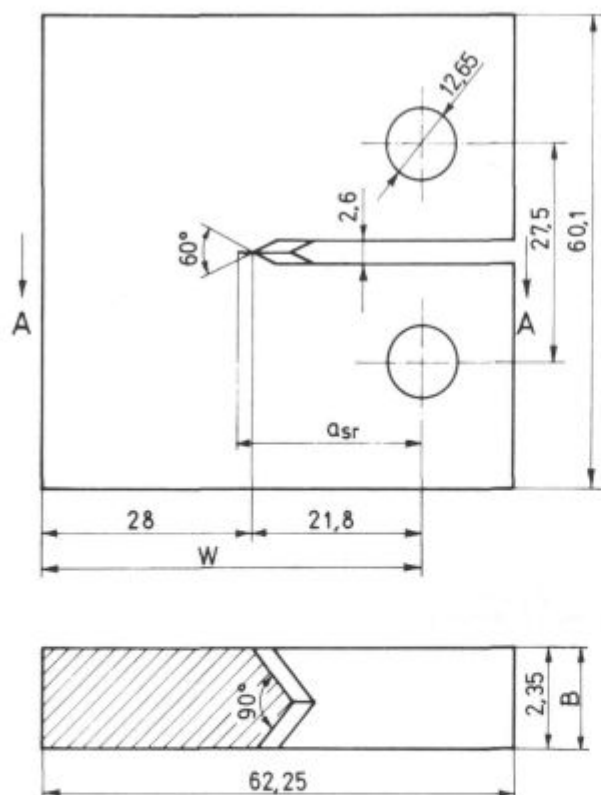
2. OPIS POSKUSOV

Preiskovani jekli sta imeli naslednjo kemično sestavo:

	(%)						
	C	Si	Mn	P	S	Cr	Mo
Č.4150 (OCRI2)	1,97	0,34	0,36	0,030	0,030	11,30	0,1
Č.4850 (OCRI2VM)	1,53	0,40	0,30	0,025	0,025	11,60	0,83
	V	Ni	Cu	Al			
Č.4150 (OCRI2)	1,53	0,19	0,15	0,016			
Č.4850 (OCRI2VM)	1,18	0,17	0,22	0,049			

Jekli smo stalili na zraku v indukcijski peči in ulili v ingote kvadratnega preseka 220 mm. S kovanjem smo dobili gredice kvadratnega preseka z robom 65 mm. Jeklo je bilo pred izdelavo epruvet mehko žarjeno.

Epruvete za mehanske preizkuse (trdnost, udarna in lomna žilavost) iz jekla Č.4150 smo kalili iz solne kopeli pri 960 °C v olje in jih dvakrat po eno uro popuščali na posameznih temperaturah; jeklo Č.4850 je bilo kaljeno na enak način s temperature 1010 °C in enako popuščano. Mikrostrukturo litega, kovanega in toplotno obdelanega jekla smo preiskali z optičnim in transmisivnim elektronskim mikroskopom, količino primarnih karbidov smo izmerili s Quantimetom 720, naravo sekundarnih karbidov z elektronsko difrakcijo, količino zaostalega avstenita pa rentgenografsko.



Slika 1

Geometrija uporabljene CT epruvete s puščičasto zarezo

Fig. 1

Geometry of the CT specimen with an arrow-like notch

2. DESCRIPTION OF EXPERIMENTS

The investigated steel qualities had the following chemical composition:

	(%)						
	C	Si	Mn	P	S	Cr	Mo
Č.4150	1,97	0,34	0,36	0,030	0,030	11,30	0,1
Č.4850	1,53	0,40	0,30	0,025	0,025	11,60	0,83
	V	Ni	Cu	Al			
Č.4150	1,53	0,19	0,15	0,016			
Č.4850	1,18	0,17	0,22	0,049			

The steels were melted in the air in the induction furnace and cast into ingots with square cross-sectional area (220 mm). Out of these, billets with square cross-sectional area were forged with the edge measuring 65 mm. Prior to the fabrication of the test specimens, the steel was annealed.

The specimens for mechanical testing (strength, impact and fracture toughness) made of steel quality Č.4150 were quenched from the salt bath at the temperature 960 °C into oil and tempered twice for one hour at each temperature. The steel quality Č.4850 was hardened in the same way from the temperature 1010 °C and also tempered in the same way. The microstructure of the cast, forged and heat treated steel was searched with the optical and TEM — the quantity of carbides was measured with Quantimet 720, the nature of secondary carbides was studied by electron diffraction, and the quantity of residual austenite from X-ray technique.

The magnitude of fracture toughness (stress intensity factor) was measured by means of CT-specimens, the geometry of which ensured a plane strain state. The specimens were cut out of billets so that the cut ran rectangularly to the direction of deformation and the tensile stress was acting in the direction of the deformation of the billet. The test bars were fabricated according to the ASTM E 399-83 standard, (1). The critical value of the stress intensity factor was determined semi-empirically by measuring the deformation on the CT-specimens (Figure 1) on which primary cracks were initiated by fatigue on the MTS 820 machine. After the fracture it was examined whether the fatigue crack fulfills the conditions of the experiment.

After the static fracture, the length and the tip shape of fatigue crack were measured as well as the forces F_0 and F_{max} . From the force F_0 we calculated the assumed value of the factor K_0 with the help of the equation:

$$K_0 = \frac{F_0}{B\sqrt{W}} \cdot \frac{(2 + a/W) \{0,886 + 4,64a/W - 13,32(a/W)^2 + 14,72(a/W)^3 - 5,6(a/W)^4\}}{\sqrt{(1 - a/W)^3}}$$

then the measuring conditions were controlled by calculating the following parameters:

$$B, a_{sr} \geq 2,5 \left(\frac{K_0}{R_{p0,2}} \right)^2, \quad (2)$$

where B is the thickness of the specimen and a the length of the crack.

Between the maximum value of the stress intensity factor $K_{I,max}$ in fatigue testing and the elasticity module, the following relationship has to hold true:

$$\frac{K_{I,max}}{E} \geq 0,00032 \sqrt{m}, \quad (3)$$

Velikost lomne žilavosti (faktorja intenzivnosti nape-
tosti) smo merili s pomočjo CT epruвет, katerih geome-
trijska je zagotavljala ravninsko deformacijsko stanje.
Epruvete smo izrezali iz gredic tako, da je bila zarezna
pravokotna na smer deformacije, natezna napetost pa je
bila v smeri deformacije gredice. Epruvete so bile izdelane
po standardu ASTM E 399-83 (1). Kritično vrednost
faktorja intenzivnosti napetosti smo določali polempiri-
čno z merjenjem deformacije na CT epruветah (slika 1),
na katerih je bila narejena primarna razpoka z utrujanjem
na stroju MTS 820.

Po prelomu smo ugotavljali, če utrujenostna razpoka
izpolnjuje pogoje poskusa.

Po statičnem prelomu smo izmerili dolžino in obliko
čela utrujenostne razpoke ter izmerili sili F_Q in F_{max} . Iz sile
 F_Q smo izračunali predpostavljeno vrednost faktorja K_Q s
pomočjo enačbe:

$$K_Q = \frac{F_Q}{B\sqrt{W}} \cdot \frac{(2 + a/W) [0,886 + 4,64a/W - 13,32(a/W)^2 + 14,72(a/W)^3 - 5,6(a/W)^4]}{\sqrt{(1 - a/W)^3}}$$

nakar smo kontrolirali pogoje merjenja še z računom na-
slednjih parametrov:

$$B, a_{sr} \geq 2,5 \left(\frac{K_Q}{R_{p0,2}} \right)^2, \quad (2)$$

kjer sta B debelina vzorca, a pa dolžine razpoke.
Med največjo vrednostjo faktorja intenzivnosti napetosti
 $K_{I,max}$ pri utrujanju in modulu elastičnosti mora veljati
odnos:

$$\frac{K_{I,max}}{E} \geq 0,00032 \sqrt{m}, \quad (3)$$

$$\text{razmerje obremenitev: } \frac{F_{max}}{F_Q} \geq 1,1 \quad (4) \text{ in}$$

velikost plastične cone na vrhu razpoke, ki mora biti
manjša od 2 % utrujenostne razpoke:

$$r_{pl} \leq 0,02 a_{sr}. \quad (5)$$

Če so izpolnjeni ti štirje pogoji, se privzame predposta-
vljena vrednost faktorja intenzivnosti napetosti K_Q kot
dejanska, kritična vrednost tega faktorja K_{IC} .

3. REZULTATI

Mikrostrukturne sestavine obeh preiskanih jekel po
toplotnih obdelavah so martenzit, primarni in sekundarni
karbidi ter zaostali avstenit (slika 2). Količina in narava
zadnjih dveh sestavin je navedena v tabeli 2.

Tabela 2:

Jeklo	T_{pop}	Karbidi (%)		Zaostali avstenit (%)
		$M_{23}C_6$	M_7C_3	
Č.4150	180	10,5	89,5	10,2
	400	11,2	88,8	5,0
	500	11,2	88,2	0
Č.4850	180	8,8	91,40	10,9
	400	7,94	92,06	10,6
	500	7,91	92,09	7,2

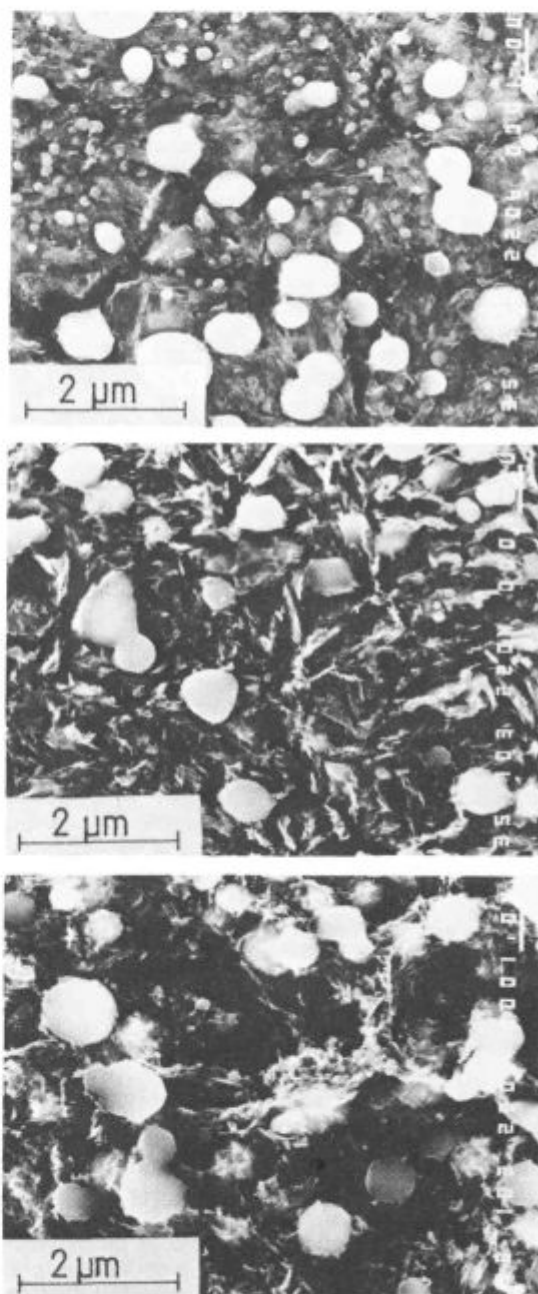
Mehanske lastnosti obeh jekel so zbrane v tabeli 3:

$$\text{the ratio of loads: } \frac{F_{max}}{F_Q} \geq 1,1 \quad (4) \text{ and}$$

the size of the plastic zone at the tip of the crack which
has to be smaller than a 2 % fatigue crack:

$$r_{pl} \leq 0,02 a_{sr}. \quad (5)$$

If the above four conditions are fulfilled, the assumed
value of the stress intensity factor K_Q can be taken as
the critical value of this factor K_{IC} .



Slika 2
Sekundarni karbidi v jeklu Č.4150 popuščenega na temperatu-
rah a) 180, b) 400 in c) 500 °C

Fig. 2
Secondary carbides in steel Č.4150 tempered at the temperatu-
res a) 180, b) 400 and c) 500 °C

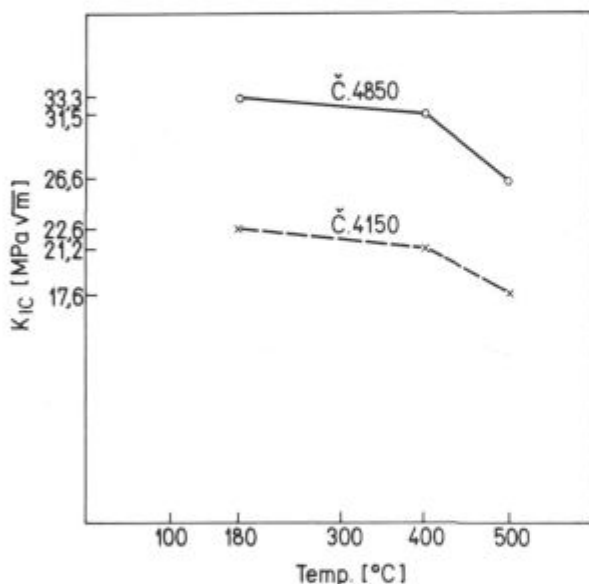
Tabela 3:

Jeklo	T_{pop}	R_m (MPa)	$R_{p0.2}$ (MPa)	E (MPa)	Trdota HRC	Žilavost MJ/m ²
Č.4150	180	1034	982	230000	62,8	0,078
	400	1024	973	230000	58,2	0,062
	500	1156	1098	230000	55	0,050
Č.4850	180	964	916	210000	62	0,075
	400	1033	981	210000	58	0,063
	500	1297	1232	210000	55	0,056

Kritične velikosti faktorja intenzivnosti napetosti K_{IC} pa so v tabeli 4. (Slika 3)

Tabela 4:

Jeklo	T_{pop} (°C)	K_{IC} (MPa√m)	Kontrola
Č.4150	180	22,6	$K_Q = K_{IC}$
	400	21,2	$K_Q = K_{IC}$
	500	17,6	$K_Q = K_{IC}$
Č.4850	180	33,3	$K_Q = K_{IC}$
	400	31,5	$K_Q = K_{IC}$
	500	26,6	$K_Q = K_{IC}$



Slika 3

Kritična vrednost faktorja intenzivnosti napetosti v odvisnosti od temperature popuščenja

Fig. 3

Critical stress intensity factor K_{IC} versus tempering temperature

4. Zaključek

Na način, ki je značilen za preizkušanje konstrukcijskih jekel, smo izmerili lomno žilavost dveh kromovih ledeburitnih orodnih jekel.

Osnovni problem pri preizkušanju je bil izdelati začetno razpoko z utrujanjem jekla. Izmerjeni faktorji intenzivnosti napetosti so odvisni od kemične sestave in mikrostrukture jekla.

Jeklo Č.4850 ima znatno boljšo lomno žilavost od jekla Č.4150. Pri obeh jeklih se lomna žilavost spreminja s temperaturo popuščenja jekla po kaljenju. Ta sprememba faktorja intenzivnosti napetosti je v dobri korelaciji s spremembo deleža zaostalega avstenita. Spremembe v

3. RESULTS

The microstructural components of both investigated steels after the heat treatment procedures are: martensite, primary and secondary carbides and residual austenite (Fig. 2). The amount and the nature of the last two components are presented in Table 2.

Table 2:

Steel	T_{pop}	Carbides (%)		Residual austenite (%)
		$M_{23}C_6$	M_7C_3	
Č.4150	180	10,5	89,5	10,2
	400	11,2	88,8	5,0
	500	11,2	88,2	0
Č.4850	180	8,8	91,40	10,9
	400	7,94	92,06	10,6
	500	7,91	92,09	7,2

The mechanical properties of the two steel qualities can be seen in Table 3:

Table 3:

Steel	T_{pop}	R_m (MPa)	$R_{p0.2}$ (MPa)	E (MPa)	Hardness HRC	Toughness MJ/m ²
Č.4150	180	1034	982	230000	62,8	0,078
	400	1024	973	230000	58,2	0,062
	500	1156	1098	230000	55	0,050
Č.4850	180	964	916	210000	62	0,075
	400	1033	981	210000	58	0,063
	500	1297	1232	210000	55	0,056

Finally, the critical values of the stress intensity factor K_{IC} are presented in Table 4. (Fig. 3)

Table 4:

Steel	T_{tem} (°C)	K_{IC} (MPa√m)	Control
Č.4150	180	22,6	$K_Q = K_{IC}$
	400	21,2	$K_Q = K_{IC}$
	500	17,6	$K_Q = K_{IC}$
Č.4850	180	33,3	$K_Q = K_{IC}$
	400	31,5	$K_Q = K_{IC}$
	500	26,6	$K_Q = K_{IC}$

4. Conclusion

A method which is typically used for testing structural steels was applied to measure the fracture toughness of two chromium ledeburite tool steels. The basic problem of the testing was how to initiate a crack by fatigue. The measured stress intensity factors are in dependence on the chemical composition and microstructure of the steel. Steel Č.4850 possesses a much higher fracture toughness than steel Č.4150. With both qualities of steel the fracture toughness varies with the temperature of tempering after the hardening procedure. This variation of the factor is in good correlation with the changing percentage of the residual austenite. The changes in the magnitude of the stress intensity factor are much more selective than the values of impact toughness measured

velikosti faktorja intenzivnosti napetosti so mnogo bolj selektivne od vrednosti udarne žilavosti, izmerjene po Charpyju na epruvetah z ostro V zarezo. Faktor intenzivnosti napetosti in vrednosti udarne žilavosti pri preiskanih jeklih se ne dajo povezati z znanimi empiričnimi obrazci.

Velikosti kritične vrednosti faktorja intenzivnosti napetosti za obe toplotno obdelani jekli dajejo v celotnem intervalu temperatur popuščanja prednost jeklu Č.4850. Te meritve posredno potrjujejo tudi znane vrednosti udarne žilavosti in prakso orodjarjev, ki dobro poznajo to prednost jekla Č.4850.

according to Charpy on test bars with a sharp V-notch. The stress intensity factor and the fracture toughness values of the investigated steels cannot be related to the known empirical patterns.

The magnitudes of the ultimate values of the stress intensity factor for both qualities of the heat treated steel examined over the whole temperature interval of tempering give priority to steel Č.4850. Thus these measurements are also an indirect confirmation of the known value of the impact toughness and the practical experience of tool makers who are well familiar with this advantageous feature of steel Č.4850.

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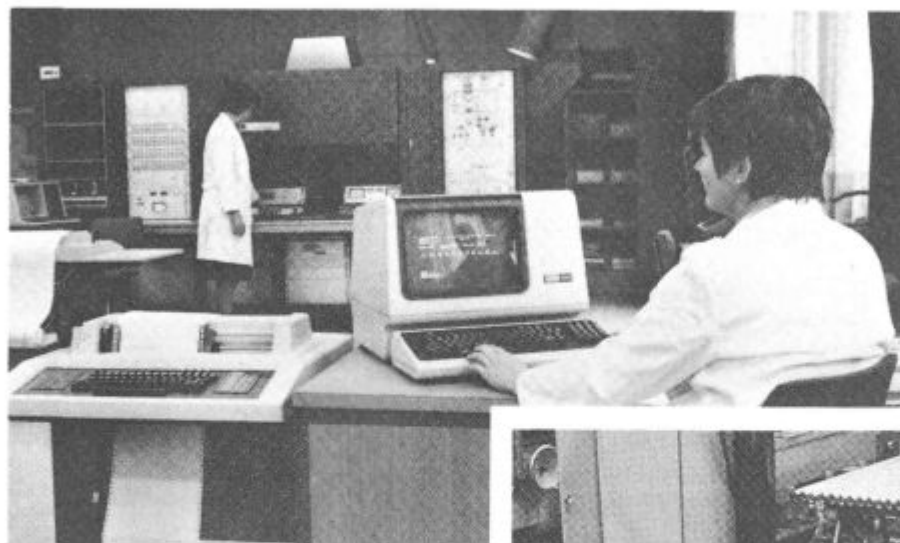


**SLOVENSKE ŽELEZARNE
ŽELEZARNA RAVNE**

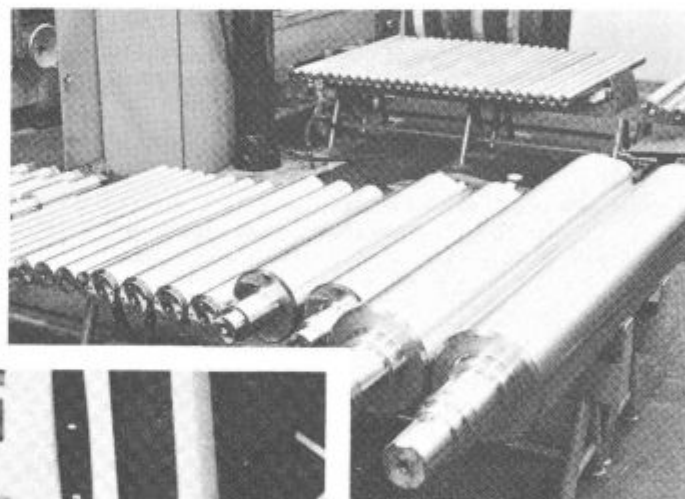
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**RAVNE NA KOROŠKEM
SLOVENIA - YUGOSLAVIA**

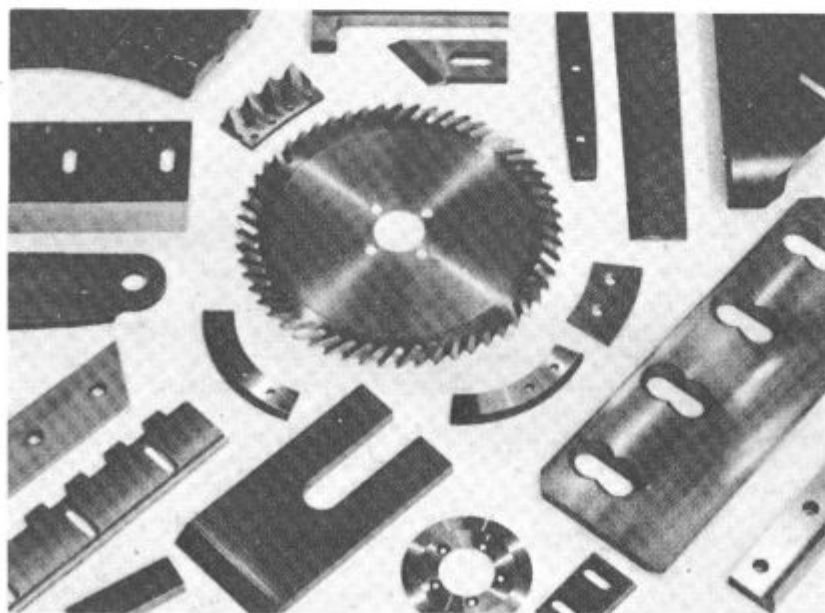
Železarna Ravne kot proizvajalec kvalitetnih in plemenitih jekel nenehno razvija in izpopolnjuje tehnološke postopke s ciljem povečevanja finalizacije, kvalitete, avtomatizacije in humanizacije dela. Izgradnjo novih tehnoloških naprav v jeklarni, kovačnici, termični obdelavi in širjenje proizvodnje finalnih izdelkov je spremljal intenziven tehnološki razvoj podprt z uvedbo procesnih računalnikov, numerično krmilnih enot ter avtomatizacije.



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Študij optimalnih pogojev za analizo kovinskih materialov z metodo ICP atomske emisijske spektrometrije

Investigation of Optimal Conditions for Metal Analysis by ICP Atomic Emission Spectrometry

A. Osojnik*, T. Lavrič*

UDK: 543.423
ASM/SLA: S11k, U2g

Študirali smo optimalne pogoje in aparativne parametre za analizo nikljevih zlitin s sekvenčno atomsko emisijsko spektrometrijo. Razvili smo metodo multielementne analize za določanje Ni, Co, Cr, Mo, Ti (60 do 2 %) ter Al, Fe, Mn, Cu in Si (1 do 0.005 %). Študirali smo spektralne interferences za vse prisotne elemente. Izbrali smo optimalne valovne dolžine, ter določili občutljivost, mejo zaznavnosti, korekcijske faktorje in reproduktivnost rezultatov. Točnost rezultatov smo preverili s certificiranimi referenčnimi materiali nikljevih zlitin podobnih sestav.

The optimal conditions and determination parameters for analysis of nickel base alloys by sequential ICP atomic emission spectrometry were studied. A method for determination of major Ni, Co, Cr, Mo, Ti (~60 to 2 w/w %) and minor components Al, Fe, Mn, Cu Si (~1 to 0.05 w/w %) using a single sample preparation technique was developed. Actual spectral interferences due to the influence of any present element were identified by wavelength scans near analyte wavelengths for Ni, Co, Cr, Mo, Ti, Al, Fe, Mn, Cu and Si. Optimal spectral lines, detection limits, sensitivities, additive correction factors and reproductivity of results were established. The accuracy of the results was checked with different certified materials of similar composition.

UVOD

Za hitro analizo kovin in zlitin se običajno najbolj uporabljata metodi emisijske spektrometrije z vzbujanjem z iskro in rentgenska fluorescenčna analiza. Alternativno možnost za analizo metalurških vzorcev predstavlja atomska emisijska spektrometrija z induktivno sklopljeno plazmo (ICP AES). Prednosti metode so predvsem možnost multielementne analize, dobra občutljivost, široko linearno koncentracijsko območje ter malo kemijskih motenj. V literaturi zasledimo številne publikacije o teoretičnih osnovah, operativnem razvoju, napredku in aplikacijah ICP AES za analizo kovinskih materialov^{1, 2, 3, 4, 5, 6, 7}. Vsak sistem zahteva specifičen način raziskovanja in kritično ovrednotenje rezultatov za izbiro optimalnih parametrov analize in dosego optimalne kombinacije občutljivosti, stabilnosti ter razmerja signal — ozadje za določen element.

To delo obsega raziskave za izdelavo analizne metode, ki omogoča določanje desetih elementov na različnih koncentracijskih nivojih v vzorcih nikljevih zlitin, tipa Nimonic.

EKSPERIMENTALNO DELO

Meritve smo izvršili s sekvenčnim vakuumskim emisijskim spektrometrom z ICP izvorom, firme Applied Research Laboratories (ARL), model 3520 OES. Karakteri-

INTRODUCTION

Routine analysis of metals and their alloys are commonly performed by spark emission spectrometry or x-ray fluorescence. Other alternative for analysis of metallurgical samples represents inductively coupled plasma atomic emission spectrometry with its multielement capability, good sensitivity, wide linear calibration ranges and freedom from chemical-type interferences. There are numerous publications on theory, progress and application of ICP atomic emission spectrometry for metal analysis^{1, 2, 3, 4, 5, 6, 7}. Each system requires specific way of investigation and critical evaluation of results to get optimal operating parameters giving the best combination of sensitivity, stability and line to background ratios for elements concerned.

The present paper reports about a single analytical method applicable to the determination of ten elements at major and minor constituent levels in samples of nickel base alloys of Nimonic type.

EXPERIMENTAL

Equipment

Applied Research Laboratories (ARL) 3520 OES vacuum sequential scanning inductively coupled plasma emission spectrometer was used for all measurements. The instrument specifications and operating conditions are given in Table 1.

* SŽ — Metalurški inštitut Ljubljana

** Originalno objavljeno: ZEB 22 (1988) 4
*** Rokopis prejet: avgust 1988

stike aparature in eksperimentalni parametri so navedeni v tabeli 1.

Tabela 1: Karakteristike aparature in eksperimentalni parametri

APARATURA:	ARL, model 3520 OES sekvenčni, vakuumski — spektrometer, ICP izvor
Spektrometer	
Monohromator:	1 m premera, Paschen-Runge nastavitev
Uklonska mreža:	1080 zarez/mm
Spektralno območje:	170—797 nm
Širina reže, primarna:	20 μ m
Širina reže, sekundarna:	50 μ m
RF generator	
Frekvenca:	27.12 MHz
Moč:	1200 W
Reflektirana moč:	< 5 W
ICP izvor	
Gorilec:	koncentričen, kremenčev, tip Fassel
Pretok Ar, hladilni:	12 l/min.
Pretok Ar, plazma:	0.8 l/min.
Pretok Ar, nosilni:	0.32 l/min.
Višina opazovanja:	15 mm nad tuljavo
Vnašanje raztopine	
Razpršilec:	steklen, tip Meinhard
Hitrost sesanja raztopine:	2 ml/min.
Analizni parametri	
Čas izpiranja:	15 s
Čas integracije:	2 s

Priprava vzorca

50 mg vzorca (v obliki finih ostružkov) zatehtamo v 100 ml čašo in previdno raztapljamo v 20 ml kislinke mešanice $H_2O : HCl : HNO_3 = 3 : 2 : 1$. Raztopino rahlo segrevamo, da se vzorec popolnoma raztopi, po potrebi filtriramo. Raztopino ohladimo na sobno temperaturo, prelijemo v 500 ml merilno bučo in dopolnimo do 500 ml z deionizirano vodo. Vzoredno pripravimo slep vzorec.

Umerjanje

Umeritvene krivulje smo izdelali s pomočjo multielementnih standardnih raztopin in s certificiranimi referenčnimi materiali nikljevih zlitin (BAS, MBH), ki smo jih raztapljali na enak način kot vzorce.

Multielementne standarde raztopine za umerjanje smo pripravili iz čistih kovin ali soli, ki smo jih raztopili v kislinski mešanici oziroma v vodi.

REZULTATI IN DISKUSIJA

Prvi korak pri razvoju analize metode je izbira in vrednotenje primernih spektralnih črt, ki so optimalne za posamezni element glede na sestavo vzorca in njegovo koncentracijsko območje. Možnost izbire med več emisijskimi črtami za posamezni element dovoljuje določanje več elementov v istem vzorcu v različnih koncentracijskih nivojih pri enakem faktorju razredčenja.

Spektralne interference, ki so posledica vpliva kate-regakoli prisotnega elementa v vzorcu zaradi prekrivanja spektralnih črt, smo ugotavljali z opazovanjem profila spektralnih črt pri ustreznih valovnih dolžinah za elemen-

Table 1: Instrumentation and operating conditions

APPARATUS:	ARL, model 3520 OES Sequential, vacuum spectrometer, ICP source
Spectrometer	
Monochromator:	1 m radius, Paschen-Runge mounting
Grating:	1080 grooves/mm
Spectral range:	170—797 nm
Slit width, primary:	20 μ m
Slit width, secondary:	50 μ m
RF Generator	
Frequency:	27.12 MHz
Incident power:	1200 W
Reflected power:	< 5 W
Plasma	
Plasma torch:	Three concentric quartz tubes, Fassel type
Argon flow rate, coolant:	12 l/min.
Argon flow rate, plasma:	0.80 l/min.
Argon flow rate, carrier:	0.32 l/min.
Observation height:	15 mm above load coil
Sample introduction	
Nebuliser:	glass concentric type (Meinhard)
Solution uptake rate:	2 ml/min.
Analysis parameters	
Flow time:	15 s
Integration time:	2 s

Sample preparation

500 mg of sample in the form of fine drillings was weighed into a 100 ml beaker and carefully dissolved in 20 ml of 3 : 2 : 1 mixture of $H_2O : HCl : HNO_3$. The solution was heated gently to complete the dissolution, and filtered where necessary. After cooling to room temperature, the solution was made up to 500 ml with deionised water in the volumetric flask. An acid blank of the appropriate concentration was also prepared.

Calibration

Calibration curves were obtained from direct intensity measurements made on multielement standard solutions or solutions of certified reference materials, supplied by the BAS (BCS) and MBH (Willan Metals Limited — Rotherham).

Stock calibration multielement standard solutions were prepared from pure metals or salts, dissolved in high purity acid mixture or deionised water, respectively.

RESULTS AND DISCUSSION

The first step of investigation was the selection and evaluation of the wavelengths that are the most suitable for each element in a particular matrix. The flexibility of utilizing many emission lines for each element allows to analyse different elements in a sample at various concentration levels with a single dilution factor. Spectral interferences due to the influence of any present element in the sample were identified by wavelength scans near analyte wavelengths (± 0.2 nm) for Ni, Co, Cr, Mo, Ti, Al, Fe, Mn, Cu and Si. The wavelengths for particular element were selected from the available lists of ICP atomic emission lines by Boumans⁸ considering their sen-

te Ni, Co, Cr, Mo, Ti, Al, Fe, Mn, Cu in Si v območju ±0.2 nm od maksimuma izbrane spektralne črte. Valovne dolžine za posamezni element smo izbrali z liste možnih ICP AES spektralnih črt po Boumansu⁸, upoštevajoč njihovo občutljivost, čim manjše interference ter nizko in konstantno ozadje.

Rezultati teh poskusov so pokazali, da korekcija ozadja ni potrebna. Kot je prikazano na **sliki 1 in 2**, smo ugotovili le spektralno interferenco kobalta na 238.204 nm Fe črti in molibdena na 251.611 nm Si črti, kar povzroča napako pri določanju železa oziroma silicija. Majhen peak, ki ga opazimo na obeh Si spektralnih črtah v prisotnosti titana (**slika 2**), pripisujemo kontaminaciji Ti standarda s silicijem, ki je nastala pri pripravi standardne raztopine z raztapljanjem titana v kislini mešanici HF-HNO₃.

Izvršili smo korekcijo za železo in silicij glede na močnejše elemente. Na **sliki 3** prikazujemo primerjalne rezultate določanja silicija v različnih standardnih vzorcih nikljevih zlitin s korekcijo motečega elementa (Mo) in brez nje.

Na osnovi rezultatov preliminarnih poskusov smo za vsak element izbrali optimalne spektralne črte, čas izpiranja, čas integracije, pretok argona in druge parametre, ki so prikazani v **tabelah 2 in 1**. Izdelali smo umeritvene krivulje s pomočjo multielementnih standardnih raztopin in certificiranih referenčnih materialov, pri čemer smo v obeh primerih dobili skoraj identične signale.

V **tabeli 2** so zbrani podatki za valovne dolžine uporabljenih spektralnih črt, občutljivost, mejo zaznavnosti, relativni standardni odklik, koncentracijsko območje in korekcijske faktorje. Meja zaznavnosti je definirana kot

sensitivities, freedom of interferences and a constant, low background structure.

Graphic spectral scans had shown that no background correction was necessary. As indicated in Fig. 1 and 2 only the presence of cobalt at 238.204 nm Fe line and presence of molibdenum at 251.611 nm Si line could introduce an error in iron and silicon determination, respectively. The small peak of Ti standard observed on the both Si lines (Figure 2) was due to the contamination of Ti standard with silicon at preparation of this standard solution by dissolution of titanium with HF-HNO₃ acid mixture.

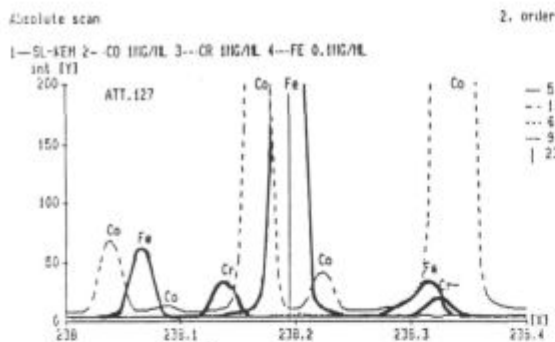
The correction for Fe and Si considering the mentioned interfering elements was made. Comparison results of Si determination in different certified reference materials with and without correction of interfering element (Mo) are presented in Fig. 3.

On basis of results obtained by preliminary study optimal spectral lines, flush time, integration time, argon carrier flow rate and other parameters were selected for each element (Table 2, Table 1).

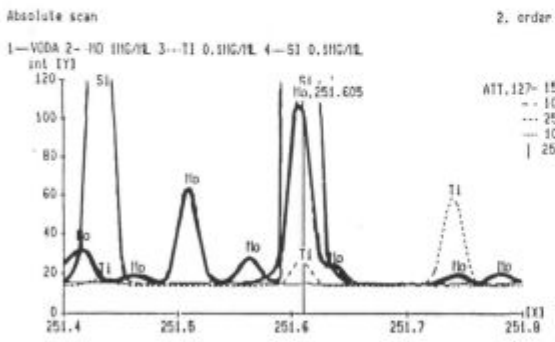
Calibration curves and regression on the basis of multielement standard solutions and certified reference materials were made. Signals of mostly identical relative intensities were obtained for multielement standard solutions and solutions of certified reference materials.

Spectral lines used, sensitivities, detection limits, relative standard deviations, concentration ranges and correction factors for investigated elements are summarized in Table 2. Detection limit is defined as twice the standard deviation of the fluctuation of the blank signal divided by the slope of the linear calibration curve⁹. It was calculated from the data of 10 successive intensity measurements of the blank value.

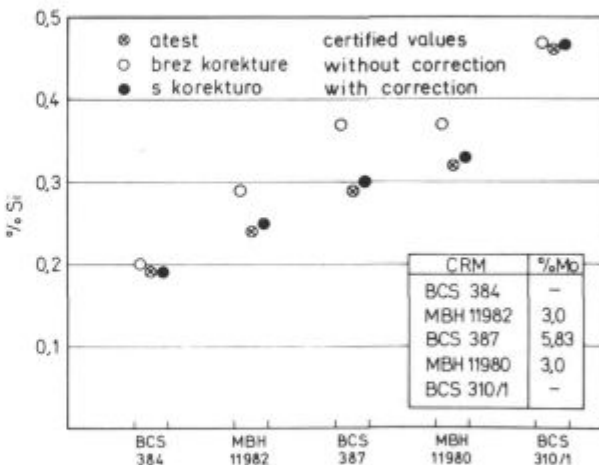
The accuracy of the method was checked with different reference materials of similar composition. Composition results of ICP and certified values for two BCS standards are given in Table 3. The presented standard deviations were obtained with frequent successive measurement of the same sample. The results generally indicated good agreement within reported standard deviations for all elements, except for nickel and copper. The worst reproducibility and accuracy of results was



Slika 1
Spektralna interferenca kobalta na Fe 238.204 nm liniji
Fig. 1.
Spectral interference of cobalt on Fe 238.204 nm line



Slika 2
Spektralna interferenca molibdena na Si 251.611 nm liniji
Fig. 2
Spectral interference of molibdenum on Si 251.611 nm line



Slika 3
Primerjalni rezultati za silicij z in brez korekcije motečega elementa (Mo)
Fig. 3
Comparison results of Si determination with and without correction of interfering element (Mo)

Tabela 2: Optimalni pogoji in ugotovljeni parametri za analizo nikljevih zlitin**Table 2:** Optimal conditions and established data for ICP analysis of nickel alloys

Element Element	Valovna dolžina (nm) Wavelength (nm)	Faktor občutljivosti Attenuator- position	Občutljivost S_{ICP} (rel. enote-za 1ppm) Sensitivity S_{ICP} (rel. units-for 1ppm)	Meja zaznavnosti D_L ($\mu\text{g/ml}$) Delection Limit D_L ($\mu\text{g/ml}$)	RSD % RSD %	Območje % Range (w/w %)	Aditivna korekcija Additive correction	
							moteči element Interfering element	koefficient Coefficient
Ni	221,647	125	9,0	0,006	0,59	58—62		
Co	228,616	127	17,1	0,006	0,73	14—17		
Cr	205,552	127	4,8	0,007	0,78	9—13		
Mo	202,030	127	3,0	0,013	0,86	3—6		
Ti	307,864	120	101,5	0,014	0,80	2—5		
Al	309,278	120	38,1	0,037	0,60	0,2—6		
Fe	238,204	120	13,5	0,008	1,0	0,2—0,8	Co	-0,0008
Si	251,616	127	21,3	0,011	2,1	0,2—0,5	Mo Mn	-0,0139 -0,0065
Mn	294,920	127	325,8	0,002	1,1	0,1—0,4		
Cu	327,396	127	298,0	0,002	2,5	0,01-0,05		

Tabela 3: ICP in certificirane vrednosti — primerjalni rezultati v %**Table 3:** ICP and certified values comparison results (all results in w/w %)

Element	BCS 310/1		BCS 387	
	ICP	Atest	ICP	Atest
Ni	58,2 ± 0,52	58,6 (58,5—58,7)	41,4 ± 0,38	41,9 (41,8—42,0)
Co	16,80 ± 0,11	17,0 (16,88—17,2)	0,23 ± 0,002	0,21 (0,21—0,23)
Cr	19,44 ± 0,14	19,45 (19,37—19,52)	12,44 ± 0,02	12,46 (12,40—12,52)
Mo	0,035 ± 0,002	n.d.	5,80 ± 0,05	5,83 (5,75—5,85)
Ti	2,41 ± 0,01	2,43 (2,39—2,47)	2,92 ± 0,016	2,95 (2,88—3,04)
Al	1,055 ± 0,003	1,06 (1,02—1,09)	0,27 ± 0,002	0,24 (0,22—0,25)
Fe	0,27 ± 0,003	0,25 (0,24—0,27)	35,72 ± 0,25	36,0 (35,8—36,1)
Mn	0,35 ± 0,004	0,35 (0,34—0,37)	0,085 ± 0,0004	0,08 (0,080—0,085)
Cu	0,04 ± 0,001	n.d.	0,045 ± 0,0003	0,032 (0,029—0,033)
Si	0,47 ± 0,01	0,46 (0,44—0,47)	0,30 ± 0,005	0,28 (0,26—0,30)

dvakratni standardni odklik slepe vrednosti, deljen z naklonom umeritvene krivulje⁸. Meja zaznavnosti je izračunana na osnovi podatkov desetkratne zaporedno izmerjene intenzitete slepe vrednosti.

Točnost metode smo preverili na različnih standardih nikljevih zlitin podobnih sestav. Primerjavo rezultatov ICP analize dveh BCS standardov nikljevih zlitin z atesti prikazujemo v tabeli 3. V tabeli naveden standardni odklik se nanaša na večkratno zaporedno merjenje istega vzorca. Rezultati v glavnem dobro sovpadajo v mejah navedenega standardnega odklika za vse elemente, ra-

chieved for Ni, where the signals of lowest stability were observed. High Cu results were probably caused by high blank value.

The main problem for precise and accurate determination by ICP emission spectrometry, especially for major elements, is maintaining the constant nebulization efficiency and other aparative conditions, wich requires frequent standardisation of calibration curves in short time intervals.

zen za nikelj in baker. Najslabšo ponovljivost in točnost rezultatov smo dobili za nikelj, kjer opažamo najslabšo stabilnost izmerjenih intenzitet. Previsoki rezultati za baker so verjetno posledica sorazmerno visoke slepe vrednosti.

Glavni problem za natančno in točno določanje z ICP AES, predvsem elementov v višjem koncentracijskem območju, je vzdrževanje konstantnih pogojev razprševanja in drugih aparativnih parametrov, kar zahteva večkratno standardizacijo umeritvenih krivulj v kratkih časovnih intervalih.

ZAKLJUČKI

Na osnovi naših opomb, praktičnih izkušenj in dobljenih rezultatov lahko zaključimo, da je predlagana metoda ICP atomske emisijske spektrometrije primerna in perspektivna tehnika za hitro multielementarno analizo večine elementov v preiskovanih nikljevih zlitinah.

CONCLUSIONS

Considering our remarks, practical experiences and results obtained, we can conclude that recommended method by ICP atomic emission spectrometry is a useful, suitable perspective technique for rapid multielement determination for most of major and minor elements in investigated nickel base alloys.

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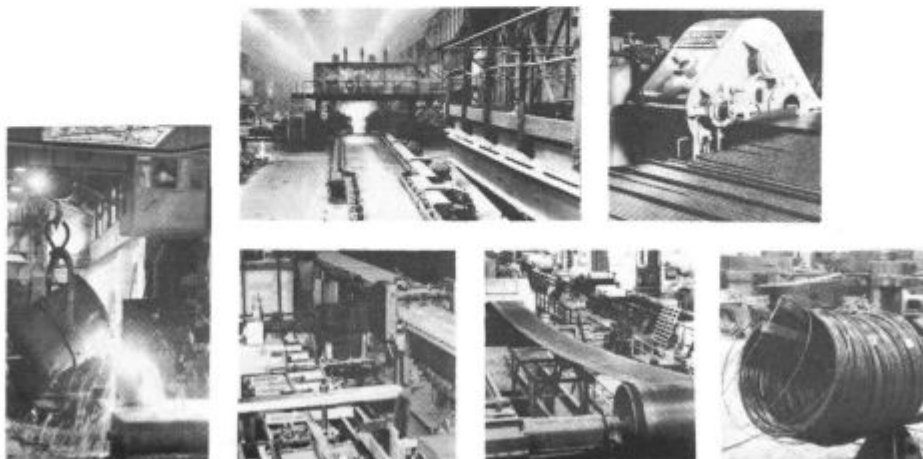
PRIKAZ

Izdelava jekel v elektro obločni peči, sekundarna rafinacija v vakuumski napravi, kontinuirno vlivanje jekla, vlivanje jekla v kokile, vlivanje odlitkov v livarni, valjanja gredic, slabov in predtrakov na valjalnem stroju bluming, valjanje žice in profilov, valjanje debele pločevine



PROIZVODNJE

Toplo valjanje trakov na valjalnem stroju (štekel), hladno vlečenje žice, hladno vlečenje profilov, hladno valjanje trakov, proizvodnja žebeljev, proizvodnja dodatnih materialov, izdelava hladno oblikovanih profilov, izdelava vratnih podbojev

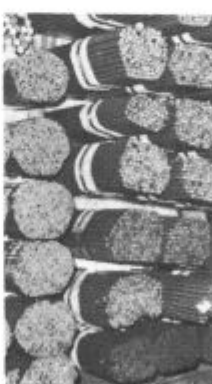


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V proizvodnem programu so naslednji izdelki:

gredice, toplo valjana debela, srednja, in tanka pločevina, hladno valjana pločevina in trakovi, toplo valjana žica, hladno vlečena žica, hladno vlečeno, luščeno in brušeno paličasto jeklo, hladno oblikovani profili, kovinski vratni podboji, dodatni materiali za varjenje, žebelji, jekleni ulitki, tehnični plini

Poleg navedenih izdelkov pa nudimo tudi storitve:

valjanje v pločevino ali trak, vlečenje v žico ali paličasto jeklo, toplotne obdelave, raziskave oziroma meritve lastnosti jekla, računalniške obdelave, psihološke, sociološke in ekološke študije, tehnološki inženiring

Določanje sledov kovin v jeklih in superzlitinah, po predhodni ločbi, s plamensko AAS

AAS Determination of Trace Metals in Steels and Superalloys with Preliminary Separation

T. Lavrič*, A. Osojnik*, Z. Kristan*

UDK: 543.064:669.14
ASM/SLA: S11d, S11g, 1—54

Delo opisuje primerjalno študijo ločbe ionsko asociiranih kompleksov Ag, Bi, Cd, Pb, Se, Sn, Te in Zn s trioktilfosfinoksidom (TOPO) in trioktilaminom (TOA) v metilizobutilketon (MIBK). Raziskujemo možnost uporabe obeh skupinskih ločb naštetih kovin za določanje nečistoč v jeklih in superzlitinah na osnovi niklja, s končnim določanjem s plamensko AAS. Separiranje in določanje preverjamo s certificiranimi referenčnimi materiali. Zbrani so tudi podatki analize sledov za nikljeve zlitine iz proizvodnje in podatki o občutljivosti, točnosti, ponovljivosti določanja ter o praktični meji zaznavnosti za vsak element.

The present work describes a comparison study of the separation of Ag, Bi, Cd, Pb, Se, Sn, Te and Zn, as iodide complexes ion-associated with trioctylphosphine-oxid (TOPO) and with trioctylamine (TOA), into methylisobutylketone (MIBK).

The efficiency of both multielement separations, followed by flame AAS determination, was investigated to determine the traces of analytes in different grade of steels and superalloys. Standard reference materials were used to test separation and determination. The sensitivity, accuracy and repeatability data, and also the practical limit of detection for each element are gathered and assessed.

UVOD

Sledovi Ag, Bi, Cd, Pb, Se, Sn, Te in Zn ter še nekaterih elementov vplivajo kvarno na mehanske, fizikalne in tehnološke lastnosti litega železa, nekaterih vrst jekla, predvsem pa so škodljivi v superzlitinah, ki se uporabljajo pri visokih temperaturah. Nezaželjene in škodljive so že primesi reda velikosti nekaj ppm ($=\mu\text{g g}^{-1}$) in manj. Pravilna ocena takih količin zahteva precizne metode določanja, ki so vezane izključno na instrumentalno tehniko. Vendar so redke in zelo drage tiste tehnike, ki imajo, brez predkoncentriranja, zadostno občutljivost za direktno analizo sledov kovin in da so, istočasno brez predhodne ločbe sledov od matrice, proste motenj glavnih komponent. Plamenska AAS, neplamenska AAS in ICP-AES zahtevajo ločbo ter skoncentriranje ppm količin kovin od osnove z namenom, da se odstranijo motnje ali/in zaradi izboljšave parametrov določanja. Primerne tehnike so ekstrakcija, hidridna tehnika, soobarjanje, redukcija do elementarnega stanja. Na izbiro ločbe vplivajo fizikalne in kemične lastnosti določenega elementa in matrice, kar vpliva tudi na to, ali je ločba lahko eno-ali večelementna.

Namen predstavljene študije je bil zbrati podatke o možnosti skupinske ločbe in skoncentriranja ppm količin jodidov Ag, Bi, Cd, Pb, Se, Sn, Te in Zn iz večje zatehte jekla oziroma superzlitine na nikljevi osnovi v 5, 10 ali 20 ml organske faze TOPO-MIBK ali TOA-MIBK. Kontrola ločbe je potekala z analizo organskih ekstraktov s pla-

INTRODUCTION

Mechanical, physical and technological properties of various types of cast iron, some low alloy steels, and especially superalloys for high temperature application strongly depended on trace metal contents such as Ag, Bi, Cd, Pb, Se, Sn, Te, Zn, and others. Because of their harmful effect already at the ppm ($=\mu\text{g g}^{-1}$) level and lower a great attention has been paid to the knowledge of ppm concentrations of trace elements. All that requires reliable, correct methods of determination, that are exclusively connected with instrumental technics. Except a few and expensive technics have satisfactory sensitivity for direct determination of trace metals without preconcentration and that they are at the same time free of interferences of the matrix without separation. The conventional flame AAS, flameless AAS, ICP-AES demand the separation and preconcentration of ppm amounts of metals from the matrix in order to avoid interferences or/and to improve parameters of determination. The convenient separation methods are solvent extraction, hydride generation, coprecipitation, reduction to elemental state. The possibility of application of these separation methods depends on physical and chemical properties of the determined trace and of the matrix, what influences also to one-or multielement separation.

The aim of the present study was to gather analytical data obtained by the use of preconcentration solvent extraction technic of iodides of Ag, Bi, Cd, Pb, Se, Sn, Te, and Zn from large weight from various kinds of steels and superalloys on nickel base by the use of 5, 10, 20 ml TOPO-MIBK and TOA-MIBK organic phase, followed by

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mensko AAS. Uvedli smo TOPO-MIBK ločbo po Burkeju^{1,2}, ki jo uporablja avtor za določanje Bi, Pb, Sb in Sn v aluminiju, železu in nikljevih zlitinah. Janoušek³ in Staats⁴ uporabljata podobno ločbo za določanje mikroelementov v jeklih. Janoušek določa le Bi, Pb, Sb in Sn v nelegiranem jeklu, medtem ko je Staats prilagodil ločbo določanju Cu, Zn, Mo, Ag, Sn, Sb, Pb in Bi za nelegirana in malolegirana jekla. Ločba TOA-MIBK je manj v rabi na področju analize jekla^{5,6}, bolj za posamezne elemente-sledove v bakru, svincu in selenu^{7,8,9}. Dodatno smo izvedli primerjalno študijo določanja Te z redukcijo do elementarnega Te. Opisane so separacijske metode in predstavljeni rezultati za certificirane referenčne materiale (CRM) ter nekaj nikljevih zlitin iz proizvodnje. V možnih primerih smo izvedli za CRM primerjavo z dosegljivimi podatki drugih avtorjev.

EKSPERIMENTALNI DEL

Aparatura

Meritve smo izvajali z AA spektrometrom Perkin Elmer model 2380, ki je bil opremljen z zunanjo izvorom za brezelektrodne žarnice. Za določanje Bi, Se, Sn in Te smo uporabljali kot primarni izvor svetlobe brezelektrodne žarnice, za določanje Ag, Cd, Pb in Zn pa votle katode. Signale smo beležili na printerju Perkin Elmer PRS-10. Za vsak element smo optimirali lego gorilca in parametre plamena na maksimalno absorbanco z razprševanjem standarda v ustreznem ekstraktu. Za vse elemente smo uporabljali plamen zrak-acetilen in »impact bead«, le za Sn plamen didušikov oksid-acetilen in »vetnico«. Čas integracije je bil vedno 1 sec pri hitrosti razprševanja organske faze ~ 5 ml min⁻¹. Meritve smo izvajali za vsak element na njegovi najbolj občutljivi-resonančni liniji. Meritve smo izvajali za vse elemente izključno samo v linearnem območju, kjer je zadoščalo umerjanje z enim standardom, čeprav je instrument sposoben sprejeti tri standarde za umerjanje in korekturo krivulje.

Reagenti in materiali

Vse kemikalije so bile nabavljene pri fa. Fluka. MIBK in kisline so bile p.a., TOA purum kvalitete. Uporabljali smo 5 % raztopino TOPO v MIBK in enako 5 % TOA v MIBK. Za pripravo vzorcev smo uporabljali sigradur čaše. Uporabljali smo CRM naslednjih dobaviteljev: BAS, NBS in MBH. Večina jih je bila kupljena v obliki finih ostružkov, nekateri v obliki diskov (MBH), iz katerih smo pripravili ostružke z ene strani diska. Kemična sestava uporabljenih CRM je razvidna iz **tabele 1**.

Postopki za jekla in nikljeve zlitine

Opisana sta dva postopka ekstrakcije Ag, Bi, Cd, Pb, Se, Sn, Te in Zn ter en postopek redukcije Te. Vsem trem so skupne tri faze: raztapljanje s pripravo vzorca, ločba in zadovoljivo določanje. Vsaj en slepi vzorec pridružimo vsakemu postopku.

— **TOPO-MIBK ekstrakcija:** Osnova postopka je ekstrakcija jodidov enega ali več elementov, kot jo navaja Burke¹, z umerjanjem z raztopinami, ki jih vodimo skozi celoten postopek². Vzorec jekla ali nikljeve zlitine (1–5 g, odvisno od vsebnosti sledov) počasi in previdno raztopimo v 3 + 1 mešanici HCl + HNO₃. Raztopino izparimo na ~ 5 ml, dodamo 10 ml HCl, razkrojimo HNO₃ z mravljinčno kislino. Raztopino izparimo do goste sirupaste konsistence, da izženemo vse dušikove okside in da se razkroji mravljinčna kislina. Dodamo HCl, askorbinsko

flame AAS. We followed the TOPO-MIBK separation of Burke^{1,2}, applied by author for Bi, Pb, Sb, and Sn determination in aluminium, iron and nickel base alloys. Janoušek³ and Staats⁴ performed similar separation for determination of trace elements in steels. Janoušek³ determined Bi, Pb, Sb, and Sn in unalloyed steel but Staats⁴ adapted separation for the determination of Cu, Zn, Mo, Ag, Sn, Sb, Pb, and Bi for unalloyed and low alloyed steels. The TOA-MIBK extraction is a little applied separation for steels^{5,6} but more for the determination of single elements in copper, lead, and selenium^{7,8,9}. For Te also a comparison with reduction to elemental Te was made. Methods of separation are shortly described and the results presented for the analytes of certified reference materials (CRMs) and elected nickel base alloys from production. Some results for CRMs are compared with available literature data.

EXPERIMENTAL

Instrumentation

Perkin Elmer atomic absorption spectrometer Model 2380, equipped with an external electrodeless discharge power supply was used. As primary light source electrodeless discharge lamps were employed for the determination of Bi, Se, Sn, Te, and for the determination of Ag, Cd, Pb, and Zn hollow cathode lamps were used. The signals were printed on a Perkin Elmer PRS-10 printer. Other conditions were as follows: the burner position and flame parameters for each element were optimized for maximum absorbance by aspirating standard organic solution. The impact bead and air-acetylene flame were used for all test analytes, except for Sn nitrous oxide-acetylene and spoiler were used. Integration times of 1 sec were used in all cases in conjunction with an aspiration time ~ 5 ml min⁻¹ of organic solution. The most sensitive-resonance line was chosen for each element. The measurements were made for all analytes exclusively in the linear concentration range where the calibration with one standard was sufficient, otherwise the instrument is capable of accepting up to three standards for calibration and curve correction.

Reagents and materials

All analytical work reagents were supplied from Fluka, MIBK and acids p.a. grade, TOPO puriss, and TOA purum grade. TOPO-5 % solution in MIBK, TOA-5 % solution in MIBK was applied. Sigradur vessels were used for sample preparation. Certified Reference Materials (CRMs) supplied by the BAS, NBS and MBH were used. The most of them were supplied in finely divided form, but some of them were in disc form (MBH). From discs fine drillings were cut on one side **Table 1**.

Procedures for steels and nickel base alloys

Two solvent extraction methods for determination of Ag, Bi, Cd, Pb, Se, Sn, Te, and Zn are described, and one procedure for reduction of Te.

All three further described procedures have three steps in common: dissolution with pretreatment of the sample, separation, and satisfactory determination. A blank was included in each of the following digestion procedures:

— **TOPO-MIBK extraction:** Procedure based on the extraction of iodides of one or more elements re-

Tabela 1: Opis uporabljenih standardnih referenčnih materialov in podatki za Ag, Bi, Cd, Pb, Se, Sn, Te ter Zn
Table 1: Description of standard reference materials used, and data for Ag, Bi, Cd, Pb, Se, Sn, Te and Zn

Oznaka vzorca Sample identification	Vrednosti v certifikatih ($\mu\text{g g}^{-1} = \text{ppm}$) / Values of certificates ($\mu\text{g g}^{-1} = \text{ppm}$)							
	Ag	Bi	Cd	Pb	Se	Sn	Te	Zn
EURO 085-1								
NBS 365	(-20 ppb)	(<0.1)	ND	0.19	(<0.1)	(0.2)	(<0.1)	$25 \pm 6[18 - 42]_{15}$ <0.1
NBS 361	4	(4)	ND	0.25	(40)	100	(6)	(1)
NBS 362	11	(20)	ND	4.8	(12)	160	(11)	(5)
NBS 363	37	(8)	ND	18.6	(1.6)	1040	(9)	(4)
BCS 345	<0.2[<0.5-0.2]_{11}	<0.2[<0.05-<0.2]_{11}	<0.1[<0.05-<0.1]_{11}	$0.2 \pm 0.05[0.12 - 0.30]_{11}$	<0.5[<0.2-<0.5]_{11}	$6 \pm 1.6[3.8 - 8.0]_{11}$	<0.2[<0.05-<0.2]_{11}	<0.5[0.3-<0.5]_{11}
BCS 346	$35 \pm 2[32.2 - 38.1]_{13}$	$10 \pm 1[9.4 - 11.6]_{13}$	$0.4 \pm 0.05[0.34 - 0.48]_{13}$	$21 \pm 2[18 - 23.2]_{14}$	$9 \pm 1[7.5 - 10.2]_{14}$	$91 \pm 7[78 - 100]_{10}$	$12 \pm 1[9.5 - 14.5]_{10}$	$29 \pm 2[25.7 - 31.5]_{10}$
MBH 11980D	<2	<0.1	<0.1	<2	<5	<10	<2	<2
MBH 11980F	0.2	<1.5	0.1	3	<1	18	<0.2	6
MBH 11980A	20	2	0.2	10	15	40	12	15

Euro: 085-1, nelegirano jeklo/unalloyed steel
 NBS: 361, 363 malo legirano jeklo/low alloy steels
 NBS: 365 elektrolitsko železo/electrolytic iron
 BCS: 345, 346 -IN 100 zlitine/IN 100 alloys
 MBH: 11980D, 11980F, 11982A-IN 100 zlitine/IN 100 alloys
 (): Vrednosti niso certificirane/Values are not certified
 []: Določitev v certifikatu v mejah/Determination in certificat within the limit, x število določitev/number of determinations.
 N.D.: ni določeno/not determined.

kislino in jodidni reagent ter ekstrahiramo v 5, 10, 20 ali 30 ml 5 % TOPO v MIBK. Čas ekstrakcije je 30 sek. Organsko fazo razpršimo v plamen. Za določitev enega samega elementa zadostuje 5 ml ekstrakta. Izkušen analitik lahko določi vseh osem elementov iz 30 ml ekstrakta.

Podrobni eksperimentalni podatki kot tudi diskusija k TOPO-MIBK ekstrakciji so na voljo v literaturi^{1, 2}. Pri naših poskusih smo povečali količino zmesne kisline za raztapljanje 5 g vzorca iz 60 na 100 ml.

2— TOA-MIB ekstrakcija: Priprava vzorca in ločba sta povsem enaki kot za TOPO-MIBK ekstrakcijo, le da smo uporabljali kot ekstraktant 5 % TOA v MIBK, čas ekstrakcije je daljši 5 min.

— Redukcija Te do elementarnega stanja s hidrazinhidrokloridom: Priprava vzorca je enaka kot opisujemo spredaj do vključno z dodatkom mravljinčne kisline. Nato dodamo ~ 25 ml HCl ter razredčimo na ~ 200 ml. Kislost raztopine naj bo 2—3 M. Dodamo dvojno količino hidrazinhidroklorida, glede na zatehto vzorca. Postavimo na vodno kopel pri 100 °C za 30 min, da se pojavi črna oborina izpadlega Te, nato pustimo čašo z oborino nadaljnih 30 min poleg vroče plošče. Koagulirano oborino zberemo na milipor filtru 0.2 µm, speremo z vodo in raztopimo v čimmanj hladne HNO₃, ohladimo, dodamo 5 ml HCl, razredčimo na 25 ml, razpršimo v plamen.

REZULTATI IN DISKUSIJA

Umerjanje in meritve

Za umerjanje aparature smo sprva v glavnem uporabljali CRM, ki smo jih pripravljali na enak način kot vzorce. Zaradi pomanjkanja CRM s ppm vsebnostjo iskanih elementov smo včasih naredili referenčne vzorce, že pred raztapljanjem, z združevanjem elektrolitskega železa (NBS 365) ali zelo čiste nikljeve zlitine (BCS 354) z različnimi CRM v različnih utežnih razmerjih.

Nadalje smo pripravljali raztopine za umerjanje iz standardnih raztopin, ki smo jih dodajali elektrolitskemu železu (NBS 365) ali superzlitini (BCS 345). Standardne raztopine smo vedno dodali šele po raztopitvi matrice. Tako pripravljene sintetske vzorce smo vodili skozi celoten postopek. Vse standardne raztopine smo pripravili iz čistih kovin ali p.a. soli (Ag). Z obema načinoma umerjanja dobimo skoraj identične rezultate za vse elemente, razen za Bi, kjer smo ugotovili, da dobimo pravilne rezultate le z umerjanjem s CRM; z umerjanjem s sintetskimi vzorci dobimo prenizke rezultate.

Pravilno umerjanje je zelo važen dejavnik celotnega postopka. Kritična točka je v pravilni izbiri ničle instrumenta. Kot ničlo instrumenta vstavimo vedno elektrolitsko železo (NBS 365) ali nikljevo zlitino (BCS 345), ki jo v nadaljnjem imenujemo delovna slepa raztopina in jo pripravimo enako kot vzorce. Dobljeni rezultati so namreč pokazali, da dobimo napačne rezultate, če vstavimo kot ničlo čisti MIBK, izmerimo koncentracijo delovne slepe raztopine in to vrednost naknadno odštejemo od celotne vrednosti za umerjalni standard ali preiskovani vzorec. Delovno slepo raztopino pripravimo za vsako skupino vzorcev in jo obvezno uporabljamo za izpiranje med posameznimi vzorci, posebno kadar merimo v bližini praktične meje zaznavnosti in pri ogrevanju gorilca.

Uporabnost obeh ekstrakcijskih sistemov

Meritve Ag, Bi, Cd, Pb, Se, Sn, in Te v TOPO-MIBK in TOA-MIBK ekstraktih so pokazale podobno učinkovitost ločbe v obeh sistemih, medtem ko se Zn ekstrahira dobro le v TOPO-MIBK, v TOA-MIBK največ 50 %, pri izbranih delovnih pogojih. Izkoristki ločb so za vse ostale ele-

ported by Burke¹, with calibration solutions that have been taken through extraction procedure², was applied. The sample of steel or nickel base alloy (1—5 g depending on amount of traces) slowly and carefully was dissolved to avoid losses by sputtering in 3+1 mixture of HCl+HNO₃. The resulting solution was then evaporated to ~ 5 ml, then 10 ml HCl was added, and nitric acid decomposed by formic acid. The solution was then evaporated nearly to dryness to sthick consistence drive off to all nitrogen oxide fumes and finally destroying of formic acid. After the addition of HCl, ascorbic acid, and iodide reagent, the extraction into 5, 10, 20 or 30 ml of 5 % TOPO-MIBK followed, extraction time 30 sec. The organic extract was aspirated into flame. For determination of one element only 5 ml of extract satisfy. An experienced analyst is able to determine all eight analytes from 30 ml of extract. Data for experimental conditions as well as discussion on the TOPO-MIBK separation may be found in the literature^{1, 2}. In our research acid mixture was increased for 5 g sample from 60 to 100 ml.

— TOA-MIBK extraction: The preparation of the sample and separation procedure are the same as under TOPO-MIBK extraction, except we added 5 % TOA in MIBK instead of TOPO the extraction time was 5 min.

— Reduction of Te to elemental state by hydrazine hydrochloride: The dissolution procedure as described above, inclusive of formic acid addition. After that hydrochloric acid was added to adjust the acidity to 2—3 M and the volume to ~ 200 ml (~ 25 ml concentrated hydrochloric acid/200 ml). Double amounts of hydrazine hydrochloride was added with regard to the sample weight. The mixture was incubated in a water bath at 100 °C for 30 min till black precipitate of Te appeared. The mixture was allowed to stand near the hot plate further 30 min. Coagulated precipitate was collected on a millipor filter 0.2 µm, washed with water and dissolved in a few ml of cold concentrated nitric acid, cooled, 5 ml of hydrochloric acid was added, diluted to 25 ml and applied to AAS.

RESULTS AND DISCUSSION

Calibration and measurements

In the first stage calibration solutions from CRMs were used for calibration of the instrument, which were prepared on the same way as the samples. To overcome the lack of standards with ppm amounts of analytes, reference materials were sometimes prepared with known amounts of traces by spiking electrolytic iron (NBS 365) or very clean nickel base alloy (BCS 345) with different CRMs in different proportions before the dissolution step.

Later also calibration solutions from varying amounts of a stock solution of respective element and electrolytic iron (NBS 365) or superalloy (BCS 345) were prepared. The stock solutions were added always after dissolution of the matrix. All standard solutions were prepared from clean metals or p.a. salts (Ag).

With both calibration made we achieved nearly identical results for all elements. Except for Bi we stated, that correct results were obtained with calibration with CRMs. Calibration with synthetic standards yields to low results.

The calibration is an important factor in all procedures. A critical point in both liquid-extraction procedures was imposed by correct choice of the zero of the instrument. The working blanc, electrolytic iron or very clean nickel base alloy taken through all procedure,

mente v obeh sistemih med 85—110 %. Če upoštevamo nizke koncentracije, lahko ugotovimo, da so izkoristki dobri.

Oba ekstrakcijska sistema sta uporabna za analizo sledov v jeklih in nikljevih zlitinah.

Prednost ločbe s TOPO-MIBK so: je izrazita večelementna ločba sledov, ki omogoča tudi določanje Zn po opisanem postopku. Odlikuje jo kratek čas ekstrakcije (30 sek) v primerjavi s 5 min ekstrakcije s TOA-MIBK.

Prednost ločbe s TOA-MIBK so: je tudi večelementna ločba, ki bi bila morda ob drugačnih pogojih preiskovane raztopine uspešna tudi za Zn. Nihanje ozadja je manj izrazito kot pri TOPO-MIBK, kar pride posebno do izraza pri Se, ki je težko določljiv s plamensko AAS, za katerega dobimo s TOA-MIBK stabilnejše odčitke za slepi vzorec in vzorec, s tem v zvezi boljši standardni odmik, kar je posebno važno, ko določamo koncentracije v bližini praktične meje zaznavnosti. Standardni odmik desetih meritev istega vzorca za 0,2 µg ml⁻¹ Se je bil v TOPO-MIBK 15—25 %, v TOA-MIBK 10—20 %.

Meritve občutljivosti za TOPO-MIBK in TOA-MIBK ekstrakte dajejo približno enake vrednosti za vse elemente, z izjemo Sn, kjer je razlika med obema sistema občutnejša, **tabela 2**. Na splošno je občutljivost do-

ločanja dobra, najslabša je za Sn. V primerjavi s klorovo *must be set as zero of the instrument used in this study. The results obtained confirmed, that it is wrong to measure the concentration of the working blank against clean MIBK separately, and subsequent its subtraction from the total signal for calibration sample and tested sample.*

A working blank should be prepared with each set of samples, and may be used obligatory for washing out between each sample, particularly by measuring near the practical limit of detection, and for burner warm up.

Application of extraction systems

Measurements of Ag, Bi, Cd, Pb, Se, Sn, and Te in TOPO-MIBK and TOA-MIBK extracts yield approximately the same degree of separation; for Zn only the extraction into TOPO-MIBK is convenient, the extraction in TOA-MIBK is less than 50 %, under chosen working conditions. 85—110 % recoveries for all analytes were afforded. Considering the low concentrations the recoveries can be regarded as acceptable. The both extraction systems are available for the analysis of trace elements, mentioned above, in steels and nickel base alloys. Advantages of TOPO-MIBK separation are: it is an expressive multielement separation technic, that hat is unable to separate and preconcentrate also Zn, under described procedure. The separation is distinguished by less time consuming for shaking, 30 sec against 5 min for TOA-MIBK. Advantages of TOA-MIBK separation are: is also a multielement separation technic, which could be useful also for Zn in other conditions of the working solution. The fluctuation of the signals of the background is smaller than of TOPO-MIBK solutions which contributes to slightly more stable signals. This is especially evident for Se, which is difficult to determine in TOPO-MIBK. This contributes to stable signals for working blank and sample solution and lower relative standard deviation, which is especially noticeable when concentrations are near the practical detection limit. Relative standard deviation for ten measurements of one sample on 0.2 µg ml⁻¹ level of Se was approximately 15—25 % in the TOPO-MIBK, and 10—20 % in the TOA-MIBK solution.

Tabela 2: Vpliv TOPO- in TOA-MIBK ter H₂O + HCL sistemov na občutljivost določanja.

Table 2: Effect of TOPO- or TOA-MIBK, and H₂O + HCL systems on the sensitivity of determination

Element	µg ml ⁻¹	Absorbanca/Absorbance		
		TOPO-MIBK	TOA-MIBK	H ₂ O + HCL
Ag	0.5	0.166	0.178	0.062
Bi	3.0	0.178	0.168	0.058
Cd	0.5	0.238	0.238	0.120
Pb	3.0	0.202	0.204	0.094
Se	3.0	0.044	0.036	0.014
Sn	10.0	0.040	0.027	0.012
Te	3.0	0.126	0.114	0.046
Zn	0.2	0.258	/	0.072

Tabela 3: Praktične meje zaznavnosti in ugotovljena linearna območja umerjanja v organskem sistemu.

Table 3: Practical limits of detection and linear ranges of calibration in organic system.

Element	Praktična meja zaznavnosti Practical detection limit		Območje linearnosti Range of linear response (µg ml ⁻¹) ^b
	(µg g ⁻¹) ^{a,b}	(%)	
Ag	0.2	2 × 10 ⁻⁵	0.05—3.0
Bi	0.4	4 × 10 ⁻⁵	0.2—6.0
Cd	0.1	1 × 10 ⁻⁵	0.1—0.5
Pb	0.4	4 × 10 ⁻⁵	0.2—4.5
Se	1.0	1 × 10 ⁻⁴	0.5—3.0
Sn	1.0	1 × 10 ⁻⁴	1 —50
Te	0.4	4 × 10 ⁻⁵	0.2—6.0
Zn	0.05	5 × 10 ⁻⁶	0.2—0.6

^a — Pri teži vzorca 5g, ekstrakt 5 ml
Using 5g sample, extract 5 ml

^b — Vse vrednosti so približno enake za TOPO- in TOA-MIBK, z izjemo za Zn
All values are approximately equal for TOPO- and TOA-MIBK, exceptly for Zn

*Measurements of sensitivity of determination for all analytes in both solvent extraction procedures were nearly the same, with exception for Sn, where the difference is grater. Generally the sensitivity of determination is good except for Sn. The effects of enhanced sensitivity of the analytes in organic phases compared with H₂O + HCl solutions are shown in **Table 2**. Proportional improvements in sensitiviry realise better practical detection limits. Practical detection limits, the lowest concentration which can be determined under routine conditions, based on 5 g sample and 5 ml organic extract are shown in **Table 3**.*

*All measurcmnts were made for all analytes exclusively in linear concentration range shown in **Table 3**.*

Repeatability test chiefly indicated a relative standard deviation of 2 % at about 100 µg g⁻¹ level, 10 % at about 6 µg g⁻¹ level and 20—30 % at about 2 µg g⁻¹ level within different batches on different days. Recommended procedures gave good reproducibility for the same organic extract from day to day for all analytes.

Application of reduction procedure for tellurium

*As can be seen from **Table 4**, the Te is determined enough precisely by the reduction method to elemental*

Tabela 4: Rezultati določanja Ag, Bi, Cd, Pb, Se, Sn, Te in Zn v CRM ($\mu\text{g g}^{-1}$).
 Tabela 4: Results of Ag, Bi, Cd, Pb, Se, Sn, Te and Zn determination on CRM_s

Element	EURO 851-1		NBS 361		NBS 362		NBS 363		BCS 345		BCS 346		MBH 11980D		MBH 11980F		MBH 11982A	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Ag	a	(4)	4.2±0.41	(11)	12.8				<0.2	0.13±0.06	35	34.2±1.7	<2	0.5±0.3	0.2	0.2	20	20.6±1.0
	b		4.1±0.36						0.16±0.04		33.7±2.4		<0.2		0.2		20.5±1.0	
	d		4.0 ^a	10.6 ^a														
Bi	a	(4)	4.4±0.6	(20)	19.8±2	8	5.4±0.7		<0.2	<0.2	10	9.9±0.9	<0.1	<0.4			2	1.8
	b		4.2±0.4	19.1			7.1±0.6		<0.2			9.7±1.2	<0.3				1.9	
	d		5.3 ^a , 5'	26 ^a , 30'			6.4 ^a , 8'											
Cd	a	N.D.	<0.1	N.D.	<0.1	N.D.	<0.1	<0.1	<0.1	<0.1	0.4	0.38±0.05	N.D.	0.1	0.08			
	b		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1		0.37±0.05			0.09			
	d		<0.1 ^a	<0.1 ^a			<0.1 ^a											
Pb	a	0.25	<0.3	4.8	5.1±0.8	18.6	18.2	02	<0.6	21	20.7±1.5	<2	<2				10	11.3±1.5
	b		<0.4	4.6			18.5		<0.6		20.6±0.8	<2					10	11.2±1.5
	d		<0.2 ^a	4.4 ^a			18.7 ^a											
Se	a	(40)	39.9±1.8	(12)	10±0.8	(1.6)	2.2±0.4			9	9.6±1.3	<1	<1				15	14.7±1.7
	b		40.6±1.7	10.1±0.7			3.1±0.8											
	d		34'	13'			1'											
Sn	a	100	103±16.5				6	5.3±0.8	91	89.2±4.1							40	41.3±3.0
	b		99.9±3				6.1±0.5			94.0±2.5								40.2±2.0
	d		93.9 ^a , 90'															
Te	a	(6)	5.9±0.2	(11)	10.2±0.7	(9)	9.6±1.0	<0.2	<0.5	12	12±1.6	<2	<1				12	13.6±0.7
	b		5.5±0.2	10.7			9.2		<0.5				<1					13.7±1.2
	d		6.3±1.5	8'	9.5±0.5	7'	10.7±1.3				13±1.2							14.0
Zn	a	25	21.8±3.5	(1)	N.D.	(5)	4.9±1.6	(4)	4.2±0.6	29	29.5±4.5	<1	40				6	7.0±1.6
	d		24.3 ^a	1.6 ^a			4.5 ^a						(?)					N.D.

A — Vrednosti v certifikatih/ Values of certificates

B — Naši rezultati/ Our results

a — TOPO-MIBK; b — TOA-MIBK; c — redukcija Te/ Values not certified

() — Vrednosti niso certificirane/ Values not certified

± ... Standardni odklik $n \geq 8$ / Standard deviation $n \geq 8$

d — Literaturni podatki/ Literature data: e — TOPO-MIBK (Lit. 4); f — hidrid/hydrid-AAS (Lit. 10)

Tabela 5: Rezultati analize elementov-sledov v raznih vzorcih iz proizvodnje.
Table 5: Analytical results of trace elements for various samples from production.

Vzorec Sample	Vsebnost/Content ($\mu\text{g g}^{-1}$ = ppm)							
	Ag	Bi	Cd	Pb	Se	Sn	Te	Zn
Aluminij Aluminium	<3	<1	0.24	160	1.2	17.4	0.6	39
Nikelj Nickel	0.8	<1	0.05	12.4	2.7	15.6	0.8	5
Kobalt Cobalt	1.5	<1	11.1	5.9	2.9	4.3	0.7	12
Krom Chromium	1.7	<1	0.04	20.5	2.1	2.0	0.9	2.4
Titan Titanium	6.9	<1	0.15	<1	18.7	220	5.6	3
Molibden Molybdenum	1.9	<1	0.13	5.1	4.5	20.0	2.4	0.08
NIMONIC 263/1 ^a	0.24	0.2	0.12	2.9	2.3	14.0	1.3	2.4
NIMONIC 263/2 ^a	0.20	<1	0.10	5.5	2.0	11.4	0.46	15.5
NIMONIC 263/3 ^a	0.28	<1	0.10	7.2	1.8	11.2	0.70	32
INCONEL ^b	0.89	5.5 ± 0.5 ^c (7)	0.16	33.7 ± 3.5(7)	3.9	96.8	2.1	13.6

^a— Ni-zlitina: 50%Ni, 20%Co, 20%Cr, 5.9%Mo, 2.5%Ti, 0.36%Al, 0.65%Fe
Ni-alloy

^b— Ni-Fe zlitina: 55%Ni, 18%Cr, 0.3%Co, 16.6%Fe, 2.8%Mo, 5%Nb, 0.6%Al, 1.0%Ti
Ni-Fe alloy

^c— Srednja vrednost ± standardni odklik od sr. vr. (n=7)
Mean ± standard deviation of the mean (n=7)

dikovo kislimi raztopinami se v organskih sistemih poveča občutljivost od 2.5 do 3-krat.

Praktične meje zaznavnosti, t.j. najnižja koncentracija, ki smo jo še lahko določili z rutinskim delom, pri uporabi 5 g zatehte vzorca in 10 ml organskega ekstrakta, so razvidne iz **tabele 3**.

Vse meritve smo izvajali za vse elemente samo v linearnih območjih, ki jih navajamo v **tabeli 3**.

Test ponovljivosti daje relativni standardni odklik 2 % na nivoju 100 $\mu\text{g g}^{-1}$, 10 % na nivoju 6 $\mu\text{g g}^{-1}$ in 20–30 % na nivoju 2 $\mu\text{g g}^{-1}$, in to glede na vzorce, ki so bili pripravljene ob različnih dnevih. Postopka, ki ju priporočamo, dajeta za vse elemente dobro ponovljivost istega organskega ekstrakta v več zaporednih dnevih.

Uporabnost postopka redukcije telurja

Kot je razvidno iz **tabele 4**, se da Te določati dovolj točno z metodo redukcije do elementarnega stanja, ki ji sledi določanje z AAS iz $\text{H}_2\text{O} + \text{HCl}$ raztopin.

Na splošno dosegamo dobra ujemanja s CRM v širokem koncentracijskem območju. Občutljivost in praktična meja zaznavnosti sta slabši v primerjavi z organskimi raztopinami. Meja zaznavnosti je 6 $\mu\text{g g}^{-1}$. Postopek je uporaben tako za analizo jekla kot zlitine na osnovi niklja.

Analiza certificiranih referenčnih materialov

Z namenom, da bi preverili pravilnost ločbe in skoncentriranja, smo analizirali večje število CRM. Vrednosti, dobljene za vrsto standardov jekel in nikljevih zlitin, se zadovoljivo ujemajo s certificiranimi vrednostmi, kar potrjuje, da se da doseči z opisanima postopkoma ločbe

state, followed by AAS determination of $\text{H}_2\text{O} + \text{HCl}$ solutions. In general, there is a good agreement with CRMs over a wide concentration range, but the sensitivity and the practical detection limit are poorer, than for the organic solutions. The limit is 6 $\mu\text{g g}^{-1}$. The procedure is available for the analysis of steels and nickel base alloys.

Analysis of certified reference materials

To assess the accuracy of the separation and preconcentration methods many CRMs were applied. The values obtained for a range of standard steels and nickel base alloys show close agreement with certified values for applied procedures, confirm a good enrichment factor and also prove that accurate results can be obtained at ppm level. The results are given in Table 4 together with those obtained by other investigators from literature. Recoveries are usually higher than 85 %. The determined values are for some CRMs higher and for some lower when compared with the certificate. It is interesting to note that also the data in certificates are in a spread, and that some values are not certified but only given for information.

Analysis of samples from production

The established methods are applied on the sample from production, see **Table 5**.

There was problem with dissolution of nickel base alloy with 5 % Nb. In this case the addition of H_2SO_4 was not sufficient, but the addition of 1 ml HF prior or after the dissolution of the sample was successful.

dobro skoncentriranje sledov in pravilne rezultate na ppm nivoju. Rezultate navajamo v tabeli 4, skupaj s podatki drugih avtorjev, ki smo jih zasledili v literaturi. Izkoristki so običajno večji od 85 %. Nekatere naše vrednosti so včasih višje, drugič nižje v primerjavi s certifikati. Opozoriti je treba, da se tudi v certifikatih gibljejo analizne vrednosti v določenih razponih, nekatere vrednosti celo niso certificirane, ampak dane le v vednost.

Analiza vzorcev iz proizvodnje

Vpeljane metode uporabljamo za analizo vzorcev iz proizvodnje, **tabela 5**.

Problem je bil z raztapljanjem nikljeve zlitine, ki vsebuje 5 % Nb. Dodatek H_2SO_4 ni zadoščal¹, popolno raztopitev vzorca je omogočil dodatek 1 ml HF.

ZAKLJUČEK

Preštudirali smo ločbi jodidov Ag, Bi, Cd, Pb, Se, Sn in Te ter ugotovili, da sta obe ločbi uporabni za vse našete elemente, medtem ko je za Zn uporabna le TOPO-MIBK ločba. Preverjeni tehniki sta uporabni za analizo tistih elementov sledov v jeklih in superzlitinah, ki so zanimivi za metalurgijo. Odlikuje ju dobra točnost, ponovljivost in odlična občutljivost.

CONCLUSION

In this study it has been shown that the solvent extraction of Ag, Bi, Cd, Pb, Se, Sn, and Te-iodides can be used as with TOPO-MIBK as with TOA-MIBK procedures of separation, only Zn can be separated only with TOPO-MIBK. The proven technics are available for the analysis of steels and superalloys for trace elements of metallurgical interest. The methods offer satisfactory accuracy, good reproducibility, and excellent sensitivity for each element determined.

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PH.D. and M.SC. Theses in Year 1987 in Metallurgy at the Department of Geology, Mining, and Metallurgy

DOKTORSKI DELI

— **Matjaž Torkar:** Vroča preoblikovalnost litega maloogljivega jekla. Vpliv Al, N, Mn in S na izoblikovanje strukture pri strjevanju in ogrevanju jekla na temperaturo vročega preoblikovanja

(Mentor: F. Vodopivec, 4/5/1987)

Številne raziskave strjevanja jekel obravnavajo kompleksne procese, ki se dogajajo pri strjevanju bloka in konti lite gredice. Manj je na razpolago podatkov o vplivu strjevalne strukture in njenih značilnosti na krhkost v vročem. Z upogibnim preskusom v vročem, z metalografskimi in kemičnimi analizami ter analizo morfologije prelomov je avtor študiral vplive med strjevalno strukturo jekla ter njegovo preoblikovalnostjo. Ugotovil je, da so poškodbe med segrevanjem blokov pred deformacijo posledica strukturnega stanja jekla ob površini. Aluminij in dušik tanjšata globulitno skorjo ob površini, medtem ko mangan in žveplo nanjo skoraj ne vplivata. Pač pa mangan povečuje debelino stebričastih kristalov, žveplo pa ima nasproten vpliv, medtem ko aluminij in dušik nimata vpliva na to. Onadva povečujeta strjevalna zrna. Ogljik močno vpliva na izoblikovanje strjevalne strukture in stebra struktura se pojavlja le v območju peritektika. Žveplo povečuje vročo pokljivost jekla, mangan pa ta vpliv zmanjšuje, ker zmanjšuje topnost žvepla v avstenitu. Mangan, aluminij in ogljik vplivajo na medsebojno oddaljenost in velikost sulfidnih vključkov, ki nastajajo med ohlajanjem s temperature strjevanja. Kaže, da je vzrok za zmanjšanje začetne plastičnosti jekla z ogljikom v intervalu peritektika tudi v vplivu aluminija in dušika na strjevalno strukturo jekla.

90 strani

72 cit.

— **Anton Zalar:** Preiskava vplivov reliefnosti površine vzorca in vpadnega kota Ar^+ ionov na globinsko ločljivost profilnih diagramov večslojnih tankih kovinskih plasti, analiziranih s spektroskopijo Augerjevih elektronov (AES)

(Mentor: I. Kosovinc, 23/4/1987)

Za raziskavo elementne sestave tankih kovinskih, polprevodnih in dielektričnih plasti po globini danes uporabljamo metode, ki so povezane z ionskim jedkanjem.

Ph. D. THESES

— **Matjaž Torkar:** Hot Workability of Cast Low-Alloyed Steel. Influence of Al, N, Mn, and S on the formation of structure in solidification and heating steel on the hot working temperature

(Supervisor: F. Vodopivec, 4/5/1987)

Numerous investigations on solidification of steel treat complex processes occurring during solidification of ingot and continuously cast billet. Less data exist on the influence of the solidification structure and of its characteristics on the hot shortness. Applying hot bending test, metallographical and chemical analyses, and the analysis of fracture morphology the author studied the influences of solidification structure of steel on its workability. He found that damages during ingot soaking before deformation are the consequence of the structural state of steel surface. Aluminium and nitrogen reduce the equiaxed-crystal layer on the surface while manganese and sulphur have nearly no influence on it. On the other hand, manganese increases the thickness of columnar crystals, sulphur has the opposite effect, while aluminium and nitrogen have no effect. They increase the equiaxed crystals in the interior. Carbon has a pronounced influence on the formation of solidification structure, and columnar crystals appear only in the peritectic region. Sulphur increases the hot shortness of steel while manganese reduces this influence since it reduces the solubility of sulphur in austenite. Manganese, aluminium, and carbon influence the distance between and the size of sulphide inclusions which are formed during cooling from the solidification temperature. It seems that also influence of aluminium and nitrogen on the solidification structure of steel contribute to the reduced initial workability of steel with carbon in the peritectic region.

90 pages

72 ref.

— **Anton Zalar:** Investigation of Influences of Relief Surface of Sample and of Incidence Angle of Ar^+ Ions on the Depth Resolving Power for Profile Diagrams of Multilayer Thin Metallic Coverings Being Analyzed by the Auger Electron Spectroscopy (AES)

(Supervisor: I. Kosovinc, 23/4/1987)

In determining elemental composition of thin metallic, semiconductor, and dielectric layers into depth the methods connected to ionic etching are used today. At

Atome s površine odstranjujemo s curkom ionov žlahtnega plina. Spektroskopija Augerjevih elektronov je ena izmed metod za analizo vrhnje plasti atomov, ki ostanejo na površini po ionskem jedkanju. Reliefnost površine zaradi različnih nagibov mikroploskev proti elektronskemu in ionskemu curku pa vpliva na natančnost preiskave. Zato je avtor pri svojem študiju na podlage silicija z različno hrapavostjo katodno napržil večslojno tanko plast kroma in niklja. Hrapavost vzorcev se je gibala med 0,012 do 2,3 μm . Ugotovil je, da je za natančno analizo AES potrebna dobra električna prevodnost vzorca in preprečitev difuzijskih procesov na analiziranem mestu. Če je možno, naj bo premer curka elektronov manjši od površine mikroploskve, ki jo analiziramo. Bistveno izboljšanje globinske ločljivosti in s tem natančnejšo profilno analizo AES je avtor dosegel z jedkanjem pri vpadu ionov na vzorec iz večih smeri. Obenem je razvil metodo vrtenja vzorca med hkratno analizo AES in ionskim jedkanjem.

86 strani

209 cit.

oms from the surface are removed by an ionic jet of noble gas. Auger electron spectroscopy is one of the method used in analysis of the upper layer of atoms which remain in the surface after ionic etching. The relief of surface influences the accuracy of analysis due to variable inclination of microareas against electron and ionic jet. The author applied silicon pads of various roughness and deposited on them multilayer thin coverings of chromium and nickel by cathodic spraying. Roughness of samples varied between 0.012 and 2.3 μm . He found that accurate AES analysis demands a well conductable sample and prevention of diffusion processes on the analyzed spot. If possible, the electron jet should be smaller than the analyzed microarea. Essential improvement in depth resolving power and a more accurate AES profile analysis was achieved by etching with ions inciding the sample from various directions. Simultaneously, the author developed the method of sample rotation during simultaneous AES analysis and ionic etching.

86 pages

209 ref.

MAGISTRSKA DELA

— Sylejman Qorrolli: *Komparativna metalografsko-rentgenska analiza napak v zvarih cevi*

(Mentor: I. Kosovinc, 9/3/1987)

Namen dela je bil s primerjalnimi preiskavami objektivno ugotavljati nastanek, razvoj in škodljive vplive notranjih napak v zvarih jeklenih cevi, vzdolžno ali vijačno zvarjenih, pri čemer je avtor preiskoval tudi najbolj kompleksne napake, ko se posamezne osnovne napake pojavljajo skupaj. Metalografska analiza je pokazala, da daje VF električno uporovno varjenje najkakovostnejše zware, pri čemer je zelo pomembna naknadna toplotna obdelava zvarov. Paziti pa je pri uporovnem varjenju, da se izognemo razogljčenju in da se znotraj pri stiskanju ne tvori rob. Le-tega dobro odkrivamo z rentgensko analizo. Avtor je tudi ugotavljal potrebne pogoje rentgenske preiskave za različne zware. Na koncu pa ugotavlja, da se obe preiskovalni metodi dobro dopolnjujeta in da ju je treba več uporabljati pri preiskavi zvarov cevovodov.

111 strani

70 cit.

M. Sc. THESES

— Sylejman Qorrolli: *Comparative metallographic/X-ray analysis of defects in the welds of pipelines*

(Supervisor: I. Kosovinc, 9/3/1987)

The intention of the project was to state the formation, progression, and harmful influences of internal defects in welds of steel pipes being longitudinally or helically welded, applying comparative testing methods. Also the most complex defects as a combination of various single defects were investigated. The metallographic analysis showed that HF resistance butt welding gives the best welds, but the subsequent heat treatment of welds is very important. In resistance welding it is necessary to take care to prevent decarburization and that internal flash is not formed during butting the sheet sections. Flash is well revealed by X-ray testing. Author determined the necessary parameters of X-ray analysis for single welds. Finally, he had stated that both testing methods are complementary and that they should be more often applied in testing welds of pipelines.

111 pages

70 ref.

— Drago Dretnik: *Mehanizem vpliva klora na kvaliteto praženca za svinčev plavž*

(Mentor: A. Paulin, 9/3/1987)

Pri predelavi izrabljenih nesepariranih akumulatorjev nastaja klor iz PVC separatorjev in gre v dimnino. Z dodajanjem te dimnine koncentratom pa klor prihaja v plavž. Avtor je skušal osvetliti vpliv klora pri pirometalurškem pridobivanju svinca ter ugotoviti mehanizme nastajanja klorovih spojin in njihovo medsebojno reagiranje pri različnih temperaturah in v različnih atmosferah. Uporabil je zmesi čistih spojin PbO_2 , PbCl_2 , PbSO_4 , PbS in Na_2CO_3 , ter jih segreval na zraku, v dušiku, v kisiku in v reduktivni atmosferi do 1150 °C. To je bil študij sistema Pb-Na-O-Cl-S . Na osnovi spreminjanja mase je zasledoval izparevanje klorovih spojin, v kombinaciji z rentgensko analizo pa njihovo medsebojno reagiranje ter reagiranje s sodo. V odvisnosti od sestave izhodnih mešanec nastajajo v različnih atmosferah različni svinčevi oksidkloridi, natrijev klorid ter deloma celo svinčevo natrijevi kloridsulfati. Za prakso je pomembno, da je treba ustvariti take pogoje pri predelavi dimnine, da izpari čim manj svinčevega klorida, ki se s tem vrača nazaj v proces, in da čim več klora reagira s sodo v natrijev klorid ali druge stabilne spojine.

— Drago Dretnik: *Mechanism of Chlorine Influence on the Quality of Blast-Furnace Sinter*

(Supervisor: A. Paulin, 9/3/1987)

In treating not separated battery scrap, chlorine is liberated from PVC separators and it goes in form of compounds into the flue dust. By adding flue dust to the burden chlorine comes into the blast furnace. Author tried to elucidate the influence of chlorine in pyrometallurgical winning of lead, and to find the mechanisms of formation of chlorine compounds and of reactions among them at various temperatures and in various atmospheres. He applied pure compounds PbO_2 , PbCl_2 , PbSO_4 , PbS , and Na_2CO_3 , and heated them in air, nitrogen, oxygen and in reducing atmosphere up to 1150 °C. It is the study of the Pb-Na-O-Cl-S system. Based on mass reductions he followed the evaporation of chlorine compounds, and in combination with X-ray analysis he studied their mutual reacting and reacting with soda. Depending on initial compositions of samples various lead oxychlorides beside sodium chloride are formed in various atmospheres, and partially even complex lead sodium chloride sulphates. The essential founding for industrial practice was that such conditions for treating flue dust must be achieved that evaporation of lead chloride

Obenem je avtor študiral tudi učinkovitost hidrometalurškega razkloriranja dimnine z različnimi raztopinami, kar je omogočilo izdelati v Žerjavu industrijsko napravo, kjer dosegajo okoli 50 %no učinkovitost.

109 strani

26 cit.

is the smallest and that the majority of chlorine reacts with soda into sodium chloride or other stable compounds.

Simultaneously the author studied also the efficiency of hydrometallurgical dechlorination of flue dust with various solutions. Based on investigations, an industrial set-up was built in the lead smelter in Žerjav which operates with dechlorination efficiency of 50 %.

109 pages

26 ref.

— Boris Ule: Zapoznili lom zaradi vodika v jeklu
(Mentor: L. Kosec, 29/6/1987)

Vse več se uporabljajo zelo trdna konstrukcijska jekla, ki pa imajo relativno majhno žilavost, zato so pomembne njihove lomne značilnosti, predvsem t. i. zapoznili lom. Avtor je v svojem delu z nateznimi preskušanci z zarezo študiral zapoznili lom jekla Č 4732, rezultate meritev kvantitativno vrednotil z metodo linearne elasto-mehanike ter raziskal vpliv majhnih mikrostrukturnih variacij jekla na njegovo občutljivost k zapoznelemu lomu. Koren zarez na preskušancu je predhodno navodil. Med poskusom je z uporovnim lističem meril odpiranje ustja zarez ter napredovanje razpoke. Ugotovil je, da mejni napetostni faktor K_{TH} pri enaki plastičnosti jekla ne zavisi od majhnih mikrostrukturnih variacij jekla in da zavisi le od plastičnosti jekla. Gonilna sila za nukleacijo mikrorazpok je enaka razliki med uporabljenimi napetostmi in faktorjem K_{TH} . Pokazalo se je tudi, da vodik v koncentraciji 0,55 ppm nima vpliva na lomno žilavost. Majhni deleži bainita v pretežno martenzitni mikrostrukturi nizkolegiranih jekel pomikajo temperaturo prehoda v krhko stanje k nižjim vrednostim in s tem je jeklo manj občutljivo na krhki lom, večji deleži pa žilavost poslabšajo. Pojavljanje zapoznelega loma pri preiskovanem jeklu z malo vodika je predvsem posledica poslabšanja njegove deformabilnosti med dolgotrajnim delovanjem mehanske obremenitve.

60 strani

65 cit.

— Boris Ule: Delayed Fracture Due to Hydrogen in Steel

(Supervisor: L. Kosec, 29/6/1987)

Application of high-strength steel is increasing, but this steel has relatively low toughness, thus the fracture characteristics are essential among which the delayed fracture is the most important. The author studied the delayed fracture of Č 4732 steel using tensile tests with notched samples. The results of measurements he evaluated quantitatively with the method of linear elastomechanics. Besides, he investigated also the influence of small microstructural variations in steel on its sensitivity to delayed fracture. The notch root on the test specimen was preliminary charged with hydrogen. Strain gauge was applied for measuring widening of notch opening and for crack propagation. He found that the threshold stress intensity factor K_{TH} at the same steel plasticity does not depend on small microstructural variations in steel, but it depends only on the steel plasticity. The driving force for nucleation of microcracks is equal to the difference between the applied stress and the factor K_{TH} . It turned out that hydrogen in concentration of 0.55 ppm has no influence on the fracture toughness. Small portions of bainite in mainly martensitic matrix of low-alloyed steel shift the transition temperature to lower values and thus steel is less sensitive to brittle fracture, while higher portions reduce the toughness. Appearance of delayed fracture in investigated steel with low hydrogen is mainly caused by the deterioration of the steel deformability due to long lasting mechanical loading.

60 pages

65 ref.

— Halil Čulov: Ionsko nitriranje jekla za poboljšanje

(Mentor: L. Kosec, 28/12/1987)

Osnovni namen naloge je bil oceniti primernost ionskega nitriranja za jekla, ki se uporabljajo za dinamično obremenjene dele dizelskih motorjev velike moči. Avtor je primerjal različne metode toplotne obdelave na kakovost strojnih delov. Izbral je nikelj krom molibdenovo jeklo in ugotovil, da ionsko nitriranje predstavlja prednost glede na dosedanje tehnološke procese površinskega utrjevanja, možnost avtomatizacije procesa pa omogoča vzdrževanje stalne kakovosti. Metalografske preiskave, mehanski preizkusi ter analiza lomov so pokazali povečanje statične in dinamične trdnosti za 20 oz. 20 do 40 %, da površinska trdota okoli 740 HV zmanjšuje obrabo, da zmanjšanje hrapavosti od 0,50 na 0,07 μm s poliranjem po nitriranju tudi povečuje dinamično odpornost ter omogoča boljše mazanje v drsnih ležajih.

153 strani

18 cit.

— Halil Čulov: Ionic Nitriding of Steel for Quenching and Tempering

(Supervisor: L. Kosec, 28/12/1987)

Basic aim of the investigation was to estimate the suitability of ionic nitriding for steel which are used for dynamically loaded parts of high-power Diesel engines. The author compared various methods of heat treatment on the quality of mechanical parts. Nickel-chromium-molybdenum steel was chosen. It was found that ionic nitriding is advantageous compared with the present technology of surface hardening. Possibility of the process automatization enables to keep the constant quality. Metallographic investigations, mechanical tests, and fracture analysis showed the increased static and dynamic strength for 20 and 20 to 40 % respectively. Surface hardness of about 740 HV reduces wear, and the reduction of roughness from 0.50 to 0.07 μm by polishing after nitriding also increases dynamic strength and simultaneously it improves the greasing characteristics in sleeve bearings.

153 pages

18. ref.

— **Svetozar Golubović: Lomna žilavost ledeburitnih jekel**

(Mentor: L. Kosec, 28/12/1987)

Ledeburitna jekla za delo v hladnem so najpogostejša orodna jekla. S povečevanjem trdote se povečuje obrabna odpornost. Namen naloge je bil osvojiti metodo preiskovanja lomne žilavosti orodnih jekel Č 4150 (OCR 12) in Č 4850 (OCR 12VM). Avtor je uporabil fraktografijo loma, analiziral je lome različno toplotno obdelanih jekel, preiskal strukturo, predvsem glede na karbide in zadržani avstenit, mehansko preskušal vzorce ter ugotovil kritični napetostni intenzitetni faktor K_{IC} za preiskovana jekla. Spreminjal je temperaturo popuščanja. Pri nizkih temperaturah je žilavost večja zaradi večjega deleža zadržanega avstenita. Večina karbidov je v heksagonalni obliki M_7C_3 , le malo kot kubični $M_{23}C_6$. Pri nizkih temperaturah popuščanja nastopa interkristalni, pri višjih pa intrakristalni lom. Kali za nastajanje mikrorazpok so predvsem prelomi karbidov. Jeklo Č 4850 je pokazalo precej boljše lomno žilavost od jekla Č 4150.

98 strani

67 cit.

— **Svetozar Golubović: Fracture Toughness of Ledeburitic Steel**

(Supervisor: L. Kosec, 28/12/1987)

Ledeburitic cold working tool steel is the most frequent tool steel. Increased hardness reduces the wear. The aim of project was to master the investigation method of fracture toughness for Č 4150 (OCR 12) and Č 4850 (OCR 12VM) tool steel. The author applied the fracture fractography, he had analyzed the fractures of variously heat treated steel, he had investigated the structures with a special emphasis on carbides and retained austenite, he made mechanical tests, and he determined the critical stress intensity factor K_{IC} for the investigated steels. The temperature of tempering was varied. At lower tempering temperatures the toughness was greater due to greater amount of retained austenite. Most carbides had hexagonal M_7C_3 form while cubic $M_{23}C_6$ carbides were in minority. At lower tempering temperatures the fracture was intercrystalline, at higher it was intracrystalline. Nuclei for microcrack formation were mainly fractured carbides. Č 4850 turned out to have much better toughness than Č 4150 steel.

98 pages

67. ref.

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669.14 — Zlitine železa z ogljikom.

- Jeklo nasploh
- Kos Ivan: Vpliv izhodnega strukturnega in trdnostnega stanja ventilskih jekel na mehanske lastnosti pri povišanih temperaturah
 ŽZB 22 (1988) 1, 1—6
- Koroušič Blaženko, J. Triplat, J. Arh: Sodobna tehnologija izdelave dinamo jekel po duplex postopku EOP + V(0) D
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669.16 — Proizvodnja gradlja

- Todorovič Gojko, B. Dobovišek, J. Lamut, L. Šketa: Vpliv alkalnih karbonatov na redukcijo železovih oksidov
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669.18 — Proizvodnja jekla

- Prešern Vasilij, M. Kmetič, A. Rozman, P. Bračun: Obdelava jekla s streljanjem oplaščene žice v štorski in ravenski jeklarni
 ŽZB 22 (1988) 4, 117—126
- Koroušič Blaženko, A. Šteblaj: Kaj prinaša nova tehnologija streljanja dodatnih materialov v jeklarsko prakso
 ŽZB 22 (1988) 4, 111—115
- Rodič Jože: Skrajševanje tehnološkega postopka od taline do žice
 ŽZB 22 (1988) 4, 101—109
- Arh Joža, J. Biček, M. Demšar, A. Koselj, I. Polak, A. Mlakar: Postavitev in obratovanje Jeklarne 2 na Jesenicah
 ŽZB 22 (1988) 3, 65—78

VSEBINA

UDK: 669.181.274.621.746.047.621.771.25
ASM/SLA: D7c, D9q, D8m, A11e, 4-61

Metalurgija — Vakuumska indukcijska peč — Horizontalno kontinuirno litje žice, palic, trakov — Vroča predelava — Specifična poraba energije — Skrajševanje tehnoloških postopkov
J. Rodič

Skrajševanje tehnološkega postopka od taline do žice
Železarski zbornik 22 (1988) 4 s 101—109

Novi materiali, materiali z izboljšanimi lastnostmi, racionalizacija tehnoloških procesov, zmanjševanje specifične porabe energije in izboljšanje izkoristkov so cilji novih usmeritev tehnološkega razvoja. Novi pristopi k razvojnim raziskavam za uveljavljanje pravih materialov in tehnologij s simulacijami in matematičnim modeliranjem se navezujejo tudi na pilotno proizvodnjo, ki je v članku nekoliko podrobneje opisana.

Poseben fleksibilen sklop pilotne proizvodnje predstavlja vakuumska indukcijska peč, naprava za horizontalno neprekinjeno litje žice in palic ter električno pretaljevanje pod žlindro.

Avtorski izvleček

UDK: 669.18.669.891
ASM/SLA: D9r, ADr, EGf41, EGr

Metalurgija — jeklarstvo — streljanje oplaščene žice
V. Prešern, M. Kmetič, A. Rozman, P. Bračun

Obdelava jekla s streljanjem oplaščene žice v štorski in ravenski jeklarni
Železarski zbornik 22 (1988) 4, S 117—126

Rezultati uvajanja postopka obdelave jekla s streljanjem oplaščene žice s CaSi v štorski in ravenski jeklarni. Narejena je primerjava s postopkom vpihovanja CaSi. Podani so zahtevani pogoji, da dobimo jeklo z majhno vsebnostjo kisika ter modificiranimi aluminatnimi vključki. Prikazan je vpliv pečne žilindre, dani so izkoristki kalcija, titana in bora, analizirano je nadušičenje in gibanje vsebnosti žvepla. Razčlenili smo osnovne stroške novega postopka in jih primerjali s postopkom vpihovanja CaSi.

Avtorski izvleček

UDK: 669.18.669.891.669.046.521
ASM/SLA: D9r, D11r, ADr, EGf41, EGr

Metalurgija — jeklarstvo — streljanje žice v talino — desoksidacija — nove tehnologije

B. Koroušič, A. Šteblaj

Kaj prinaša nova tehnologija streljanja dodatnih materialov v jeklarsko prakso

Železarski zbornik 22 (1988) 4 s 111—115

Metoda streljanja različnih materialov v tekoče jeklo, kot so: Ca, Al, Ti, C, B . . . prinaša vrsto prednosti v jeklarsko tehnologijo. Tehnika streljanja polne ali polnjene žice omogoča izvajanje desoksidacije taline, toda tudi legiranje manjših količin elementov z visoko afiniteto do kisika in modifikacijo nekovinskih vključkov, kar je posebej zanimivo za kontilitet jekla.

Avtorski izvleček

UDK: 621.771.8.669.14.018.23/29
ASM/SLA: L22, F23, K5j, TSb, SGBs

Metalurgija — plativanje jekel — vroče valjanje — fizika kovin
D. Kmetič, J. Gnamuš, F. Vodopivec, B. Ralič

Plativanje orodnih jekel na konstrukcijska jekla

Železarski zbornik 22 (1988) 4 s 127—136

Prispevek obravnava plativanje različnih vrst orodnih jekel na nosilno konstrukcijsko jeklo. Preiskave smo naredili na žarjenih vzorcih in na vzorcih, valjanih pri različnih termomehanskih pogojih.

Poleg metalografskih preiskav prehodne difuzijske plasti med orodnim in konstrukcijskim jeklom smo v elektronskem mikroanalizatorju opredelili koncentracijske profile legirnih elementov. Raztržna trdnost plativanih jekel je odvisna od trdnosti šibkejšega gradnika in od mikrostrukturnih značilnosti prehodne plasti.

Avtorski izvleček

CONTENTS

UDK: 669.18.669.891
ASM/SLA: D9r, ADr, EGf41, EGr

Metallurgy — steelmaking — injection of cored wire
V. Prešern, D. Kmetič, A. Rozman, P. Bračun

Treatment of Steel in Štore and Ravne Steelworks by Injection of Cored Wire

Železarski zbornik 22 (1988) 4 P 117—126

Paper presents the results of the introduction of steel-treatment technology by the injection of CaSi cored wire in Štore and Ravne steelworks. A comparison with the injection of powdery CaSi was made. The conditions to obtain steel with low oxygen content and modified aluminate inclusions are given. Influence of furnace slag, and calcium, titanium and boron yields are given, pick-up of nitrogen and variation of sulphur contents are analyzed. Basic costs of the new method were estimated, and comparison with the injection of powdery CaSi was made.

Author's Abstract

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ASM/SLA: D7c, D9q, D8m, A11e, 4-61

Metallurgy-Vacuum induction furnace-Horizontal continuous casting of wire, rods and strips-Hot working-Specific energy consumption-Shortening of technological procedures.

J. Rodič

Shortening of Technological Procedures

Žel. zbornik 22 (1988) 4 P 101—109

New materials, materials with improved properties, rationalization of technological processes, reduction of specific energy consumption and increase in yield are the targets of technological development. New concepts to research and development for the promotion of proper materials and technologies with mathematical modelling and computer simulation are connected with pilot production which is described in more details.

Specially flexible pilot plant consist of a vacuum induction furnace, horizontal continuous caster for wire and rods, and electro-slag remelting unit.

Author's Abstract

UDK: 621.771.8.669.14.018.23/29
ASM/SLA: L22, F23, K5j, TSb, SGBs

Metallurgy — Plating of Steel — Hot Rolling — Metals Science
D. Kmetič, J. Gnamuš, F. Vodopivec, B. Ralič

Plating Tool Steel on Structural Steel

Železarski zbornik 22 (1988) 4 P 127—136

The paper treats plating of various tool steels on the bearing structural steel. Investigations were made with annealed samples and samples rolled at various thermomechanical conditions. Next to the metallographic investigations of the transition diffusion layer between the tool and the structural steel, also concentration profiles of alloying elements were determined by electron microanalyzer. Tensile strength of plated steel depends on the strength of weaker component and on the microstructural characteristics of the transition zone.

Author's Abstract

UDK: 669.18.669.891.669.046.521
ASM/SLA: D9r, D11r, ADr, EGf41, EGr

Metallurgy — steelmaking — wire injection — deoxidation — advanced technologies.

B. Koroušič, A. Šteblaj

Advanced Technology in Steelmaking — Injection of Additions

Železarski zbornik 22 (1988) 4 P 111—115

The injection of different materials such as Ca, Al, Ti, C, B... into liquid steel have a series of advantages. The method using cored or coreless wire is very efficient and useful for deoxidation, small additions of alloying elements with a high affinity for oxygen as well as for modification of non-metallic inclusions which is of interest specially for continuous casting.

Author's Abstract

VSEBINA

UDK: 620.178.2:539.211.669.15
ASM/SLA: Q26r, M23p, AY

Metalurgija — mehanika loma — J integral
J. Vojvodič-Gvardjančič, Š. Strojnik, B. Ule, A. Ažman

J integral in morfologija preloma mikrolegiranih — drobnostnatih jekel Nionical 70 in Niomol 490

Železarski zbornik 22 (1988) 4, s 137—145

Merjenja lomne žilavosti drobnostnatih mikrolegiranih jekel z metodo J-integrala zahtevajo, v primerih pojavljanja večje lateralne kontrakcije preizkušancev, rabo ostrejših dimenzijskih kriterijev, kot pa jih predpisuje veljavni ASTM standard.

Ne glede na le orientacijske vrednosti J_{IC} pa mikrofraktografske preiskave kažejo, da se velikosti jamic na frakturnih površinah v grobem ujemajo z izmerjenimi žilavostmi.

Avtorski izvleček

UDK: 543.423
ASM/SLA: S11k, U2g

Metalurgija — kemijska sestava — ICP emisijska spektrometrija — nikljeve zlitine

A. Osojnik, T. Lavrič

Študij optimalnih pogojev za analizo kovinskih materialov z ICP atomsko emisijsko spektrometrijo

Železarski zbornik 22 (1988) 4 s 153—157

Študirali smo optimalne pogoje in analize parametre za določanje elementov Ni, Co, Cr, Mo, Ti (60-2 %) in Al, Fe, Mn, Cu, Si (1 do 0.05 %) v nikljevih zlitinah s sekvenčno ICP atomsko emisijsko spektrometrijo.

Ugotavljali smo spektralne interference za vse prisotne elemente. Identificirali smo spektralno interferenco Co pri 138.204 nm Fe liniji in Mo pri 251.611 nm Si liniji. Izvršili smo korekcijo za Fe in Si glede na moteče elemente. Izbrali smo optimalne valovne dolžine ter določili občutljivost, mejo zaznavnosti, korekcijske faktorje (za Fe in Si) in ponovljivost rezultatov. Točnost metode smo preverili s standardi nikljevih zlitin podobnih sestav.

Avtorski izvleček

UDK: 620.178.2:669.15-196.58
ASM/SLA: Q6, Q7, Q26q, TSh, 2-64

Metalurgija — preiskava materiala — mehanika loma
S. Golubović, L. Kosec

Lomna žilavost ledeburitnega kromovega jekla

Železarski zbornik 22 (1988) 4 s 147—151

S poskusi smo ugotovili kritično vrednost faktorja intenzivnosti napetosti pri ravninski deformaciji za kromovi ledeburitni jekli Č.4150 in Č.4850. Jekli sta bili kaljeni in popuščeni pri temperaturah 180, 400 in 500° C.

Kritično vrednost faktorja intenzivnosti napetosti K_{IC} smo določali s polempirijsko metodo. Uporabili smo CT epruvete, v katerih smo z utrujanjem ustvarili začetne razpoke. S temperaturo popuščenja se lomna žilavost obeh jekel zmanjšuje. Jeklo Č.4850 ima skozi ves interval temperatur popuščenja boljše lomno žilavost.

Avtorski izvleček

UDK: 543.064.669.14
ASM/SLA: S11d, S11g, 1-54

Metalurgija-analiza jekel in superzlitin — določanje sledov — separiranje in skoncentriranje — AAS določanje

T. Lavrič, A. Osojnik, Z. Kristan

Določanje sledov kovin v jeklih in superzlitinah, po predhodni ločbi, s plamensko AAS

Železarski zbornik 22 (1988) 4 s 159—166

Preštudirali smo ločbo, skoncentriranje in določanje sledov Ag, Bi, Cd, Pb, Se, Sn, Te in Zn za razna jekla in superzlitine. Izvedli smo primerjalno študijo ekstrakcije jodidov preiskovanih elementov s trioktilfosfinoksidom (TOPO) in trioktilaminom (TOA) v metilizobutiketon (MIBK). Organsko fazo smo analizirali s plamensko AAS. Učinkovitost separacije je, vključno z določanjem, za oba ekstrakcijska sistema, za vse elemente približno enaka, in to 85-110 %. Samo za Zn so bili doseženi izkoristki s TOA-MIBK sistemom pod 50 %. Za Se smo dobili s TOA-MIBK ekstrakti, v primerjavi s TOPO-MIBK, občutno stabilnejše signale. Za Te smo izvedli tudi primerjavo določanja z AAS, po redukciji do elementarnega stanja in naknadnem raztapljanju. Vse metode so dale pravilne rezultate za uporabljene certificirane materiale. Praktične meje zaznavnosti se gibljejo pri ločbi z ekstrakcijo, če izhajamo iz 5 g vzorca, odvisno od občutljivosti elementa, ki ga določamo, v območju 0.05—1 ppm.

Avtorski izvleček

CONTENTS

UDK: 543.423
ASM/SLA: S11k, U2g

Metallurgy — chemical composition, ICP emission spectrometry — nickel base alloys

A. Osojnik, T. Lavrič

Investigation of Optimal Conditions for Metal Analysis by ICP Atomic Emission Spectrometry

Železarski zbornik 22 (1988) 4 P 153—157

The optimal conditions and analysis parameters for determination of Ni, Co, Cr, Mo, Ti (60-2%) and Al, Fe, Mn, Cu, Si (1 to 0.05%) in nickel base alloys by sequential ICP atomic emission spectrometry were studied.

Spectral interferences due to the influences of any present element were identified by wavelength scans near analyte wavelengths for all ten elements. It was established that only the presence of cobalt at 238.204 nm Fe line and the presence of molybdenum at 251.611 nm Si line could introduce an error in iron and silicon determination, respectively. Therefore a correction for these two elements considering the interfering elements was made. Optimal spectral lines, detection limits, sensitivities, additive correction factor (for Fe and Si) and reproductivity of results were established. The accuracy of the method was checked with different certified reference materials of similar composition.

Author's Abstract

UDK: 620.178.2.539.211.669.15
ASM/SLA: Q26r, M23p, AY

Metallurgy — Fracture Mechanics — J-Integral

J. Vojvodič-Gvardjančič, Š. Strojnik, B. Ule, A. Ažman

J-Integral and Fracture Morphology of Micro-alloyed Fine-grained Steels Nionical 70 and Niomol 490

Železarski zbornik 22 (1988) 4, P 137—145

Fracture toughness measurements of fine-grained micro-alloyed steels by the J-integral method show that whenever severe lateral contractions appear on sides of a specimen it is necessary to apply a more rigid size criteria than those set by the ASTM standard.

Regardless of the approximative J_{IC} values it was shown by microfractographic investigations that the sizes of dimples on fracture surfaces on the whole agree with measured toughness values.

Author's Abstract

UDK: 543.064.669.14
ASM/SLA: S11d, S11g, 1-54

Metallurgy-analysis of steels and superalloys — trace elements — separation and preconcentration-flame AAS

T. Lavrič, A. Osojnik, Z. Kristan

AAS Determination of Trace Metals in Steels and Superalloys With Preliminary Separation

Železarski zbornik 22 (1988) 4 P 159—166

Separation, preconcentration and determination of trace metals Ag, Bi, Cd, Pb, Se, Sn, Te, and Zn in different grades of steels and superalloys was investigated. A comparison study was carried out to evaluate the extraction of iodides of analytes using trioctylphosphineoxid (TOPO) and trioctylamine (TOA) into methylisobutylketone (MIBK). The organic phase was analysed by flame AAS. The effectiveness of separations, inclusively the determination, was approximately equal for both extraction systems, and thus 85—110%, only for Zn the recoveries in TOA-MIBK system were under 50%. For Se significantly better stability of the signals was obtained with TOA-MIBK extractants as with TOPO-MIBK. For Te also a comparison with reduction to elemental Te with subsequent dissolution and AAS determination was made. All methods gave accurate results for the certified materials used. The practical limits of detection based on extraction separation of 5g sample are of the order 0.05-1 ppm, depending on sensitivity of analyte.

Author's Abstract

UDK: 620.178.2.669.15-196.58
ASM/SLA: Q6, Q7, Q26q, TSh, 2-64

S. Golubović, L. Kosec

Metallurgy — Material Testing — Fracture Mechanics

Železarski zbornik 22 (1988) 4 P 147—151

The magnitude of the critical stress intensity factor in plane strain state was found out experimentally for ledeburite chromium steels Č.4150 and Č.4850. The two steel qualities were hardened and subsequently tempered to temperatures 180, 400 and 500° C. The critical stress intensity factor K_{IC} was determined by a semi-empirical method. In the experiments CT-specimens were used which were fatigued to create initial cracks. It was found out that with increasing temperature of tempering the fracture toughness of both steel qualities decreases.

Author's Abstract