UDK 669.18
Professional article/Strokovni članek

ISSN 1580-2949
MTAEC9, 44(4)223(2010)

INFLUENCE OF VACUUM PROCESSING ON THE CONTENT OF SOME ELEMENTS IN MOLTEN METAL

VPLIV VAKUUMSKEGA PROCESIRANJA NA VSEBNOST NEKATERIH ELEMENTOV V KOVINSKIH TALINAH

Derviš Pihura, Derviš Mujagić

University of Zenica, Metallurgical institute "Kemal Kapetanović" Zenica, Bosnia and Herzegovina
dervis.pihura@gmail.com

Prejem rokopisa – received: 2008-09-22; sprejem za objavo – accepted for publication: 2010-03-15

Residual and trace elements can affect physical, chemical and mechanical properties, especially those of high-alloy materials and steels. With a treatment of the molten metal in a vacuum-induction furnace and an electron-beam furnace the content of residual elements is diminished, depending on the treatment time and the vacuum pressure.

Key words: vacuum treatment, trace elements, electron-beam furnace, vacuum-induction furnace

Rezidualni elementi in elementi v sledovih vplivajo na kemične in mehanske lastnosti, posebno pri visokolegiranih zlitinah in jeklih. Pri obdelavi taline v vakuumski indukcijski peči in v peči z elektronskim curkom se vsebnost rezidualnih elementov zmanjša v odvisnosti od trajanja obdelave in od tlaka.

Ključne besede: vakuumska obdelava, elementi v sledovih, peč z elektronskim curkom, vakuumska indukcijska peč

1 INTRODUCTION

A vacuum is a powerful tool for improving the physical and chemical properties of ferrous and nonferrous alloys with vacuum melting, re-melting and treatment. Depending on the vacuum process used, the physical and chemical properties of the alloys can be improved. For this reason, it is important to select the vacuum treatment process, keeping in mind the required change in the properties of the alloy.

2 VACUUM PROCESSES

Vacuum melting is applied for the melting of raw materials in coreless induction furnaces, and is particularly suited to the melting and casting of different high-alloyed materials because it enables an exact control of the temperature and the chemical composition.[1–6] In this way, the physical characteristics and properties of the melted alloys can be tailored. The charged components are melted in vacuum or a protective atmosphere (Ar, N or H) and then vacuumed with a partial pressure of down to 10^{-4} mbar. Since the alloy may contain elements with a high vapour pressure, by selecting the proper vacuum partial pressure the chemical composition of the alloy must be kept in mind. With a vacuum treatment, the alloy is refined and its physical, chemical and mechanical properties as well as cleanliness may be changed. It is possible, in a vacuum furnace, to also treat the alloy with vacuum de-oxidation using appropriate additions or, through the effect of the vacuum itself, to decrease the content of the gasses N_2 and H_2 as well as to change the content of elements such as Sb, As, Bi, Sn, Cu, etc. By decreasing the content of some elements, non-metallic inclusions and gases, physical and mechanical properties that are better suited to a particular application are obtained.

Arc furnaces and electron-beam furnaces are mostly used for the re-melting of previously produced alloys applying a non-vacuum process. The best, which must be used for such an operation, are the electric arc furnace and electron-beam furnace, which is of particular interest for the aim of this paper. The electron-beam vacuum furnace is applied on the pilot and industrial scales for ingots up to 20 t. In this furnace, droplets of the molten alloy, or electrode, solidify rapidly in a water-cooled copper mould. The heat for melting is obtained with 3 to 12 electron beams targeted on the re-melted electrode. Depending on the energy consumption, the local electrode temperature may be increased to a few thousand degrees and, in this way, the conditions for evaporation of the high-partial-pressure components of the alloys are achieved. The high local temperature makes it difficult to measure the exact temperature of the molten drops. The evaporation may be considered as one of the advantages of the re-melting process, especially as the melt droplets form in a vacuum of different grades down to $1 \cdot 10^{-6}$ mbar. In this way, the molten metal is exposed to vacuum for a sufficient time and the extraction of the gases and the evaporation of high-vapour-pressure components is ensured. After re-melting, the alloy density and cleanliness are improved and the physical properties are substantially improved. The re-melted alloys can then be used for high-temperature and high-stress applications, as well as for the parts of jet engines.

A good technology for the vacuum treatment of molten metal is the circulating or RH process that is applied only on an industrial scale. In this process the molten metal is lifted from the container in the vacuum chamber, processed for the determined time and re-flown in the melting furnace. As part of the process the surface of the alloy surface in direct contact with the vacuum is increased and the rate and the extent of extraction is also increased. This process is also suited to the highest quality of steel grades.

3 EFFECT OF VACUUM TREATMENT

In a vacuum some of the physical properties of a molten metal are changed. Dissolved gases behave in accordance with Sieverts' and Nernst's laws and their extraction becomes possible. Nitrogen and hydrogen are extracted directly, while the extraction of oxygen occurs through vacuum de-oxidation with carbon and the extraction of CO.

Specific interactions between the elements present in the melt may help to displace some elements from the solution in the molten mother metal. The interaction coefficients are a measure of the mutual bonding energy of the dissolved X and Y atoms relative to the X-Fe and Y-Fe bonding. For dilute solutions, the bonding energies are independent of each other and additive, whereas in more concentrated solutions, Z atoms may affect the X-Y bonding. For multi-components solutions, the total activity coefficient for each element will depend on the mutual effect of each component. For a diluted solution the interaction can be described with a simple relation.

In the extraction process, the effect of the partial pressure of elements in the melt is of essential importance. For a number of elements, the effect of temperature on the partial pressure is shown in **Figure 1**. Generally, elements with a higher partial pressure are extracted more quickly from the melt; however, the evaporation also depends on the geometry, the vacuuming time and the ferro-static pressure in the reacting part of the melt. At the melting temperature of iron, the vapour pressure of the impurities and the alloying elements decreases in the order Ba > Pb > Sn > Mn > Si > Fe = 0.84 > 0.45 > 0.45 > 0.035 > $8 \cdot 10^{-4}$ > $2 \cdot 10^{-4}$ bar.[5,6]

4 RESULTS

In this work the results of investigations of the effect of the vacuum treatment of several alloys – low carbon iron and steel, alloys with about 60 % Ni and 18 % Cr, with 50 % Ni, steel with 18 % Cr and 10 % Ni and a low-alloy steel – in a vacuum-induction furnace and an electron-beam furnace are presented. In **Figure 1** the dependence of the partial vapour pressure on temperature is shown for different elements, as well as for elements found as impurities in the investigated alloys.

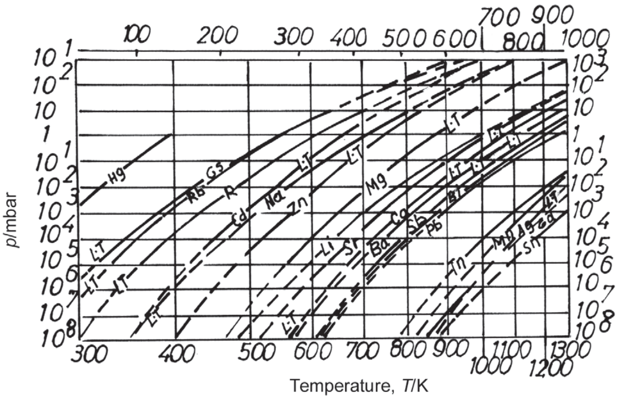

Figure 1: Dependence of the vapour or partial pressure for different elements on the temperature[5,6]

Slika 1: Odvisnost parcialnega parnega tlaka od temperature za različne elemente[5,6]

In **Figures 2 and 3** the effect of electron-beam melting on the content of some elements are shown – impurities in low-carbon iron, low-carbon steel, nickel or nickel chromium alloy types such as perm-alloy, Cr/Ni – 18/8 or 18/10, Cr/Ni – 18/60.

Figure 2 presents the results of the content change of tin, arsenic, copper and antimony, while in **Figure 3** the effects of the melting rate (kg/min) and the power ((kW h)/kg) are shown for arsenic and different groups of alloys. The content of all the investigated elements is diminished by maintaining the melt in vacuum; however, the extent and the kinetics of evaporation are different for the different alloys.

For the three elements with greater evaporation rates, two phases are seen on the kinetics curve: an initial phase of rapid evaporation down to a determined critical content and a phase with a much lower evaporation rate. For antimony the evaporation rate is 5.5 times lower in the second than in the first phase. The shape of the kinetics curves in **Figure 2** is related to the activity in the elements in solution in the molten iron. It is assumed that the evaporation rate is greater down to the equilibrium

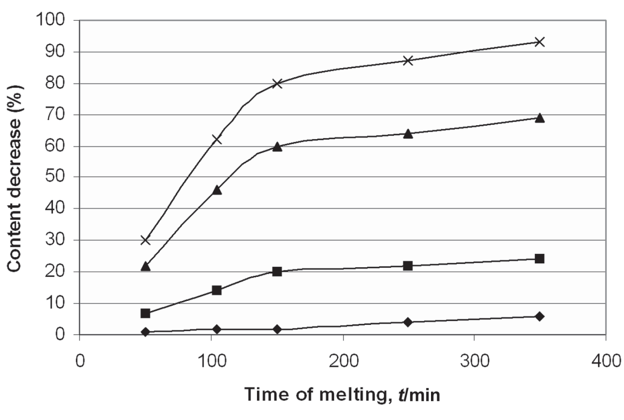

Figure 2: Decrease of some residual elements during electron-beam melting: Sn (◇), As (□), Cu (Δ) and Sb (x) in low-carbon iron

Slika 2: Zmanjšanje vsebnosti nekaterih elementov pri taljenju z elektronskim curkom: Sn (◇), As (□), Cu (Δ) in Sb (x)

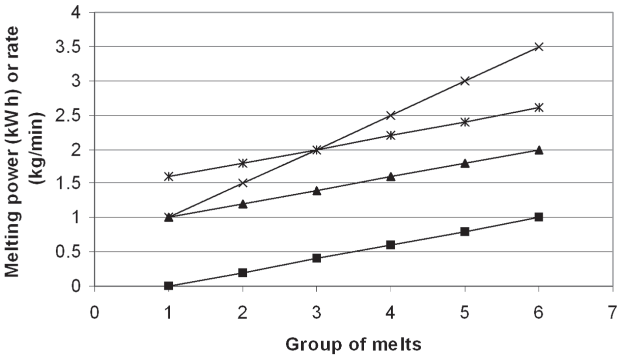

Figure 3: Loss of 22 % of arsenic by electron-beam melting for different group of melts and different melting rate MIZ (*) [6], As (□)[4] & lit. (Δ)5; low-carbon iron (1), steel (2), Cr/Ni – 18/8 (3) or 18/10 (4), Cr/Ni – 18/60 (5), perm-alloy (6) elemente

Slika 3: Izguba 22 % arzena pri taljenju v peči z elektronskim curkom za različne skupine zlitin pri različni hitrosti taljenja; MIZ (*) [6], As (□)[4], ref.5 (Δ). Malooglјično železo (1), jeklo (2), Cr/Ni 18-8 (3 in 18-10(4), Cr/Ni 18/60 (5), perm. zlitina (6)

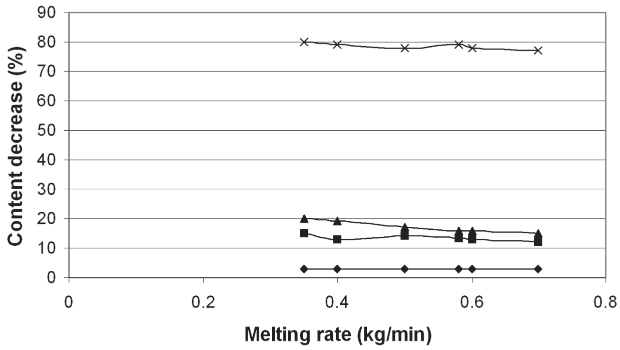

Figure 5: Decrease of some elements during melting in an electron-beam vacuum furnace: P (◇), Si (□), S (Δ) and Mn (×) depending on the melting rate of Cr/Ni – 18/8 (3), 18/10 (4) and perm-alloy6

Slika 5: Zmanjšanje vsebnosti nekaterih elementov pri taljenju v peči z elektronskim curkom; P (◇), Si (□), Cu (Δ) in Mn (×) v odvisnosti od hitrosti taljenja Cr/Ni – 18/8 (3), 18/10 (3) in perm. zlitine[6]

activity, which depends on the bath's chemical composition and the temperature.

The evaporation of antimony was the largest, but it is also large for copper. It is low for arsenic, while it is scarcely discernible for tin. In **Figure 3** the effect of the melting power and rate is shown for arsenic for the groups of melts of low-carbon iron (1), steel (2), perm-alloy (6), Cr/Ni – 18/8 (3) or 18/10 (4) and Cr/Ni – 18/60 (5). It indicates that an average decease of arsenic of 22 % for different groups of materials depends on the content of the alloying elements and on the influence of their physical properties on each material. The dependences are based on our own experimental findings[6] and reference.[5] The comparison of melting characteristics indicates a simple relation between the melting rate and the power consumption for different materials for the same average loss of arsenic.

The effect of melting in the vacuum induction furnace is, in principle, similar to the electron-beam furnace, with the higher evaporation rate for antimony and the lowest for tin (**Figure 4**). The evaporation rate increases with the increasing content of the element in the alloy and it is quite different for the same content of different elements in the alloy. Compared with the evaporation rate of tin, the evaporation rate is 2.5 times greater for arsenic, five times greater for copper and 10 times greater for antimony. The difference is very probably related to the difference of the activity of the elements in solution in the molten metal and their partial pressure and depends on the interaction coefficient of some element also, as the activity of the impurities in molten metal is affected by the presence of other components. To describe this phenomenon it is convenient to maintain the same standard state as with the binary melts, and to introduce an activity coefficient (f_x), which describes the effect of the third component. This coefficient depends on the interaction coefficients, which differ greatly,[5] and is the product of the interaction coefficients and the content of the third component in the melt.

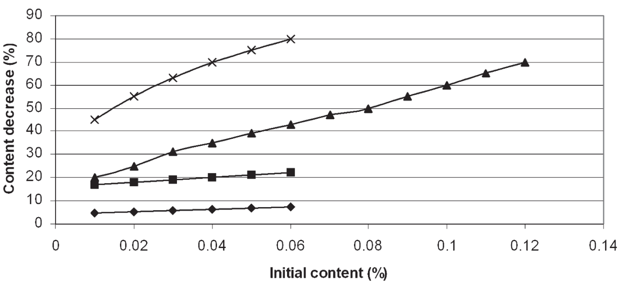

Figure 4: Decrease of some residual elements during the melting of low-carbon steels and alloys[1,2,6] in a vacuum induction furnace: Sn (◇), As (□), Cu (Δ) and Sb (×)

Slika 4: Zmanjšanje vsebnosti nekaterih rezidualnih elementov pri taljenju malooglјičnih jekel in zlitin[1,2,6] v vakuumski indukcijski peči: Sn (◇), As (□), Cu (Δ) in Mn(×)

It is assumed that with a vacuum treatment on the industrial scale the relative differences in the evaporation of elements would be similar to those presented in this work, while the absolute rate of evaporation and the change of element contents would depend for all elements on the conditions specific to the processing, especially the presence of the slag layer on the surface of the molten alloy.

The evaporation rates of sulphur, silicon and phosphorus by melting in an electron-beam vacuum furnace is low and are virtually unaffected by the melting rate, while the evaporation of manganese is large and again independent on the melting rate (**Figure 5**). Again, the difference is very probably related to the activity of the elements in solution in the iron bath. With respect to the loss of elements during other methods of vacuum processing of iron alloys, for phosphorus, sulphur, silicon and manganese a similar conclusion seems to be justified, as was earlier suggested for tin, arsenic, copper and antimony. It should also be considered that the slag could have a positive effect on the change of the content of phosphorus and particularly sulphur in the melted iron alloy.

In vacuum, the gases are extracted from the metal bath according to Sieverts' law. The degassing intensity also depends on the metal bath temperature and the chemical composition, which determine the coefficients of interaction. This is confirmed by the data in **Table 1**, showing that the degassing constant is different for alloys with different chemical compositions and temperatures.

Table 1: Constant nitrogen-degassing rate ($K_N \cdot 10^{-4}$)[1,2,6]
Tabela 1: Konstanta hitrosti degazacije dušika ($K_N \cdot 10^{-4}$)[1,2,6]

Temperature T/°C	Material				
	Cr/Ni – 18/8	Cr/Ni – 18/60	Perm alloy	LAS	Cr/Ni – 18/10
1450	0.41	2.51	2.91	–	–
1500	1.11	1.82	–	1.41	0.81
1550	1.45	1.12	1.09	1.35	1.39
1600	1.82	0.75	0.81	1.21	1.83

5 CONCLUSION

The experimental data presented show the loss of elements as a result of evaporation in vacuum is very different; it is below the detection limits for some elements, while it is significant for other elements present in the iron bath. The evaporation rate is particularly high for antimony, copper and manganese, while it is virtually null for tin and low sulphur, phosphorus and silicon. The findings show that the evaporation rate depends on the interaction coefficient of the elements in solution in the metal bath and the temperature. When extrapolating the experimental findings to other vacuum processes for iron alloys, it should be kept in mind that the evaporation process also depends on the geometry of the vacuum exposure of the melt, and remembering that the presence of the slag on the metal bath surface would significantly affect the evaporation loss in two ways: by preventing a contact between the bath surface and the atmosphere and by a direct chemical reaction of the slag with some elements in solution in the molten bath, especially sulphur and phosphorus.

6 REFERENCES

[1] Pihura D. at al. Promjena sadržaja dušika u vakuumskoj peć (Change of nitrogen content in the vacuum furnace), Zenica, 2008

[2] Pihura D. at al. Osvajanje proizvodnje legura tipa nimonic i nitronic u vakuumskoj peći (Manufacturing of nimonic and nitronic type alloys in a vacuum furnace), Zenica, 2007

[3] Pihura D. Kazanska metalurgija (Ladle metallurgy) – VI-VIII dio; Met. Inst., Zenica, 1986/9

[4] Pihura D. Vacuum Melting Technology Monogr., UNIDO, Vienna, 1980

[5] Winkler O, Bakhish Vacuum metallurgy, Elsevier, London 1971

[6] Pihura D. Vakuumske tehnike i tehnologije (Vacuum technique and technology), Met. Inst., Zenica, 1979