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ALLOYS WITH MODIFIED CHARACTERISTICS

ZLITINE Z MODIFICIRANIMI LASTNOSTMI

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Industry has a permanent need for new materials to improve the performance of constructions. However, the development of new materials is a complicated and costly process, and in many cases the existing materials with modified characteristics are used. By the use of certain technological processes of producing liquid metals, deformation processes, thermal and surface treatments, the mechanical and exploitation characteristics of existing materials can be improved. In this paper is an overview of several research activities at the Institute in Zenica with the goal to improve the characteristics of some materials in use in the air and car industries. With semi-industrial facilities and in laboratories of the institute some researches where conducted on stainless steels and maraging steels as well as on superalloys based on nickel and iron.

Key words: new materials, new technologies, stainless steels, maraging steels, super alloys

Industrija potrebuje nove materiale, če želi izboljšati lastnosti konstrukcij. Razvoj novih materialov je zapleten in drag proces in so zato mnogokrat uporabljeni materiali s spremenjenimi lastnostmi. Z spremembami v tehnologiji obdelave taline, procesov predelave, toplotne in površinske obdelave je mogoče izboljšati mehanske in uporabne lastnosti materialov. V tem delu je kratek pregled raziskav na Inštitutu v Zenici, ki so bile izvršene s ciljem izboljšanja materialov, ki so v uporabi v industriji vozil in letal. Na polindustrijskih in laboratorijskih napravah na inštitutu so bile opravljene raziskave na nerjavnih in maraging jeklih in na superzlitinah niklja in železa.

Ključne beside: novi materiali, nove tehnologije, nerjavno jeklo, maraging jeklo, superzlitine

1 INTRODUCTION

Modern industry has a permanent need for new materials to improve the performance of their constructions. The introduction and application of new materials for the improvement of existing structures with a higher level of exploitation properties is related to new material development and the mastering of these materials. In some cases designers, in cooperation with research and development institutions, use simple and economically reasonable solutions. One possibility is a modification (improvement) of some of the properties of existing materials with the aim to increase the exploitation and mechanical properties at room and elevated temperatures or improve the corrosion, heat and wear resistance. The term modification used here includes specific changes in chemical composition and microstructure, achieved with changes of technology during the production of liquid metal, hot, warm and cold processing and heat treatment.

This paper reviews several studies conducted on experimental equipment and in laboratories of the Institute of Metallurgy "Kemal Kapetanović", University of Zenica, aimed at improving the properties of some special steels and superalloys used in the automotive industry: austenitic stainless steel, maraging steel and some nickel- and iron-based superalloys. Application of the remelting process in the case of maraging steel, the optimization of the chemical composition of austenitic stainless steel, and the application of modified rolling technology of the superalloy Nimonic 80A, lead to an improvement of some properties. The application of metallic coatings on iron-based superalloy A286 also leads to a significant improvement of the exploitation properties.

2 APPLICATION OF REMELTING TECHNOLOGY IN MARAGING STEEL MAKING

High-strength maraging steels are strengthened to a high level with the coherent precipitation of the intermetallic phase $Ni_3(Mo,Ti,Al)$ in a carbon-free, nickel-martensite matrix by aging at temperatures of 480 °C. They are intended to provide high values of tensile strength and typically have a high content of nickel, cobalt and molybdenum, but a very low carbon content. In fact, carbon and nitrogen are impurities limited to very low levels.

The high strength of maraging steel is achieved by the strengthening of the soft and ductile low-carbon nickel martensite with aging and the forming of a high density of very fine coherent intermetallic precipitates Ni_3 (Mo, Ti, Al). The basic martensitic matrix with a high density of disoriented dislocations interacting with fine, uniformly distributed precipitates, forms a structure particularly resistant to local slip and premature breaking by stretching. The primary goal in making liquid maraging metal is to achieve a high-purity microstructure with a low content of non-metallic inclusions and particularly low levels of harmful elements such as carbon, nitrogen, sulfur and phosphorus. Carbon, nitrogen and sulfur tend to form brittle carbides, carbonitrides, sulfides and carbosulfides that could strongly reduce the absorbed impact energy. For this reason, the technology of liquid metal production is a process of fundamental importance for further processing and the achieving of the optimal mechanical and exploitation properties.

The elaboration of several maraging steel types (18Ni 200, 18Ni 250, 18Ni 300 and 18Ni 350) was developed in semi-industrial facilities and laboratories of the Institute and special attention was given to the manufacturing technology of 18Ni250 maraging steel. Respecting the highly complex final processing by means of cold flow turning, it was necessary to achieve the maximum purity and an extremely low content of carbon, nitrogen and sulfur and high levels of strength and ductility. These properties were achieved with remelting, especially electron-beam remelting [1].

The elaboration of the steel consists of three technologically related stages:

- Melting the charge in open induction furnaces (OIP);
- Remelting in vacuum induction furnaces (VIP);
- Remelting under inert-gas-protected electric conductive slag (ETP) and under electron beam remelting (ESP);

Here, only the final results for remelted melts during ETP and ESP are presented.

Electrolytic iron, pure metals and the standard technology of liquid metal manufacturing in the OIP were used to obtain the basic charge. A high steel purity and a low content of undesirable elements were obtained by remelting of the basic charge in induction vacuum furnaces. The remelting on ETP led to a further reduction of the sulfur content and electron beam remelting to a further purity increase and a gas content reduction. In addition, both methods (ETP and ESP) achieve solidification grains very suitable for deformation. The maraging steel manufacturing and processing scheme, with basic reactions during molten metal processing is shown in **Figure 1**, and the chemical composition and mechanical properties are shown in **Table 1**.

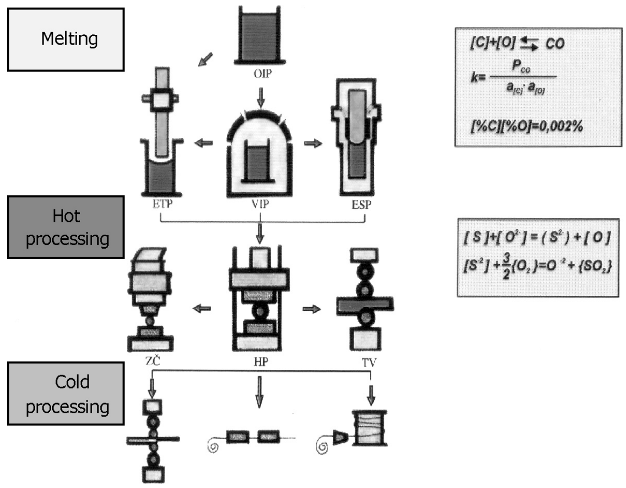


Figure 1: Technological scheme of production with variations in the processes of melting (remelting) and deformation

Slika 1: Tehnološka shema proizvodnje s spremembami v procesih taljenja (pretaljevanja) in predelave

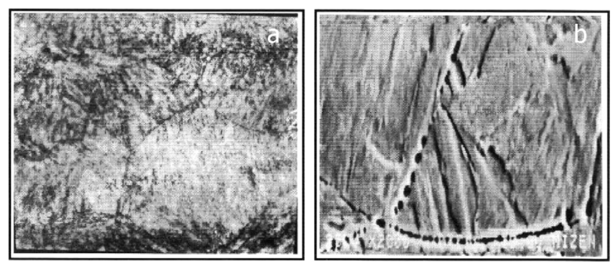


Figure 2: Microstructure of maraging steel: a) optical microscopy (500-times), b) SEM microscopy (2000-times)

Slika 2: Mikrostruktura maraging jekla: a) optični posnetek (povečava 500-kratna), b) SEM posnetek (povečava 2000-kratna)

The mechanical properties, especially the impact energy and fracture toughness K_{1C}, clearly show the effects of remelting that allow very good further processing with cold working. In **Figure 2** the maraging steel microstructure is shown. The examination in the optical and scanning electron microscopes showed that the microstructure consisted of a lath nickel martensitic matrix.

Table 1: Chemical composition and mechanical properties of maraging steel X2NiCoMo 18 9 5 (18Ni 250) according to WL 1.6354 (AMS 6514) in heat treated condition*

Tabela 1: Kemična sestava in mehanske lastnosti maraging jekla X2NiCoMo 18 9 5 (18Ni 2 50) po WL 1. 63 54 (AMS 6514) v toplotno obdelanem stanju*

Making	Content of elements, *w*/%										Mechanical properties				
	Ni	Co	Mo	Ti	Al	C	S	P	B	N	$R_{p0.2}$/ MPa	R_m/ MPa	A_5/%	*K*V/J	K_{1c}/ (MPa m$^{0.5}$)
Prescribed WL1.6354	17–19	8.0–9.5	4.6–5.2	0.6–0.9	0.05–0.15	max 0.03	max 0.010	max 0.010	max 0.03	0.001–0.15	1910	1960	4.5	12	
VIP+ETP	18.4	8.3	5.2	0.55	0.16	0.01	0.001	0.009	0.002	0.004	1905	1940	8.5	21.5	76
VIP+ESP	18.4	8.4	5.0	0.72	0.12	0.01	0.006	0.008	0.002	0.003	1893	1970	10.0	29.4	80.5

*Heat treatment: Triple quench from temperature 920 °C/water and aged at 480 °C/ 34 h/air

3 INFLUENCE OF NITROGEN ALLOYING ON THE MECHANICAL AND EXPLOITATION PROPERTIES OF AUSTENITIC STAINLESS-STEEL AISI 316

Austenitic stainless steel type AISI 316 has a very wide range of applications due to its good technological and exploitation properties. The possibilities of a variation of the chemical composition and the regime of technical processing for maintaining the austenitic structure and constant demands for cleanliness and corrosion resistance, have initiated an active research activity on this type of steel.

A significant role in these studies was played by the possibility of alloying with nitrogen for the replacement of part of the nickel content for the stabilization of the austenitic structure and the affect of nitrogen on the increase of the strength properties. A reduction of the nickel content has its economic justification and the increase in the yield and tensile strength is necessary for the production of structural components operating in aggressive media under high loads.

For the purposes of this research six experimental melts were produced in a vacuum induction furnace with three different variations of nitrogen content, i.e., (0.03, 0.06 and 0.12) %. For each variation of alloying with nitrogen, two melts were made with nickel contents of approx. 10.5 % and 13.5 %. This experiment enabled the simultaneous testing of the effect of alloying with

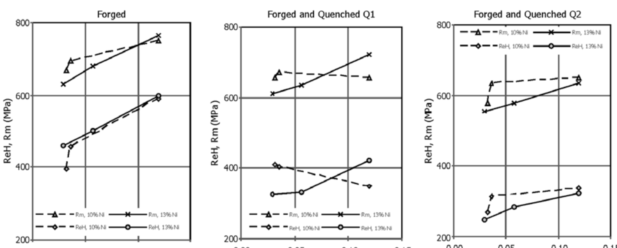


Figure 3: Yield and tensile strength of experimental melts depending on the nitrogen content and the heat-treatment condition (Q1 – 950 °C, Q2 – 1100 °C)

Slika 3: Meja plastičnosti in raztržna trdnost eksperimentalnih talin v odvisnosti od vsebnosti dušika in pogojev toplotne obdelave (QI – 950 °C, Q2 – 1100 °C

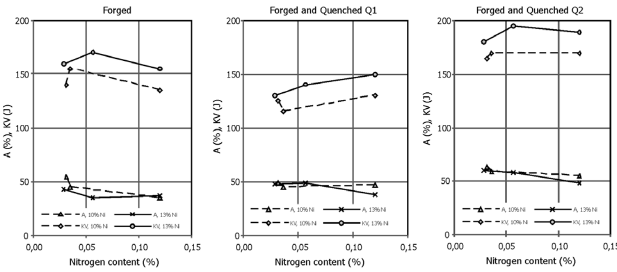


Figure 4: Elongation and absorbed energy of experimental melts depending on the nitrogen content and heat-treatment condition (Q1 – 950 °C, Q2 – 1100 °C)

Slika 4: Raztezek in absorbirana energija eksperimentalnih talin v odvisnosti od vsebnosti dušika in toplotne obdelave (QI – 950 °C, Q2 – 1100 °C)

nitrogen and to evaluate the possibility of reducing the nickel content within the limits prescribed for the steel AISI 316. The content of the basic elements and the achieved mechanical properties in the wrought and quenched conditions are given in **Table 2** and in **Figure 3 and 4**. The obtained results show that alloying with nitrogen in amounts up to 0.12 % has a favorable effect on the strength properties of the steel AISI 316 [2].

4 METALLIC ALLOYS FOR WORK AT ELEVATED TEMPERATURES

4.1 Austenitic stainless steel Nitronic 60

In recent years, based on conventional austenitic stainless steel 18/8, steels under the commercial name Nitronic, with the addition of manganese, nitrogen and silicon, have been developed. These steels are intended to operate at elevated temperatures and extended the exploitation area of austenitic stainless steel. In addition, it is significant that the austenitic structure is achieved with less-expensive stabilizing alloying elements, manganese and nitrogen.

Research results show that the occurrence of δ-ferrite in steel Nitronic 60 can be prevented with elements that stabilize austenite, nickel, and especially nitrogen, closer to the upper permitted limits, while the content of ferrite stabilizing elements is maintained in the middle of the allowed range. If the content of a ferrite stabilizing

Table 2: Content of the basic elements and mechanical properties in the forged and quenched condition of the experimental melts
Tabela 2: Vsebnost baznih elementov in mehanske lastnosti eksperimentalnih talin po kovanju in gašenju

Melts	Content of elements*, *w*/%				Mechanical properties											
	C	Cr	Ni	N	Forged (F)				Quenched 950 °C (F+Q1)				Quenched 1100 °C (F+Q2)			
					R_{eH}/MPa	R_m/MPa	A_5/ %	KV/J	R_{eH}/MPa	R_m/MPa	A_5/ %	KV/J	R_{eH}/MPa	R_m/MPa	A_5/%	KV/J
1	0.07	16.5	10.5	0.032	395	670	55	140	410	655	49	125	270	580	63	165
2	0.07	15.8	13.2	0.029	460	630	43	160	325	610	48	130	250	555	60	180
3	0.08	16.4	10.1	0.036	475	695	45	155	405	670	45	115	315	635	59	170
4	0.07	15.9	13.1	0.057	500	680	35	170	330	635	49	140	285	580	58	195
5	0.08	17.5	10.6	0.120	590	750	35	135	350	655	47	130	340	650	55	170
6	0.07	16.7	13.7	0.120	600	765	37	155	420	720	38	150	325	635	48	190

* The contents of other elements Mo, Mn, Si, S i P is approximately equal in all melts

Table 3: Chemical composition of the experimental melts of steel S 218 00 (Nitronic 60)
Tabela 3: Kemična sestava eksperimentalnih jekel S 218000 (Nitronic 60)

Making	Content of elements, *w*/%								Cr_{ekv}[1]	Ni_{ekv}[2]	δ-ferrite[3]
	C	Mn	Si	P	S	Cr	Ni	N			
Prescribed ASTM A 276	max. 0.10	7.0–9.0	3.5–4.5	max 0.06	max. 0.03	16.0–18.0	8.0–9,0	0.08–0.18	–	–	–
Melt 1	0.06	7.0	3.6	0.002	0.015	16.5	8.1	0.113	21.9	16.8	3
Melt 2	0.07	7.8	4.2	0.002	0.012	18.0	9.0	0.109	24.3	18.3	8
Melt 3	0,08	7.8	3.6	0.001	0.012	16.8	9.0	0.178	22.2	20.6	0

NOTE:
1. $w(Cr_{ekv}) = w(Cr) + 1,5\ w(Si)$
2. $w(Ni_{ekv}) = w(Ni) + 30\ w(C) + 30\ w(N) + 0,5\ w(Mn)$
3. According to revised Schaeffler constitution diagram[3]

Table 4: Chemical composition of experimental melts of superalloy Nimonic 80A
Tabela 4: Kemična sestava eksperimentalnih talin superzlitine Nimonic 80 A

Variant	Content of elements, w/%										
	C	Cr	Si	Mn	Fe	Co	S	P	Ti	Al	Ni
Variant I	0.05	19.7	0.25	0.03	2.10	1.25	0,007	0.005	2.52	1.32	Balance
Variant II	0.04	20.8	0.23	0.16	1.48	1.30	0,006	0.005	2.68	1.44	Balance

element would be close to the upper limit to achieve the specific use characteristics, the content of the other ferrite stabilizing elements should be lower. Otherwise, the purely austenitic structure cannot be achieved, regardless of the content of the austenite stabilizing elements. The revised Schaeffler diagram [3] can be used to optimize the chemical composition at which the formation of δ-ferrite will be prevented [4].

4.2 Nickel-based superalloy Nimonic 80A

The superalloy Nimonic 80A is a nickel-base alloy intended for use at elevated and high temperatures where significant creep may occur. The primary strengthening mechanism of this superalloy is based on the precipitation of fine and coherent particles of intermetallic γ' phase $Ni_3(Al,Ti)$ that increase the creep resistance. This strengthening mechanism for such a superalloy is more favorable than other strengthening mechanisms [5]. The effect of hardening that can be achieved by the γ' phase depends on the amount, dispersion, and size of the γ' phase and it is controlled by heat treatment. The standard heat treatment includes a solution annealing at 1080 °C 8 h and precipitation aging at 700 °C 16 h. The maximal hardness of the superalloy Nimonic 80A achieved after this treatment is around 360 HV, but certain applications in the automotive industry require higher hardness. Since by long-lasting solution annealing at high temperature coarsening of grains occur, it is not possible to increase the hardness (additional strengthening) significantly with a reduction of the grain size. The increase of the dislocation density after solution annealing and before precipitation aging, with cold or warm deformation, increases the strength, but the ductile properties are reduced significantly. A partial recrystallization after such a deformation results in a significant increase in the ductile properties and retains a high level of strength properties.

For additional strengthening of the superalloy Nimonic 80A the application of warm deformation is considerably more favorable than cold deformation, because the warm deformation can be done on a hot-rolling mill. In addition, the dislocation substructure obtained after the warm deformation is more favorable than that obtained after cold deformation, because the

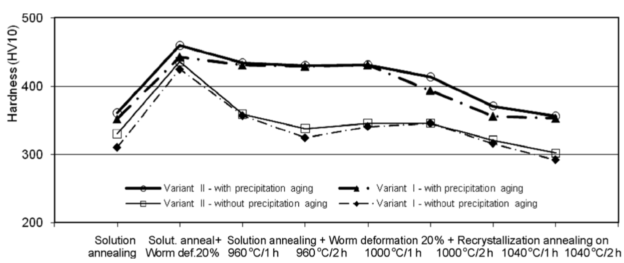
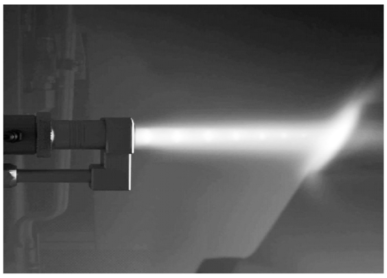


Figure 5: Hardness (HV10) after corresponding treatment
Slika 5: Trdota (HV10) po označeni toplotni obdelavi

Table 5: Chemical composition and structure of the base material A286 and NiCrAlY metal powders
Tabela 5: Kemična sestava in struktura osnovnega materiala A286 in prhov NiCrAlY

Material	Content of elements, *w*/%							Structure
	C	Ni	Cr	Mo	Al	Ti	Y	
A 286	0.05	26.0	15.5	1.3	0.2	2.1		$\gamma' + \gamma + K$
NiCrAlY	–	67	22.0	–	10.0	–	1.0	$\gamma'+\gamma+Al_2O_3+Y_3O_3+\beta$



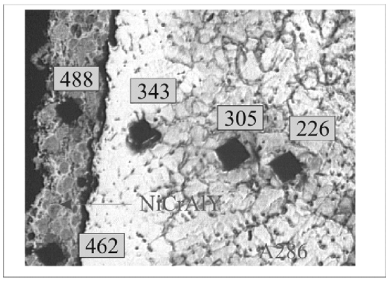


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Figure 6: Applying metallic coatings with the HVOF process and the microstructure of superalloy A286 and coatings after the thermal treatment (solution annealing at 1080 °C and hardening at 740 °C for 8 h)

Slika 6: Nanašanje metalnih prekritij z HVOF-procesom in mikrostruktura superzlitine A286 in prekritja po toplotni obdelavi (topilno žarjenje pri 1080 °C in utrditev pri 740 °C 8 h)

structure after cold deformation is characterized by chaotically distributed dislocations.

A change of the hardness of the two experimental melts (**Table 4**), subjected to solution annealing (1080 °C 8 h) after hot rolling, and then to 20 % warm deformation and recrystallisation annealing at different temperatures (960 °C, 1000 °C and 1040 °C in duration of one or two hours) and finally to precipitation aging (700 °C 16 h) is shown in **Figure 5**. The hardness of the alloy can be significantly increased through warm deformation after solution annealing. With the subsequent partial recrystallization the values of the hardness and the ductile properties can be controlled [5].

5 IMPROVEMENT OF THE CHARACTERISTICS OF IRON-BASED SUPERALLOYS WITH METALLIC COATINGS

A surface-enhanced structural element can be obtained with the application of surface-engineering technologies [6]. The coated element combines the good properties of the base material and of the applied metallic layer. The combined properties could not be achieved using only one type of coating material. The selection of the base material and the metal coating is based on the requirements from manufacturers in the automotive industry that needed a cold-deformed iron-based superalloy A286 for some structural parts. However, the idea of rationalization with use of this as cast did not give satisfactory results, primarily because the required strength properties (hardness at the surface) could not achieved. The required surface hardness with improved resistance to high-temperature corrosion was achieved by applying HVOF technology (High velocity oxyfuel) for forming metallic coatings (**Figure 6**). The process of applying the metallic powder NiCrAlY on the superalloy A286 was carried out by using a Diamond Jet technology in cooperation with the Development Department of "ORAO" Bijeljina.

The microstructural constituents of the base material A286 and the NiCrAlY coatings are given in **Table 5**. Aluminum and yttrium oxides improve the resistance to high-temperature corrosion and yttrium oxide particles act as a strengthening phase. The percentage of 40% of γ' phase in the coating increases the surface hardness to values that exceed the hardness that can be achieved with the superalloy A286 [7].

6 CONCLUSION

The producer's requirements ensured that particular structural elements satisfy the exploitation conditions were the starting base for this work. The concept of research included a preliminary analysis of the content and the interaction of the alloying elements, the structure analysis and the analysis of the relationship between the microstructure and the properties. Depending on the properties to be modified, the corresponding chemical composition and microstructure of the alloy, and then corresponding manufacturing technology, were designed. Well-known methods of designing (modeling) technologies were tested experimentally. In this article an overview of the modification of the properties of some materials suited for structural parts with improved performance is presented.

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