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NONDESIRABLE ADDITIVES CONTENTS REDUCTION IN CONTINUOUSLY CAST STEEL

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The result of the dynamic growth of the continuously cast steel ratio is the significant decrease in the waste from production in the metallurgical plants. The increasing significance of the metallic waste in the steel production under the conditions of 100% continuous casting in plant U.S.Steel Košice and Iron works of Podbrezová, a.s., is not the typical case only for the Slovak metallurgical industry. It has the common feature which is the consequence of the scientific development of the metallurgical production in all industrially developed countries of the world.

Key words: *metallic waste, recycling, metallic impurities, non-desirable elements*

Reduciranje nepoželjnih aditiva u kontinuirano lijevanom čeliku. Rezultat dinamičkog porasta omjera kontinuirano lijevanog čelika je značajno smanjenje otpada u proizvodnji metalurških pogona. Sve veće značenje metalnog otpada u proizvodnji čelika, do njegovog 100 % učešća u pogonu U. S. Čeličana Košice i željezari u Podbrezova a. s., nije tipičan samo za slovačku metaluršku industriju. To je zajednička karakteristika koja je posljedica znanstvenog razvoja metalurške proizvodnje u svim industrijski razvijenim zemljama svijeta.

Ključne riječi: *metalni otpad, recikliranje, nečistoće u metalu, nepoželjni elementi*

INTRODUCTION

In relation to the changes in the structure of the processed metallic waste intensively are discussed the aspects of its physical and chemical quality and on possible risk of the degeneration as the result of the gradual metallic waste contamination in course of its recycling. The probability of its contamination is proportional to the complexity and metals residual period in their cycle of the owner companies. The general type of the metallic waste is considered to be least pure. The impurities from the metallic waste will be in the course of the melting process transformed in the impurities in the steel.

The conclusions of the renown institution Batelle Columbus Laboratories in USA [1] and UN-Economic Commission for Europe [2] are similar ones and they have general nature:

- the residual elements in steel, origin of which is in the metallic waste, represent complex problem and this can be controlled and managed under high costs;
- demand for the clean metallic waste will grow along with the increase in the price difference among the individual types;
- the pressure for the clean metallic waste be higher proportionally with the increasing ratio of the scrap in the charge for the steel production;
- there is permanent and typical tendency of growth in the micro-alloyed steels production ratio, which bring another impurities in the steel;
- at the present time there is no risk of new residual elements occurrence.

The reduction in the solid pig iron import increases the pressure on the metallic waste for steelworks redistribution and this means significant importance increase regarding to its purity.

IMPURITIES IN STEEL

Subject to their chemical composition, the impurities in the steel may be divided as follows:

metallic impurities
- usable in the form of the alloying elements,
- unusable,
- non-desirable;

non-metallic impurities.

The metallic waste purity is as the rule characterised by the selected residual elements content [3]. There are four groups of elements in the charge for the steel produc-

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tion, that will be in the course of the refinement eliminated or will remain in the steel, Tab. 1..

Table 1. **Elements procesing by steelmaking**
Tablica 1. **Procesiranje elemenata pri proizvodnji čelika**

Method of Elements Removal	Elements	Origin
To slag	Al, B, Ti, Si, V, Zr	Pig iron, de-oxidation, alloying elements
Partially to slag	Mn, P, S, (Cr)	Pig iron, alloying elements
Remain in steel	Ni, Mo, W, Co, Cu	Alloying elements, addition heterogeneous
Fully to dust	Cd, Pb, Zn	Addition from heterogeneous coats

The extensive papers dealing with the non-desirable elements content reduction which accompany the additives in the steel applying the method of the fluidised bed melting [4] confirmed the possibilities of Bi, Sb and Cu easy evaporation, Sn difficult evaporation and As very difficult evaporation. In the studied systems of the concrete steel grades evaporation there have been gained various degrees of the non-ferrous metals elimination:

Bi 90.44 to 85.91 %;
Sb 64.93 to 95.19 %;
Cu 55.48 to 94.92 %;
Sn 19.67 to 69.17 %;
As 04.24 to 15.26 %.

The gained results [4] represent the actual theoretical and scientific base of the possible exploitation of new processes of the plasma technology in future.

Number of authors pay attention to the impurities impact on the steel quality and utility properties. The negative impact of the above mentioned elements on the steel utility properties can be considered as confirmed [5,11].

SOURCES OF IMPURITIES IN THE METAL BEARING CHARGE FOR THE STEEL PRODUCTION

High content of non-ferrous elements in the amortisation and consumers metallic waste is the objective fact and contribution can be subscribed to the pressed bundles and steel chips. This fact is confirmed by the studies subject to the many realised observations in the practical sphere. The contents of the non-desirable elements in variety of metallic scrap are according to Chvátal [6] as rule as follows in Table 2..

The highest average contents - in average up to 0.37% Cu are present in bundles of old amortising metallic scrape. More significant criterion, as the estimated annual mean Cu content, is its variability according to the batches [7]. The bundled old waste gains along with the highest mean values of Cu contents its highest variability as well.

Table 2. **Content of non-desirable elements in iron scrap**
Tablica 2. **Sadržaj nepoželjnih elemenata u starom željezu**

Grade of iron scrap	Contents, percentage		
	Cu	Sn	Ni
Cutting non-selected	0.17	0.02	0.05
Selected over 100x100 mm	0.15	0.02	0.05
Crushing light-weight	0.15	0.02	0.08
Shreder Becker	0.15-0.25	0.04	0.11
Piace	0.18	0.02	0.07

The metallic waste processing by grinding or crushing with the subsequent magnetic separation creates the conditions for non-magnetic heterogeneous components only partial elimination. It does not solve the non-ferrous metals present in steel, coats and others type of contamination elimination. The source of the impurities forms the non-selected alloying elements.

LIMIT CONTENTS OF THE NON-FERROUS METALS IN STEEL

The limit contents of the non-ferrous metals in the steel are different in different states. Limits provided in STN do not rank in the group of the most strict limits. Highly strong limits are implemented in USA and Australia.

From the point of the optimum conditions in the course of the hot steel forming the following limit relationship contents of Cu, Sn and As are recommended:

$Cu + 4\ Sn \leq 0.4$,
$Cu + 8\ Sn + 3\ As \leq 0.3$,
$Cu + 7.76\ Sn \leq 0.326$,
$Cu + 8\ Sn \leq 0.3$,
$0.008 \leq Sn \leq 0.026$.

When are evaluated the effects of the former non-ferrous metals present on the phase boundaries on the defects occurrence in the hot formed steel, the decisive role plays Cu given his content exceeds 0.2 % wt in connection with Cu enriched surface. The result of the exceeded limit is the increased liability to the inter-granular micro-cracks for austenite grains being effected [10]

In connection with the steel liability to the micro-cracks occurrence with increased Cu solubility in austenite, there should be respected the possible superposition effect of the further elements and steel chemical constitution. For example, Ni may compensate the harmful effect of Cu increased content in steel. On the contrary, Sn plays an important role in the steel liability to the surface micro-cracks formation in course of steel hot forming under high temperatures [11]. Under the conditions of the material surface exposition to the oxidizing atmosphere is originated the phase with increased Sn content.

Cu content of 0.3 % wt and Cu of 0.040 % wt create in the low carbon steel under the temperature of 1100 °C melted phase on the interface steel-scale with 0.82 % Cu wt and 7.0 % Sn wt. With the increased Ni content - above 0.30 % wt, the formation of the above melt is suppressed and the elimination of the cracks formation is gained. The phase formed in such a manner is in solid state after Ni 0.30 % wt addition even at the temperature of 1100 °C.

From the study [11] on the effect of addition small quantities of the above elements on the copper solvability in austenite, it follows:

- arsenic effect is relatively weak;
- oxidation rate and the selected heating temperature before forming have significant effect on the micro-cracks formation.

The copper content in steel effect may be compensated meeting so called Cu equivalent [10]:

$$Cu + 6\,(Sn + Sb) - Ni < 9/E$$

where E is enrichment factor, defined as the ratio of the mean concentration of the previous elements on the interface matrix-scale and their volumetric concentrations.

Under the fulfilment of the above condition given in the equation, is suppressed the melt formation on the interface metallic surface - scale. The surface enrichment by the surface active elements is controlled by Gibbs mechanism of the surface segregation. Atoms of elements with the atom diameter greater than the diameter of iron, diluted in the steels, are of particular interest. Among them rate Sn, Sb and As, which segregate intensively to the free surfaces under the grains boundary and phase interface active attenuation.

The increased carbon content causes the high-temperature ductility reduction and this effects the degradation effect of Cu, Sn, Sb. In case of the Sn independent action (0.04 % wt) with no Cu intervention, surface defects were not observed, such defects were observed with Cu, Sn or Sb intervention. Presented results were obtained after the preliminary de-oxidation on the air under the temperature of 1100 °C/3h with the subsequent cooling on the normal temperature and after the linked heating in the protective Ar atmosphere before the tensile deformation under the temperature of 1100 °C [12].

POSSIBILITIES OF NON-FERROUS METALS CONTENTS REDUCTION IN STEEL

At the present time a number of the methods verified in laboratory and plant is elaborated for the steel production and processing with the limited non-ferrous metals content. The considered non-ferrous metals are with problems removable and so far no operation technology exists for active reduction of their content in steel. The above problem is particularly actual for the mini-mills operating on the contaminated steel scrap as the base for the charge. The most frequently used steel scrap selection or melted steel “dilution” by clean raw materials (for example by pig iron), is as the rule the only practically executed measure. However, it is not sufficiently effective and efficient.

For the future in the field of the non-desirable non-ferrous metals content reduction in steel perspective are the following methods:

- evaporation of the non-desirable additives from the melts under increased temperatures and reduced pressures;
- binding such elements in the steel melts with the Ca or CaC_2 under the reduction conditions with the active slag phase;
- copper parts dilution in the steel waste by the aluminium melt.

So far no concrete industrial technology exists exploiting the evaporation method. There are numerous literature sources dealing with the methods of the levitation melting and the inductive (resistance) vacuum furnaces in the laboratory conditions or technology exploiting the plasma heating. With the objective to eliminate non-desirable non-ferrous metals it has been constructed the semi-plant facility in VÍTKOVICE a.s. exploiting the plasma heating to disintegrate the steel stream when poured from the ladle to the ladle in vacuum [12].

THE OUTLET NODE BLOCKING IN CONTINUOUSLY CAST STEEL

The outlet node blocking by the aluminium oxide causes the significant problems in constant casting rate regulation in the course of the continuous casting of the by aluminium killed steel. The optimum method of the outlet node blocking by the aluminium oxides elimination is CaSi modification on x CaO x Al_2O_3. To eliminate the node outlet blocking needed is the addition of such amount of Ca which will prevent CaO x $6Al_2O_3$ formation. Such condition is met in the industry by the heats where the ratio Ca/Al_{total} reaches the values in the range 0.12 to 0.13 [9].

CONCLUSION

Presented paper provides the review of the present possibilities and trends in the non-desirable accompanying elements reduction in the continuously cast steel. It analyzes the impact of the chemical composition of the metallic scrap and charge composition on the steel production in minimills. It provides in the industry applied limit contents of the non-desirable elements causing degradation of steel products quality parameters. Reasonable attention is paid to the outlet node blocking in the killed steels continuous casting and intrusions modification by dosing CaSi.

REFERENCES

1. Scrap and the Steel Industry, Brusseles, International Iron and Steel Institute, 1983
2. Impact of Developments in Scrap Reclamation and preparation on the World Steel Industry, ECE Steel Series, 84, 1983
3. I. Žádný: Čistota oceli v čs.národním hospodářství - obecné zákonnitosti a vlivy Hutnické aktuality, 27 (1986) 1, 17
4. L. Válek: Snižování obsahu nežádoucích příměsí v ocelích, Dizertační práca FMMI VŠB-TU Ostrava, 1997, 73-74
5. M. Longauerová, S. Longauer,M. Pivovarči: Vplyv škodlivých prímesí na skrehnutie oceľových rúr. Hutnické listy, (1993) 12, 27-30
6. V. Chvátal: Zvýšení čistoty a zkvalitnění vsádzky ocelového šrotu a zvýšení ekonomie jeho příprav. Záverečná správa, Karlštejn, VÚHŽ, 1978
7. J. Váchal: Vědeckotechnický rozvoj úpravy azpracování ocelového odpadu, Štúdia PKO, Praha, 1983
8. B. Hoh, H. Jakobi, E. Wiemer: Verbesserung des Reinheitsgrades von Stahl beim Strangiesen. Stahl und Eisen, 109 (1989) 2, 69-76
9. J. Šmíd: Ústne informácie o prácach okolo blokovania výlievok komplexnými fázami, 1995
10. J. C. Herman,V. Leroy: Iron and Steelmaker, 23 (1996), 35
11. E. Mazancová, Z. Bůžek, K. Mazanec: Hutnické listy, 53 (1998) 2, 19
12. N. Imai, N. Komatsubara,K. Kunishige: ISI Jap. Internat, 37 (1997), 217
13. L. Dobrovský: Použití vápniku v mimopecní metalurgii, Hutnické aktuality, (1989) 9, 35
14. Z. Motloch: Sekundární metalurgie s plazmovým ohřevem, Štúdia VÍTKOVICE, š. p., č. z. CS-15/91, Ostrava, 1991, 305