O vplivu oligoelementov pri električnem pretaljevanju visoko kvalitetnih jekel pod žlindro

On behaviour of residual elements in electro-slag-remelting of high quality steels

B. Koroušić*

UVOD

Električno pretaljevanje kvalitetnih jekel in posebnih zlitin pod žlindro sodi v t.i. sekundarne (pretaljevalne) postopke, pri katerih se s pretaljevanjem elektrode z definirano kemično sestavo doseže znatno višja kvaliteta pretaljenega materiala.

Med prednostmi, ki jih prinaša postopek električnega pretaljevanja pod žlindro, naj omenimo: a) odpravo žvepla, b) znatno boljšo porazdelitev in manjšo velikost nekovinskih vključkov, c) direktno predelavo površine ingota, d) izboljšanje izkoristka pri nadaljnji termomehanski predelavi, e) izboljšanje strukturne in kemične homogenosti in f) znižanje anizotropije mehanskih lastnosti.

Poleg omenjenih prednosti ima EPŽ-postopek tudi vrsto tehnoloških pomanjkljivosti, med katere prav gotovo sodi dokaj zahtevna kontrola kemične rafinacije, in posebej kontrola elementov z visoko afiniteto do kisika (Al, Ti, Zr, B, Ca), vodika in nekaterih škodljivih primesi.

Čeprav se je EPŽ postopek razširil na številna področja proizvodnje kvalitetnih jekel in superzlitin, je splošni vtis, da elektrožlindrni proces ni še dovolj raziskan, kar opozarja tudi večina EPŽ publikacij.

Namen tega članka je opisati dosedanje izkušnje na področju kompleksnih raziskav elektrožlindrnega procesa s posebnim poudarkom na kemizem reakcij, ki potekajo med žlindro in kovino pri EPŽ-procesu.

OBNAŠANJE ELEMENTOV PRI ELEKTRIČNEM PRETALJEVANJU KVALITETNIH JEKEL POD ŽLINDRO

Osnovna značilnost EPŽ-procesa je simultani potek procesov rafinacije in kristalizacije: ogrevanje in taljenje elektrodnega materiala v kemično aktivni žlindri, rafinacija tekoče kovine in strjevanje v bakreni, vodno hlajeni kokili (slika 1).

Ravno ta značilnost EPŽ-postopka znatno komplicira izbiro optimalnih tehnoloških pogojev, ki so med seboj tesno povezani in odvisni[1]. Na sliki

INTRODUCTION

Electro-slag remelting (ESR) of quality steels and special alloys belongs to secondary (remelting) processes by which a significantly improved quality of remelted metal is attained by remelting a metal electrode of definite chemical composition. Among the advantages of ESR process the following should be mentioned: a) efficient desulphuration, b) better distribution and a lower size of nonmetallic inclusions, c) direct working of ingot surface, d) improved yield in further termomechanical processing, e) improved structural and chemical homogeneity and f) reduced anisotropy of mechanical properties.

Naturally, ESR process have also a series of technological disadvantages, namely a strict control of chemical refining and specially the control of the content of elements with high affinity to oxygen (Al, Ti, Zr, B, Ca) as well as the control of hydrogen and certain harmful impurities is required.

There is a general impression that the proces has not yet been sufficiently investigated although it has been very widely applied in the manufacture of quality steels and superalloys which can be seen from a majority of corresponding publications.
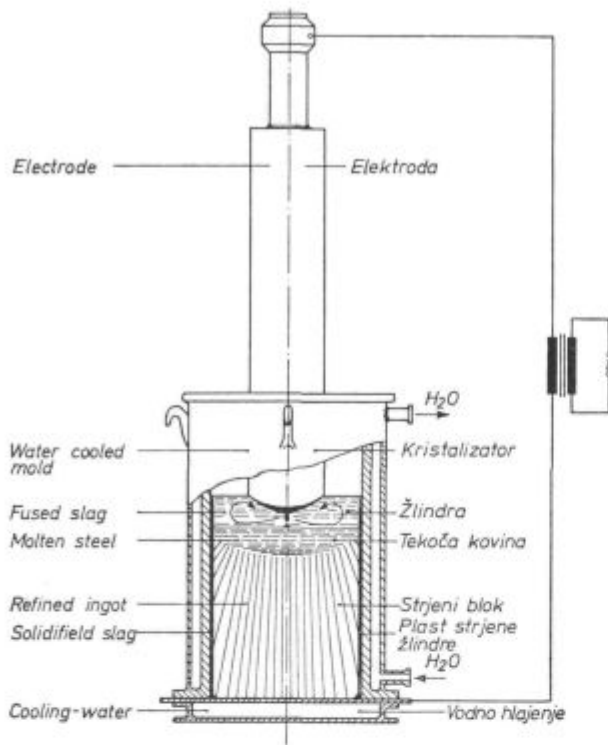
The aim of this paper is to describe the experience obtained in complex investigations of ESR proces with special regard to the chemistry of reactions between slag and metal.

BEHAVIOUR OF ELEMENTS IN ELECTRO SLAG REMELTING OF QUALITY STEELS

Main characteristic of ESR is simultaneous proceeding of refining and crystallisation: heating and melting of electrode material in chemically active slag, refining of molten metal and solidification in a copper water-cooled mould (fig. 1).

This characteristic of ESR proces significantly complicates the selection of optimum technological parameters which are mutually correlated and interdependent[1]. In fig. 2 a principal sketch is given of the information path which should be taken in account in ESR process in order to ensure a high quality of remelted metal[2, 3].

* Metalurški inštitut, Ljubljana

Slika 1
Shematski prikaz električnega pretaljevanja pod žlindro
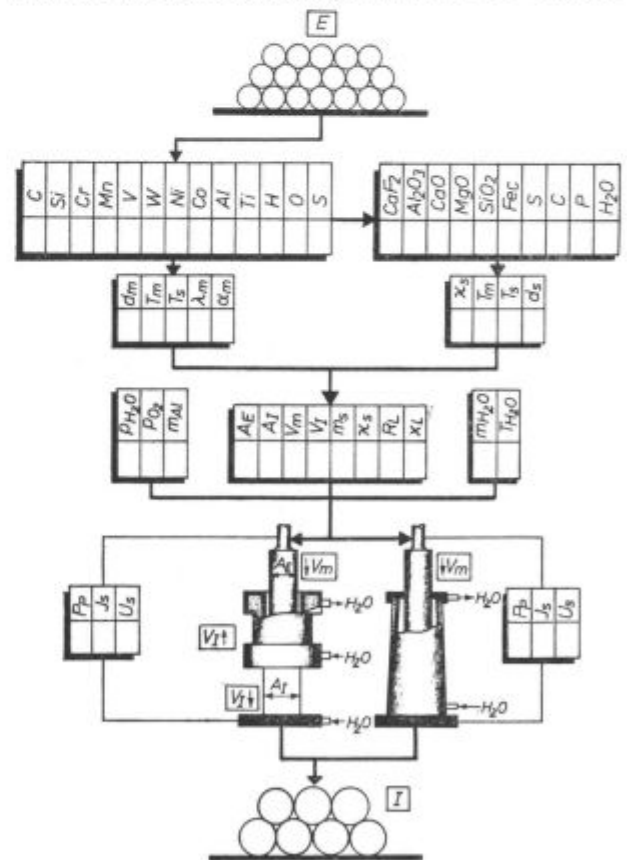Fig. 1
Sketch of ESR proces

Special care should be devoted to the knowledge of physicochemical proceses since the optimum selection of the chemical composition of slag from practical and economic viewpoint depends on the composition of electrode material and on the proceeding during remelting (gaseous atmosphere above slag, slag additions, etc.)

The experience obtained in ESR practice clearly show that the control of chemical composition of refined metal is of various importance for different quality of steels and super-alloys [4, 5].

When processing quality structural steels the control of refining, specially the control of aluminium and hydrogen content is of a primary importance[6]. As will be shown, difficulties are the bigger is ingot and the narower are the tolerance limits specified [2, 7, 8, 9]. The problems in the control of residuals in tool steels are quite different [10, 11, 12]. Therefore, it is very difficult to make any generalization in respect to the behaviour and control of particular element in ESR process.

A principal review of the behaviour of elements in ESR process is given in fig. 3. The elements are grouped in three groups as follows:

a) elements the content of which practically remains the same or changed within ±10 % limits

2 smo poskušali shematsko nakazati poti informacij, ki jih je potrebno upoštevati pri EPŽ-procesu, če želimo zagotoviti visoko kvaliteto pretaljene kovine [2, 3].

Posebno poglavje predstavlja poznavanje fizikalno-kemičnih procesov, ker je optimalna izbira kemične sestave žlindre glede na sestavo elektrodnega materiala ter spremljajočih procesov med taljenjem (plinska atmosfera nad žlindro, dodatki v žlindro itd.) povezana s praktičnimi in ekonomskimi pogledi.

Dosedanje praktične izkušnje pri EPŽ so pokazale, da ima kontrola kemične sestave pretaljenega jekla različen pomen pri različnih kvalitetah jekel in superzlitinah [4, 5].

Pri kvalitetnih konstrukcijskih jeklih predstavlja kontrola rafinacijskih postopkov, med katerimi je treba posebej poudariti pomen kontrole aluminija in vsebnosti vodika, primarni pomen[6]. Ti problemi so, kot bo kasneje pokazano, tem večji, čim večji je ingot in čim bolj so ozke predpisane specifikacije[2, 7, 8, 9]. Povsem drugačen pristop h kontroli rezidualnih elementov zasledimo pri tehnologiji pretaljevanja orodnih jekel [10, 11, 12]. Zato je zelo težko podati splošno sliko glede obnašanja in kontrole posameznih elementov pri EPŽ-procesu.

Na sliki 3 smo poskušali dati pregled obnašanja elementov, ki smo jih razdelil v tri skupine:

a) elementi, ki se med pretaljevanjem skoraj ne spreminjajo, oziroma ostanejo v mejah ±10 %

Slika 2
**Principielna shema toka informacij pri izbiri optimalnih tehnoloških parametrov pri EPŽ-procesu**
Fig. 2
Principal sketch of information paths in selection of optimum technological parameters of ESR proces.

(C, P, Ca, V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Sn, Sb, W, Pb, Bi),

b) elementi, ki med procesom pretaljevanja oksidirajo, oz. je njihova vsebnost v ingotu nižja kot v elektrodnem materialu (O, Mg, S, Si, Ti, Al, Zr, Nb, Ta, B, N),

c) elementi, pri katerih obstaja nevarnost, da se njihova koncentracija med pretaljevanjem poveča (naj omenimo predvsem H_2 in Al).
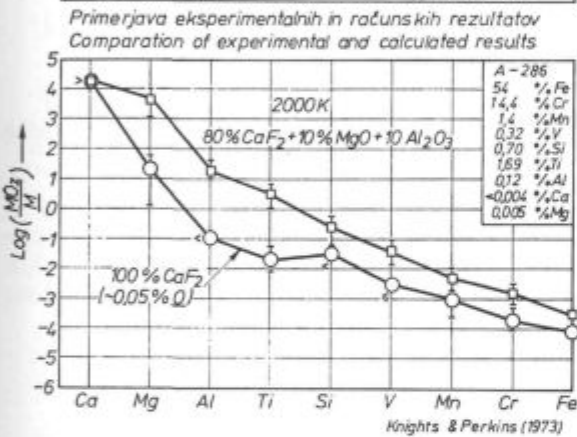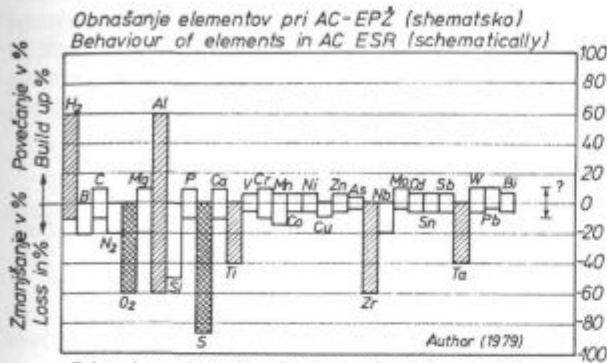
Slika 3

Obnašanje elementov pri AC-EPŽ procesu (shematsko) in primerjava eksperimentalnih in izračunanih rezultatov (Knights & Perkins 1973)[13]

Fig. 3

Behavior of elements in AC-ESR proces and comparison of experimentally obtained and theoretically calculated results (Knights & Perkins 1973)[13]

Na spodnjem delu slike 3 smo prikazali rezultate Knightsa in Parkinsa[13], ki kažejo na dejstvo, da se na fazni meji žlindra-kovina pri visokih temperaturah odvijajo reakcije v skoraj termodinamičnih pogojih.

Iz tega lahko zaključimo, da imajo na obnašanje kemičnih elementov med pretaljevanjem zelo velik vpliv oksidacijsko-redukcijski procesi (pri normalni AC-EPŽ praksi*), medtem ko moramo pri DC-EPŽ procesu* upoštevati tudi elektrokemične reakcije, ki potekajo na faznih površinah[6].

---

* Pri uporabi izmeničnega toka (AC), oziroma enosmernega toka (DC)

in ESR processing (C, P, Ca, V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Cd, Sn, Sb, W, Pb and Bi).

b) elements the content of which is lower in obtained ingot than in electrode because of oxidation (O, Mg, S, Si, Ti, Al, Zr, Nb, Ta, B and N) and

c) elements the content of which can be increased during remelting, as hydrogen and aluminium.

In the lower part of fig. 3 the results of Knights and Perkins[13] are presented showing that high-temperature reactions on the slag-metal interface proceed in accord to thermodynamical conditions.

Consequently, it may be concluded that oxidation-reduction proceses in normal AC-ESR* practice exert very strong influence on the behaviour of residuals whereas in DC-ESR*, electrochemical reactions on slag-metal interfaces should also be considered[6].

THEORETICAL MODEL OF OXIDATION-REDUCTION PROCESSES IN AC-ESR

Recent investigations showed that the behaviour of certain residuals in AC electro slag remelting can be described with sufficient accuracy by thermodynamical analysis of reactions between slag and metal[3, 4, 5, 13, 14]. This makes it possible to obtain important information on limitations imposed by the nature of ESR process.

The deficiency of thermo-kinetics data on slag and metal systems at high temperatures limits the application of thermodynamic and kinetics analysis.

In our investigations of oxidation-reduction reactions proceeding in AC-ESR a thermodynamic model has been devised and successfully applied. The model is based on the following assumptions[4, 5]:

— Diffusion rate at high temperatures is extremely high, therefore the time required for the formation or destruction of concentration gradients on reaction interface boundaries is very short.

— The elements present in electrode material react with liquid slag on reaction interface according to thermodynamic laws which hold for a general reaction:

$$/Me/ + x /O/ = (MeO_x),$$

or explicitly:

$$a_O = /\% \ O/ \ . \ f_O = \frac{a_{FeO}}{K_{Fe}} = \frac{a_{MnO}}{a_{Mn} \cdot K_{Mn}} = \sqrt{\frac{a_{SiO_2}}{a_{Si} \cdot K_{Si}}} =$$

$$= \sqrt{\frac{a_{TiO_2}}{a_{Ti} \cdot K_{Ti}}} = \sqrt[3]{\frac{a_{Al_2O_3}}{a_{Al}^2 \cdot K_{Al}}} = \ldots$$

Thermodynamical activity of slag and metal compounds can be estimated as follows: The acti-

---

* AC — Alternating current, DC — Direct current

TEORETIČNI MODEL OKSIDACIJSKO-REDUKCIJSKIH PROCESOV PRI AC-EPŽ

Raziskave zadnjih nekaj let so pokazale, da se obnašanje nekaterih elementov med procesom pretaljevanja pod žlindro da dokaj natančno opisati s termodinamično analizo reakcij med tekočo žlindro in kovino [3, 4, 5, 13, 14]. Na ta način je mogoče dobiti pomembne informacije o omejitvah, ki so pogojene z naravo EPŽ-procesa.

Širšo uporabo termodinamične in kinetične analize omejuje dejstvo, da obstaja zelo malo termokemičnih podatkov žlindrinih in kovinskih sistemov pri visokih temperaturah.

Pri naših dosedanjih raziskavah smo aplicirali termodinamični model pri študiju oksidacijsko-redukcijskih reakcij, ki potekajo pri AC-EPŽ. Model se opira na nekaj osnovnih hipotez [4, 5]:

— Pri visokih temperaturah je difuzija izredno hitra in je čas, ki je potreben za vzpostavitev, oziroma razkroj koncentracijskih gradientov na reakcijskih faznih mejah, zelo kratek.

— Elementi, prisotni v elektrodnem materialu, reagirajo z žlindro na reakcijskih površinah v soglasju s termodinamičnimi zakoni, ki veljajo za splošno reakcijo:

$$/Me/ + x\,/O/ = (MeO_x),$$

oziroma v eksplicitni obliki:

$$a_O = /\% \text{ O}/\,.\,f_O = \frac{a_{FeO}}{K_{Fe}} = \frac{a_{MnO}}{a_{Mn}\,.\,K_{Mn}} = \sqrt{\frac{a_{SiO_2}}{a_{Si}\,.\,K_{Si}}} =$$

$$= \sqrt[3]{\frac{a_{TiO_2}}{a_{Ti}\,.\,K_{Ti}}} = \sqrt{\frac{a_{Al_2O_3}}{a^2_{Al}\,.\,K_{Al}}} = \ldots$$

— Termodinamično aktivnost kovinskih in žlindrinih komponent lahko ocenimo na osnovi:

a) Kovinske komponente s parametri interakcije:

$$\log f_j = \sum_{i=1}^{n} /X/_i\,.\,e_j^i$$

b) žlindrine komponente na osnovi statistične termodinamike realnih ionskih raztopin (model Koževurova).

Detajlen opis apliciranega termodinamičnega modela je v literaturi že opisan [4, 5, 15], zato na tem mestu želimo poudariti le uporabnost teoretičnih izvajanj pri oceni aktivnosti SiO₂ v večkomponentnem sistemu: CaF₂-CaO-SiO₂ (slika 4).

vity of metal compounds can be calculated by taking into account corresponding interaction parameters:

$$\log f_j = \sum_{i=1}^{n} /X/_i\,.\,e_j^i$$

The activity of slag compounds can be obtained on the basis of statistical thermodynamics of real ionic solutions (model of Kozheurov).

Detailed description of the thermodynamic model has already been given [4, 5, 15] therefore we want only to underline the applicability of theoretical considerations in estimation of the activity of SiO₂ in the multicomponent system CaF₂-CaO-SiO₂ (fig. 4).

Slika 4
Primerjava teoretično izračunanih vrednosti a₍SiO₂₎ (teoret.) in eksperimentalnih vrednosti a₍SiO₂₎(exp.) v sistemu CaF₂-CaO-SiO₂ pri 1450° C

Fig. 4
Comparison of calculated theoretical values for a SiO₂ (theor.) and experimental values for a SiO₂ (exp) in CaF₂-CaO-SiO₂ system at 1450° C
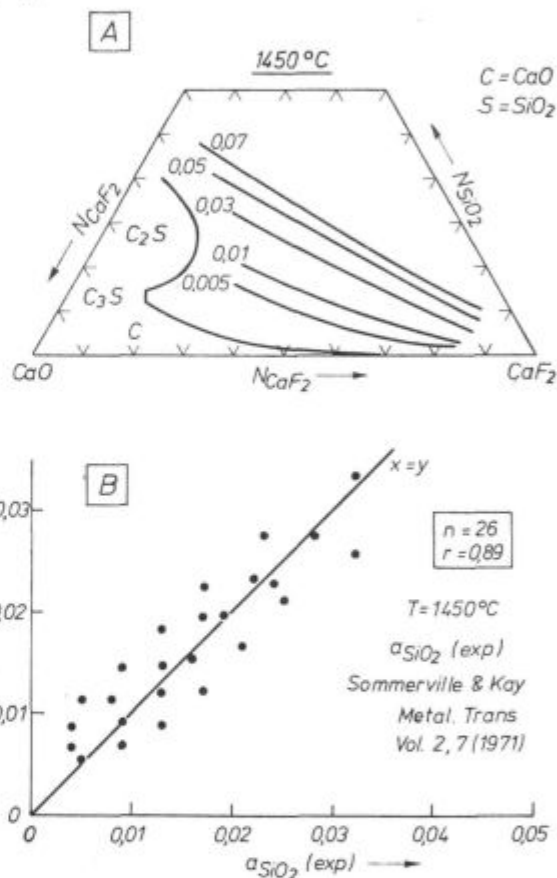
REZULTATI

V tem poglavju bomo poskušali opisati nekatere praktične izkušnje, ki smo jih pridobili pri pretaljevanju kvalitetnih jekel po postopku EPŽ v laboratorijskih in industrijskih pogojih.

RESULTS

Here we shall try to describe some practial experience obtained in electro-slag remelting of quality steels in laboratory and industrial conditions.

Vodik

Kontrola vodika pri EPŽ-postopku sodi med najbolj resne procesne probleme, zlasti pri izdelavi velikih ingotov, prečnega preseka nad 500 mm[5, 16]. Prav gotovo, da (v literaturi že opisani) problemi v zvezi z obnašanjem vodika predstavljajo znatno oviro za nadaljnjo razširitev EPŽ-tehnologije, zlasti na področju pretaljevanja posebnih in superzlitin.

Praktične izkušnje so pokazale, da je naraščanje vsebnosti vodika kritično zlasti v začetni fazi EPŽ-procesa[17]. Dosedanje raziskave so pokazale[16], da imajo dominanten vpliv na vsebnost vodika v pretaljeni kovini trije procesni parametri (slika 5):

a) bazičnost žlindre,

b) parni tlak H_2O v plinski atmosferi nad žlindro,

c) vsebnost vodika v elektrodnem materialu.

Naše raziskave so bile usmerjene v študij vpliva parnega tlaka p_{H_2O} nad plinsko atmosfero na vsebnost vodika v EPŽ-žlindrah[17].
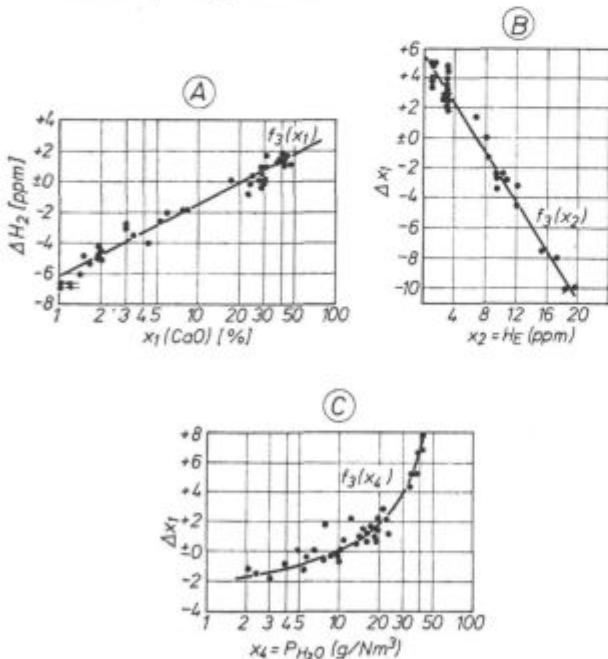
Kot izhodišče za študij smo izbrali reakcijo:

$$\{H_2O\}_g + (O^{2-}) = 2\,(OH-)$$
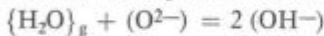
Ravnotežno konstanto za to reakcijo lahko zapišemo v obliki:

$$(\%\,H) = (\%\,H^0)\,\sqrt{p_{H_2O}}$$

Kot žlindro smo izbrali sistem: CaF_2-Al_2O_3-CaO, oziroma standardno sestavo: 33 % CaF_2 + 33 % Al_2O_3 + 33 % CaO. Poskuse smo delali pri dveh vrednostih parnega tlaka:

Hydrogen

The control of hydrogen is very serious proces problem especially in the manufacture of big ingots with cross-section over 500 mm[6, 16]. Well known hydrogen problem is certainly a considerable obstacle to further development of ESR technology especially in the field of special and superalloys. Practical experience has shown that first phase of ESR processing is most critical as regards the hydrogen problem[17]. Investigations which have been carried out to the present show[16] the dominant influence of the following three process parameters as regards the hydrogen content of refined metal (fig. 5):

a) slag basicity,

b) partial pressure of H_2O in gaseous atmosphere above slag,

c) hydrogen content of electrode material.

The aim of our investigation was to study the influence of partial pressure of water vapour p_{H_2O} on the hydrogen content of slag[17]. The base for considerations was the equation:

$$\{H_2O\}_g + (O^{2-}) = 2\,(OH-)$$
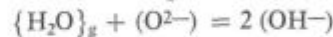
The equilibrium constant for this reaction can be written in the form:

$$(\%\,H) = (\%\,H^0)\,\sqrt{p_{H_2O}}$$

The slag belonging to the CaF_2-Al_2O_3-CaO system of standard composition 33 % CaF_2, 33 % Al_2O_3 and 33 % CaO was used. Two different partial pressures of water vapour were utilised namely 8 mm Hg and 35.6 mm Hg which correspond to air moisture in winter and summer time, respectively.

The relationship between maximum hydrogen content (H^0) and slag basicity at 1620 °C is presented in fig. 6. Practical results obtained by refining of low alloyed steel with the use of the same slag and ∅ 100 mm crystallizer are also given.

Slika 5
Vpliv različnih tehnoloških parametrov na vsebnost vodika pri pretaljevanju konstrukcijskih jekel pod žlindro

Fig. 5
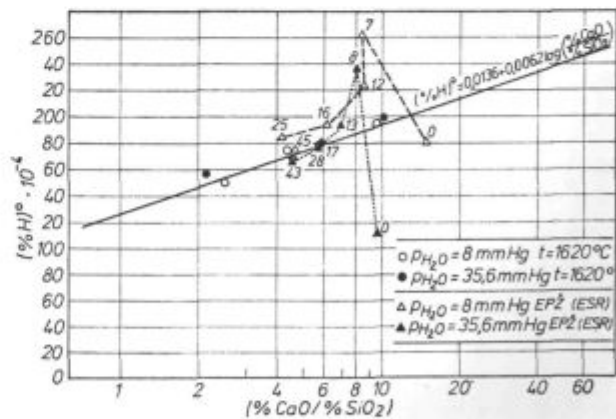Influence of various technological parameters on hydrogen content in ESR processing of structural steels

Slika 6
Odvisnost maksimalne topnosti vodika v žlindri s 33 % CaF_2 — 33 % Al_2O_3 — 33 % CaO od bazičnosti žlindre pri temperaturi 1620 °C.

Fig. 6
Relationship between maximum hydrogen solubility in 33 % CaF_2—33 % Al_2O_3—33 % CaO slag and slag basicity at 1620 °C

$p_{H_2O} = 8\,mm\,Hg$ in 35,6 mm Hg, kar približno ustreza vlažnosti v zimskem in poletnem času. Na sliki 6 je grafično prikazana odvisnost maksimalne vsebnosti vodika (H^0) od bazičnosti žlindre pri temperaturi 1620 °C. V diagram smo vrisali tudi praktične rezultate pretaljevanja nizko legiranega jekla pod enako žlindro v kristalizatorju $\emptyset$ 100 milimetrov.

Iz dobljenih rezultatov sledi, da se sistem žlindra-plinska faza s časom taljenja približuje neki ravnotežni vrednosti. Ta ugotovitev in dejstvo, da obstoja določeno razmerje (koeficient porazdelitve) med vodikom v kovini in žlindri (% H)/% H, ki pri manjših presekih ingota znaša 8—10 in pri večjih prečnih presekih 3,5—4,5, so povsem v soglasju s praktičnimi izkušnjami, kakor tudi z nekaterimi eksperimentalnimi raziskavami drugih avtorjev [16—21].

Čeprav danes obstajajo nekatere racionalne tehnološke rešitve (uporaba suhega zraka, optimalna izbira EPŽ-žlinder, prepihovanje tekoče žlindre z inertnimi plini itd.), velja zaenkrat še mišljenje, da je kontrola vodika pri EPŽ-postopku dominanten metalurški problem.
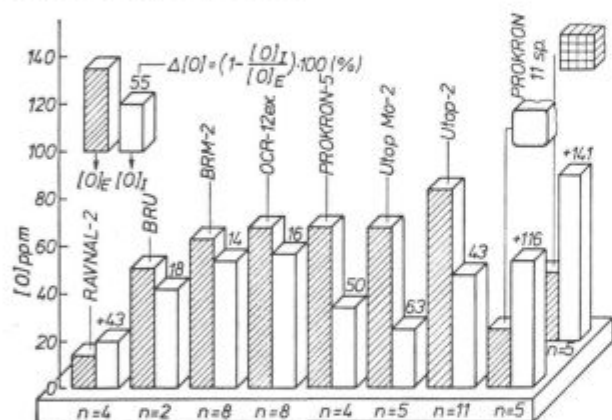
Slika 7

Obnašanje kisika pri električnem pretaljevanju kvalitetnh jekel pod žlindro

Fig. 7

Behaviour of oxygen in electro-slag remelting of quality steels

Kisik

Za razliko od vodika je kontrola kisika pri izdelav velikih EPŽ-ingotov povsem dognana. Na splošno ugotavljamo, da se vsebnost kisika med pretaljevanjem zniža tudi do 60 % (slika 7). Pri kontroli kisika je pomembno poudariti dejstvo, da je odgor elementov z visoko afiniteto do kisika v tesni zvezi z vsebnostjo kisika v EPŽ-ingotu in oksidne komponente ustreznega elementa v žlindri [4, 5]. Kot primer navajamo odvisnost med kisikom in nekaterimi parametri EPŽ-procesa, ki v celoti potrjuje veljavnost že omenjenega teoretičnega modela.

From the results it can be seen that the slag-gas system gradually approaches to a definite equilibrium value.

This finding together with the fact that there is a definite ratio (coefficient of distribution) between the hydrogen content of metal and slag (% H)/% H which lie within 8—10 and 3.5—4.5 range for ingots of low and high cros-section, respectively is in complete agreement with practical experience as well as with experimental results of other authors [16—21]. The control of hydrogen content in metal refined by ESR proces remains to be a principal metallurgical problem in ESR process although some rational technological measures have been applied, e. g. the selection of optimum slag, the use of inert gasses for blowing out slag, etc.

Oxygen

For the difference from hydrogen the control of oxygen even in the manufacture of large ESR ingots is completely obtainable. Generally, it can be said that the oxygen content of metal is decreased even by 60 % as seen from fig. 7. As regards the control of oxygen it should be stressed that oxidation losses of the elements with a high affinity to oxygen are closely connected to the oxygen content of ESR ingot and the corresponding oxide content of slag [4, 5]. As for instance, dependence of certain parameters of ESR process on the oxygen content can be mentioned which completely confirms the validity of the theoretical method mentioned.

Nitrogen

As seen from fig. 3 the nitrogen content of refined metal is normally decreased or remains the same as that in electrode material. At high temperatures nitrogen dissolves in liquid metal and only
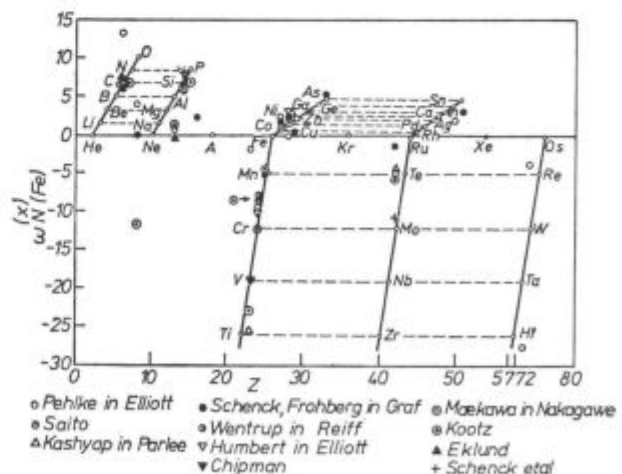
Slika 8

Odvisnost koeficienta interakcije dušika v sistemu Fe-X-N od atomskega števila elementa X

Fig. 8

Depedence of interaction coefficient of nitrogen in Fe-X-N system on atomic number of element X

Dušik

Kot je pokazano na sliki 3, se vsebnost dušika med pretaljevanjem pod žlindro normalno nekoliko zniža ali ostane enaka vsebnosti elektrodnega materiala. Dušik se pri visokih temperaturah raztaplja v tekoči kovini. V prisotnosti nekaterih nitridotvorcev, kot so V, Nb, Ti, Zr, poteka disociacija nitridov le delno (slika 8)[22, 23].

Značilnosti nitridov v primerjavi z oksidi so:

a) dokaj visoka gostota: AlN (3,1 g/cm³), TiN (5,2 g/cm³), NbN (8 g/cm³), kar otežkoča proces njihovega prenosa iz kovine v žlindro (asimilacija z žlindro),

b) zelo majhne dimenzije (NbN, TiN) ter ugodne strukturne lastnosti (kubična ali tetragonalna oblika), kar je posebej pomembno za modifikacijo nekaterih jekel.

in the presence of certain nitride formers like V, Nb, Ti and Zr their dissociation proceed only partially (fig. 8)[22, 23].

Characteristic features of nitrides as compared to oxides are as follows:

a) rather high density: AlN (3.1 g/cm³), TiN (5.2 g/cm³), NbN (8 g/cm³) which hinders their transfer from metal to slag (assimilation by slag),

b) very fine size (NbN, TiN) and favorable structure properties (cubic or tetragonal form) which is specially important in the modification of certain steels.

When remelting certain tool steels and high-speed steels the additions of nitrogen (e. g. in the form of FeMnN or FeCrN) can be used in order to exert an influence on crystallisation conditions. As for illustration the following results of the modification of high-speed steel can be mentioned:

<div align="center">
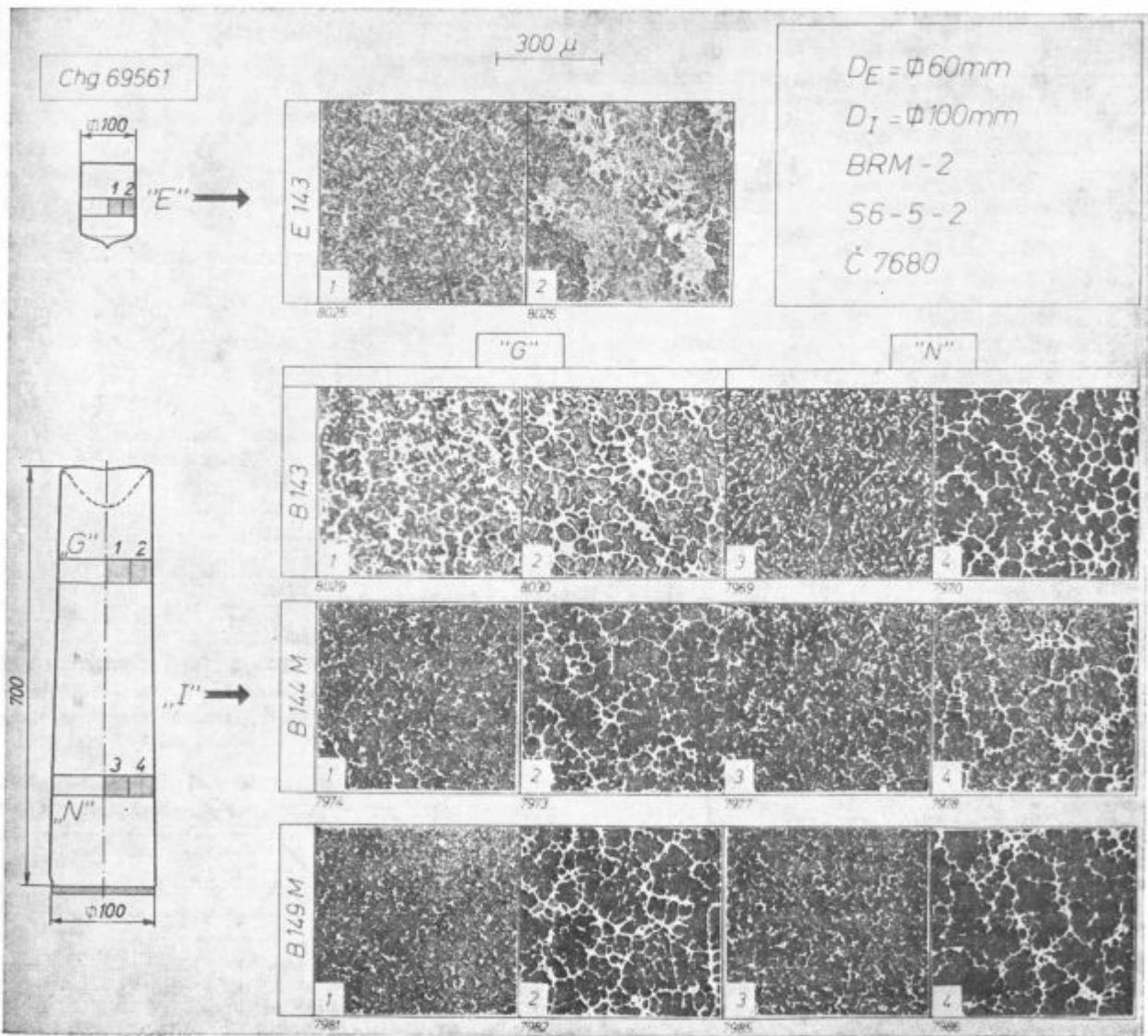
Slika 9

Mikrostruktura brzoreznega jekla S 6-5-2 (M. 2) modificiranega z različnimi variantami (Ti + dušik)

Fig. 9

Microstructure of high-speed S 6-5-2 (M. 2) steel modified in different ways (Ti + nitrogen)

</div>

Pri pretaljevanju brzoreznih in nekaterih drugih orodnih jekel je mogoče z dodatki dušika (npr. v obliki FeMnN ali FeCrN) vplivati na pogoje kristalizacije. V ilustracijo navajamo rezultate modifikacije brzoreznega jekla:

S 6-5-2 (M. 2) v treh variantah (slika 9)

B.143 Ti dodan v elektrodo v količini 0,1 %

B.144 Ti dodan v elektrodo (0,1 %) + dušik v obliki FeCrN (0,03 % N)

B.149 Ti dodan v elektrodo (0,1 %) + dušik v obliki FeCrN (0,06 % N)

Na koncu naj omenimo, da poteka intenzivni razvoj osvajanja tehnologije legiranja kvalitetnih jekel z dušikom preko plinske faze pri visokih pritiskih. Ta tehnologija ima veliko perspektivo na področju izdelave nerjavnih jekel[24, 25].
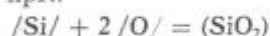
Žveplo

Značilno za žveplo je, da se zelo lahko odstranjuje iz tekoče kovine med EPŽ-procesom. Transport žvepla poteka v smeri kovina-žlindra-plinska faza. Simultano poteka proces prenosa kisika iz žlindre v kovino po reakciji:
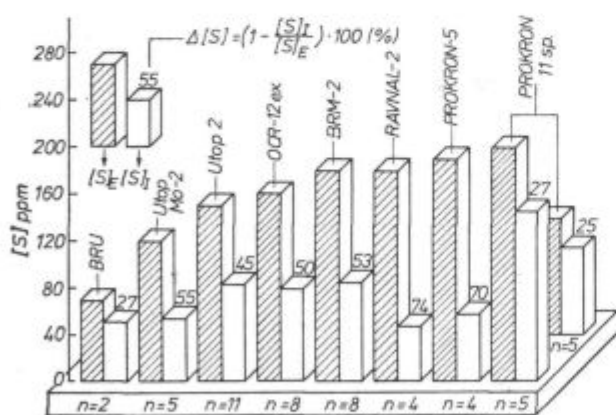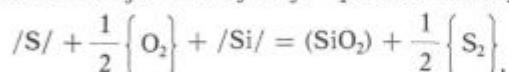
$$/S/ + (O^{2-}) = /O/ + (S^{2-}),$$
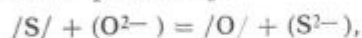
oziroma pri sodelovanju plinske faze

$$/S/ + \frac{1}{2}\left\{O_2\right\} = /O/ + \frac{1}{2}\left\{S_2\right\}$$
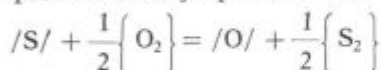
Pri standardni EPŽ praksi je vsebnost kisika pod kontrolo reakcij, ki potekajo med dezoksidanti in kisikom, npr.:

$$/Si/ + 2\,/O/ = (SiO_2)$$

Kombinacija reakcij daje splošno reakcijo:

$$/S/ + \frac{1}{2}\left\{O_2\right\} + /Si/ = (SiO_2) + \frac{1}{2}\left\{S_2\right\},$$

Slika 10

Obnašanje žvepla pri pretaljevanju nekaterih visoko legiranih kvalitetnih jeklih pri konstantni sestavi žlindre in geometriji elektrode in kokile

Fig. 10

Behaviour of sulfur in electro-slag remelting of certain high-alloyed steels at the same slag and the same electrode-mould geometry

S 6-5-2 (M. 2) Three variants-presented in Fig. 9,

B. 143 Ti added to electrode (0.1 %).

B. 144 0.1 % Ti added to electrode + 0.03 % N added in the form of FeCrN.

B. 149 0.1 % Ti added to electrode + 0.06 % N in the form of FeCrN.

Finally it should be mentioned that investigations are being undertaken in the alloying of quality steels by high pressure nitriding. This technology has a great future especially in the manufacture of stainless steels[24, 25].
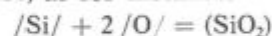
Sulfur

Sulfur is very easily removed from liquid metal in ESR proces. The transport of sulfur proceeds in the metal-slag-gas direction. Simultaneously the transport of oxygen from slag to metal proceeds according to the following reaction:
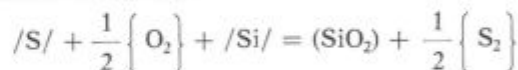
$$/S/ + (O^{2-}) = /O/ + (S^{2-})$$
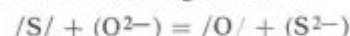
as well as by reaction with gaseous phase:

$$/S/ + \frac{1}{2}\left\{O_2\right\} = /O/ + \frac{1}{2}\left\{S_2\right\}$$
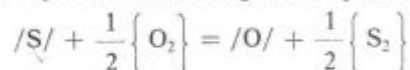
In standard ESR practice the oxygen content is controlled by reactions occuring between oxygen and deoxidizers, as for instance:

$$/Si/ + 2\,/O/ = (SiO_2)$$

By combining the two reactions a general reaction is obtained:

$$/S/ + \frac{1}{2}\left\{O_2\right\} + /Si/ = (SiO_2) + \frac{1}{2}\left\{S_2\right\}$$

The equilibrium constant of this reaction is:

$$a_S = \frac{a_{SiO_2}}{a_{Si} \cdot K}\left(\frac{P_{S_2}}{P_{O_2}}\right)^{1/2}$$

From the above equation it follows that the degree of desulfuration in ESR process depends on the following important parameters:

a) the basicity of slag,

b) the chemical composition of steel, most of all the silicon content of steel,

c) the partial pressure of oxygen in atmosphere above the slag.

The results of desulfuration of different grades of steel obtained in electro-slag remelting at the same slag and air atmosphere are presented in fig. 10[1]. Ingot dimensions and the fill factor was also the same. It is clearly seen that desulfuration degree actually depends on steel composition, i. e. on oxygen activity of the liquid metal.

The influence of slag composition i. e. of the slag basicity all other parameters being constant is seen in fig. 11[17]. At the basicity of slag (% CaO)/ /(% SiO$_2$) $\geq$ 3, the ratio between the amounts of sulfur distributed on metal-slag-gaseous phase is practically constant.

oziroma ravnotežno konstanto:

$$a_S = \frac{a_{SiO_2}}{a_{Si} \cdot K} \left(\frac{P_{S_2}}{P_{O_2}} \right)^{1/2}$$

Iz te enačbe sledi, da je stopnja odžveplanja pri EPŽ-postopku odvisna od treh pomembnih parametrov:

a) bazičnosti žlindre (vpliv na aktivnost SiO_2),

b) kemične sestave jekla (predvsem vsebnosti silicija v jeklu),

c) parcialnega tlaka kisika v zračni atmosferi.

Na sliki 10 so ponazorjeni rezultati odprave žvepla pri pretaljevanju različnih kvalitet jekla pri enaki sestavi žlindre in zračni atmosferi[1]. Tudi dimenzije ingota in polnilni faktor sta bila identična. Iz teh rezultatov sledi, da je stopnja razžveplanja dejansko funkcija sestave jekla, oziroma aktivnosti kisika v tekoči kovini.

Vpliv sestave žlindre, oz. bazičnosti žlindre pri vseh ostalih konstantnih parametrih kaže slika 11[17]. Pri bazičnosti žlindre (% CaO)/(% SiO_2) ≥ ≥ 3 je razmerje med količino žvepla, ki se porazdeli med kovino-žlindro-plinsko fazo, skoraj konstantno.
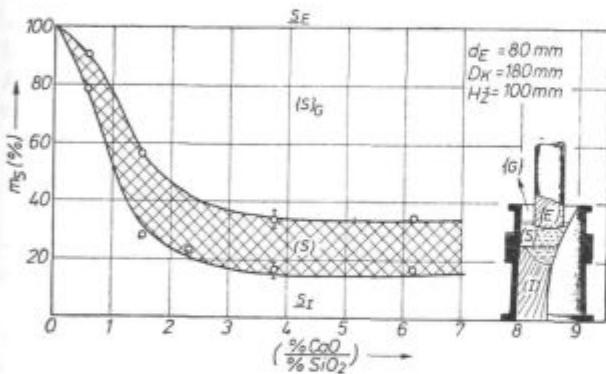
Slika 11

Porazdelitev žvepla med kovino-žlindro-plinsko fazo med pretaljevanjem nizko legiranega jekla. S_I, (S), S_G in S_E so vsebnost žvepla v ingotu, žlindri, plinski fazi in elektrodi

Fig. 11

Distribution of sulfur between metal-slag-gas plases in remelting of low alloyed steel. S_I, (S), S_G, S_E — sulfur content of ingot, slag, gaseous phase and electrode, respectively
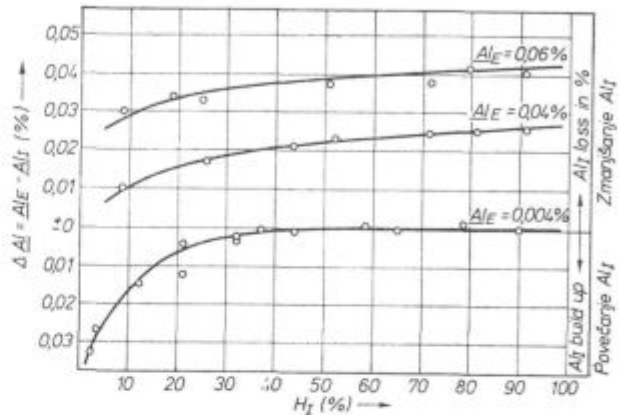
Aluminij

Dosedanje praktične izkušnje pri pretaljevanju konstrukcijskih jekel, posebej velikih kovaških ingotov, so pokazale, da je kontrola aluminija pri EPŽ-ingotih zelo dominanten metalurški problem[4,5,6,16]. Pri standardni praksi, tj. uporabi žlinder z visoko vsebnostjo Al_2O_3 in kontinuirani dezoksidaciji žlindre z Al, se opaža padec vsebnosti Al od noge proti glavi ingota[11,16].

Slika 12 kaže spremembo vsebnosti aluminija Al_E-Al_I (E = elektroda, I = ingot) z višino ingota pri različnih izhodnih aluminijih v elektrodi[11].

Aluminium

Practical experience obtained to the present in electro-slag remelting of structural steels, specially heavy forge ingots has shown that the control of aluminium content in ESR ingots is a dominant metallurgical problem[4,5,6,16]. In standard practice i. e. when using slag with a high Al_2O_3 content and at continuous deoxidation of slag with Al additions a decrease in the aluminium content of ingot has been observed in leg-head direction[11,16].

Slika 12

Spremembe vsebnosti aluminija Al_E - Al_I (E = elektroda, I = ingot) z višino ingota pri različnih vsebnostih aluminija v izhodni elektrodi[11]

Fig. 12

Difference in aluminium content of electrode and ingot Al_E—Al_I in depedence from ingot heigth at various initial aluminium content of electrode[11]

The difference in the aluminium content of electrode and ingot Al_E — Al_I (E — electrode, I — ingot) in dependence on ingot heigth at different initial aluminium content of electrode is presented in fig. 12[11].

A part of aluminium added to slag (approximately 15 %) is transfered to metal which makes it possibble to control the aluminium content of obtained ingot[5].

Slag composition exerts much higher influence on the aluminium content of ESR ingot. Due to the complexity and high research costs a theoretical model has been developed which together with the use of a mini-computer makes it possible to estimate the influence of various parameters.

The results of the investigations of this type in comparison with practical results obtained in electro slag remelting of a series of structural steels in laboratory and industrial conditions are given in fig. 13[5,15].
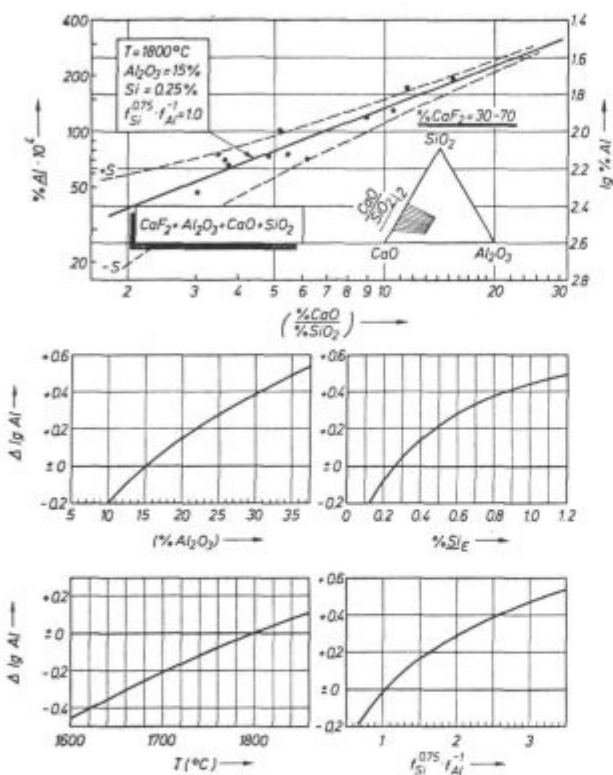
Titanium

The behaviour of titanium in ESR proces is rather similar to that of silicon. Its control is specially problematic in stainless steels with about 0.6 % Ti and up to 0.1 % Al[26]. The control of titanium is very important in refining maraging steels and certain super-alloys.

Pri dodatku Al v žlindro del tega (okoli 15 %) prehaja v kovino in na ta način lahko vpliva na vsebnost Al v pretaljenem ingotu[5].

Neprimerno večji vpliv na vsebnost aluminija v EPŽ-ingotu ima sestava žlindre. Zaradi kompleksnosti in dokaj visokih raziskovalnih stroškov takih raziskav smo razvili teoretični model, ki omogoča z uporabo mini-računalnika oceniti vplive različnih parametrov.

Na sliki 13 smo prikazali rezultate tovrstnih raziskav in jih primerjali s praktičnimi podatki pri pretaljevanju konstrukcijskih jekel v laboratorijskih in industrijskih pogojih[5, 15].
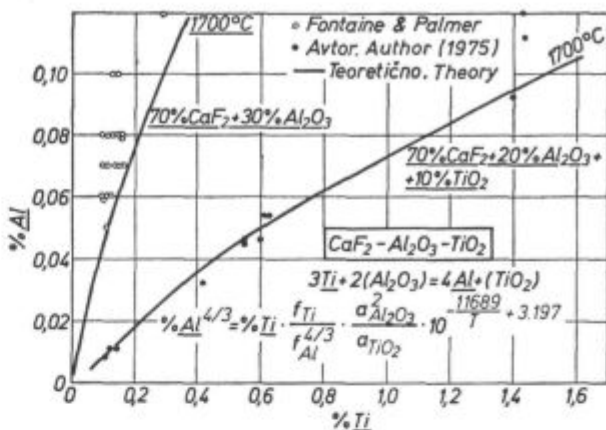

Slika 13
Vpliv različnih tehnoloških parametrov na vsebnost aluminija pri EPŽ-postopku

Fig. 13
Influence of various technological parameters on aluminium content of steel in ESR proces

Titan

Obnašanje titana pri EPŽ-postopku je dokaj podobno obnašanju silicija. Njegova kontrola je posebej problematična pri pretaljevanju nerjavnih jekel z vsebnostjo titana okoli 0,6 % in aluminija, nižjega od 0,1 %[26]. Tudi pri pretaljevanju maraging jekel in nekaterih superzlitin je kontrola titana velikega pomena.

Naše izkušnje se nanašajo na pretaljevanje nerjavnih jekel tipa AISI 321 in različnih kvalitet maraging jekel[5, 15]. Na sliki 14 je prikazana odvisnost med aluminijem in titanom za nekatera ma-

Slika 14
Odvisnost med aluminijem in titanom pri pretaljevanju maraging jekel vrste 18 NiCoMo

Fig. 14
Relationship between aluminium and titanium in electro-slag remelting of maraging 18 NiCoMo steel

Our experience concerns electro slag remelting of AISI 321 steel and different grades of maraging steel.

The relationship between aluminium and titanium in maraging steel of 18 NiCoMo type is presented in fig. 14. The relationship has been calculated on the basis of the theoretical model and then compared to practically obtained data. A detailed description of these investigations has already been published[5, 15].

Other elements

A general review of the behaviour of other elements during electro-slag remelting can be seen in fig. 3.

Practical experience obtained to the present has shown that the control of a majority of residuals such as Pb, As, Sb, Sn, Cu, ... is not necessary if the slag composition is maintained within definite specified limits.

Although producers of ESR-slag give certain specifications for particular elements these informations are deficient and inaccurate. As for instance the following table 1 presents a specification of the standard ESR slag of CaF_2-Al_2O_3-CaO type[6].

Lead

In electro-slag remelting of steel and superalloys lead is reduced and transfered to gaseous atmosphere in the form of vapour. Therefore PbO content is limited to 0.02 % maximum.

Arsenic

According to the thermodynamic stability of arsenic oxides arsenic starts to reduce after the melting of slag and leaves the melt in the form of As and As_2O_3 vapour[6]. Generally speaking there is only a few data on the behaviour of arsenic.

raging jekla, vrste 18 NiCoMo. Odvisnosti so izpeljane na osnovi teoretičnega modela in nato primerjane s praktičnimi podatki. Obširno so te raziskave opisane v literaturi[5, 15].

Ostali elementi

Splošni pregled o obnašanju ostalih elementov pri EPŽ-procesu je razviden iz slike 3. Dosedanje praktične izkušnje so pokazale, da kontrola večine rezidualnih elementov, kot so: Pb, As, Sb, Sn, Cu ni potrebna, če sestavo žlindre ohranimo v določenih, predpisanih mejah.

Čeprav proizvajalci EPŽ-žlinder navajajo določene specifikacije za posamezne elemente, so te informacije pomanjkljive in premalo precizne. Kot primer navajamo nekatere specifikacije za standardno EPŽ-žlindro, tipa $CaF_2\text{-}Al_2O_3\text{-}CaO$[6]. (Tabela 1)

Tabela 1: Nečistoče v EPŽ-žlindrah
Table 1: Impurities in ESR slags

Nečistoča Impurity	%
C	0,03
P	0,005
S	0,02
PbO	0,02
Si_2O_3	0,002
$Na_2O + K_2O$	0,20
FeO	0,20
MnO	0,20
MgO	0,20

Svinec

Med pretaljevanjem jekel in superzlitin se svinec reducira in v obliki pare zapušča žlindro, oziroma prehaja v plinsko atmosfero. Zato je vsebnost PbO omejena na maksimalno vrednost 0,02 % PbO.

Arzen

Sodeč po termodinamični stabilnosti njegovih oksidov, se ta takoj, ko je žlindra raztaljena, začne reducirati in zapušča žlindro kot As ali As_2O_3 — pare[6]. Na splošno o njegovem obnašanju ni veliko podatkov.

Fosfor

Pri standardni EPŽ-praksi niso dani pogoji za odpravo fosforja, ker je oksidacijski potencial žlindre zelo nizek. V literaturi obstaja nekaj po-

Phosphorus

In standard ESR practice dephosphorization is not possible due to a very low oxidation potential of ESR slag. However, certain data have been published on dephosphorization in electro-slag remelting obtained by the use od CaF_2-CaO slag with a high FeO and low SiO_2 content.

Carbon

The control of carbon represents no problem in electro slag remelting of steels with carbon content over 0.1 %. However, certain measures have to be taken to assure a low carbon content of slag when remetling steel with a low carbon content (e.g. stainless steels with carbon content below 0.04 %) and specially in the case of super alloys. It has been determined that carbon present in slag can be easily transported to metal during remelting. This transport of carbon probably proceeds by diffusion of carbide ions which are subsequently oxidised to carbon.

CONCLUSIONS

The presented review of the behaviour of elements in electro-slag remelting of quality steels and superalloys can not be considered as complete, however it offers certain informations and suggestions which can help to better understanding of the problem which has become very actual due to the introduction of computer control of ESR proces.

Generally, it can be stated that there is a serious deficiency in the data on the behaviour of particulate elements during electro-slag remelting. Data on high-temperature thermochemistry of ESR-slags are also lacking. As a result of such situation ERS-practice is still based on empyrical work in a higher extent than on corresponding theoretical models, which help to deepen our knowledge and represent much better basis for the introduction of computer control of ESR proces[5, 15].

Literatura — References

1. B. Koroušić: Želez. zbornik 7, št. 1 (1973), 23—29.
2. W. Holzgruber, M. Kroneis, A. Schneidhofer: In Proc. Second International Symposium on Electroslag and Other Special Melting Technologies, Vol. I. Pittsburgh: Mellon Institute, 1969.
3. W. Holzgruber, E. Ploeckinger: Stahl u. Eisen 88, 12 (1968), 638—48.
4. B. Koroušić: Berg- und Hüttenmännische Monatshefte J. 122, H. 7 (1977), 287—291.
5. B. Koroušić, W. Holzgruber: BHM. J. 123, H. 1 (1978), 17—22.
6. R. H. Nafzieger et al: The electroslag melting process, U. S. Bureau of Mines, Bulletin 669 (1976).
7. W. Holzgruber: Paper No. 139 presented at Electro-Heat Conference, Brighton, England, 1968.
8. A. Choudhury, R. Jauch, H. Hinze, H. Scheidig: Proc. Third International Symposium on Electroslag and Other Special Melting Technology, Vol. II, p. 159. Pittsburgh: Mellon Institute, 1971.

datkov o odpravi fosforja pri EPŽ-postopku z uporabo žlinder CaF_2-CaO z visoko vsebnostjo FeO in nizko vsebnostjo SiO_2.

Ogljik

Pri pretaljevanju jekel z vsebnostjo ogljika nad 0,1 % ni problematična njegova kontrola. Toda pri pretaljevanju jekel z nizko vsebnostjo ogljika (npr. nerjavnega jekla z vsebnostjo ogljika pod 0,04 %), in posebej pri pretaljevanju superzlitin, so potrebni določeni ukrepi, da je vsebnost ogljika v žlindri nizka. Ugotovljeno je, da ogljik, ki je prisoten v žlindri, dokaj lahko prehaja v kovino med procesom pretaljevanja. Transport ogljika verjetno poteka preko karbidnih ionov, ki se nato oksidirajo v ogljik.

ZAKLJUČKI

Opisani pregled o obnašanju elementov pri elektrožlindrnem postopku pretaljevanja kvalitetnih jekel in superzlitin ne predstavlja zaokroženo celoto. Toda nadejamo se, da daje informacije in sugestije, ki naj bi vodile do boljšega razumevanja problema, ki je danes z uvajanjem računalniškega vodenja EPŽ-procesa postal zelo aktualen.

Na splošno lahko ugotovimo, da so informacije o obnašanju posameznih elementov, predvsem pa o termokemiji EPŽ-žlinder pri visokih temperaturah zelo pomanjkljive. Posledica tega stanja je, da se praksa še vedno opira bolj na empirične izkušnje in znatno manj na teoretične modele, ki omogočajo poglobitev znanja, predvsem pa nudijo boljšo osnovo za računalniško vodenje procesa rafinacije.

9. M. Wahlster, R. Schumann: In Proc. Fourth International Symposium on Electroslag Remelting Processes, pp. 337—45. Tokyo: The Iron and Steel Institute of Japan, 1973.
10. B. Koroušić: Železarski zbornik 2 (1974), 89—99.
11. H. Kajioka, K. Yamaguchi, N. Sato, K. Soejima, S. Sakaguchi: In Proc. Fourth International Symposium on Electroslag Remelting Processes, pp. 102—14. Tokyo: The Iron and Steel Institute of Japan, 1973.
12. F. A. Kirk: Recent Developments in Tool Steels, Part 2. The Electroslag Process. Steel Times, v. 192, No. 2, February 1969, pp. 87—90.
13. C. F. Knights, R. Perkins: In Electroslag Refining London. The Iron and Steel Institute (1973).
14. M. M. Klyuey, A. E. Kablukovskii: (Metallurgy of Electroslag Remelting). Metallurgia, Moscow, 1969, 256 pp.
15. B. Koroušić: Congres International sur la Physico-Chimie de la fonte et de l'acier Versailles (1978).
16. H. Jäger, G. Kühnelt: Berg- und Hüttenmänn. Monatshefte 120 J. H. 9 (1975) S. 423—429.
17. B. Koroušić: Poročilo Metalurškega inštituta v Ljubljani, Nal. 720 (1979)
18. W. Holzgruber, A. Schneidhofer, L. Jäger: International Symposium of Special Electro-Metallurgy, Kiev, 1972.
19. B. I. Medovar, V. L. Artamanov in ostali: International Symposium of Special Electro Metallurgy, Kiev, 1972.
20. Ju. V. Lataš, B. I. Medovar: »Elektrošlakovi pereplav«, Metallurgija (Moskva), 1970, 29.
21. Y. Nakamura, K. Haroshima: 92nd Meeting of ISIJ, Oct. 2—4 (1976) Sendai.
22. C. Gatellier, M. Olette: Revue de Metallurgie — Juin (1979) s. 377—386.
23. K. Narita: Trans. ISIJ. Vol. 15 (1975) S. 145—152.
23a. B. Koroušić, F. Vodopivec, J. Rodič, A. Rodič, J. Pšeničnik: Žel. zbornik 12, št. 3 (1978), 87—97.
24. Ch. Kubisch, W. Holzgruber: In Proc. Third International Symposium on Electroslag and Other Special Melting Technology, Vol. III. pp. 267—84. Pittsburgh: Mellon Institute, 1971.
25. W. Holzgruber: Personal Communication.
26. I. Kašik, I. Petrman: Proc. 2th Czechoslovak — Japanese yoint symp. on metallurgical problems of nuclear power equipment production (1979).