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CHROMITE SPINEL FORMATION IN STEELMAKING SLAGS

NASTANEK KROMITNIH SPINELOV V JEKLARSKIH ŽLINDRAH

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During the processing of stainless-steel grades in an electric arc furnace (EAF) a considerable amount of chromium can be lost due to oxidation. These chromium oxides form different phases in the slag, the most stable being the spinel phase. The basicity of the slag has a major impact on the composition of the chromium oxide phase. A phase analysis revealed two types of chromium oxide phases, calcium chromites and chromite spinels, which are dependent on the chemistry and the basicity of the slag. The calcium chromites only form at a high slag basicity, while the chromite spinels form at both high and low basicity. The effects of ferrosilicon additions were observed as they have a profound effect on both the slag and the chromite spinel chemical composition.

Keywords: chromite spinel, calcium chromite, stainless steel slag, chromium loss

Med izdelavo nerjavnih jekel v EOP lahko pride do znatnih izgub kroma zaradi oksidacije. Kromovi oksidi v žlindri tvorijo različne faze, najstabilnejša je spinelna faza. Bazičnost žlindre ima velik vpliv na fazno sestavo kromitnih oksidov. Fazna analiza je pokazala prisotnost dveh vrst kromovih oksidov, odvisnih od kemijske sestave žlindre in bazičnosti, to sta kalcijev kromit in kromitni spinel. Kalcijevi kromiti so prisotni ob visoki bazičnosti, medtem ko so spineli prisotni tako ob visoki kot nizki bazičnosti. Opazovani so bili učinki dodatkov ferosilicija, ki odločilno vplivajo na kemijsko sestavo žlindre in kromitnih spinelov.

Ključne besede: kromitni spinel, kalcijev kromit, nerjavna žlindra, izguba kroma

1 INTRODUCTION

Chromium promotes ferrite[1] and is an important alloying element in steels, especially stainless steels. Stainless steels contain chromium in excess of the mass fraction $w = 10$ %;[2] higher amounts of chromium in steel leads to a higher corrosion resistance.[3] Chromium is added through the melting of stainless-steel scrap and ferrochromium additions. Ferrochromium is available in different grades that contain different amounts of chromium and other alloying elements. Carbon plays the most important role as an alloying element in ferrochromium besides chromium, because oxygen blowing is needed to remove the carbon from the melt, which can cause chromium losses.

Chromium-rich slags typically form during the melting of stainless-steel grades. Studies show that 97 % of the chromium losses are attributed to the electric arc furnace (EAF),[2] during melting and to a large extent during the blowing of oxygen into the melt in order to remove the carbon.[4,5] The oxidation of chromium takes place alongside that of other alloying elements in the steel, such as aluminum, carbon, silicon, manganese and a certain amount of iron itself. The reaction of chromium and oxygen dissolved in steel can be described as:[6]

$$2\mathrm{Cr}_{(s)} + 3[\mathrm{O}] = \mathrm{Cr}_2\mathrm{O}_{3(s)} \qquad (1)$$
$$\Delta G_1^0 = -1\ 127\ 100 + 250.80T\ (\mathrm{J})$$

The dominant chromium oxide in the slag at the melting temperature, without a protective atmosphere, is Cr_2O_3.[7] Oxides of alloying elements, among them chromium oxides, along with slag-forming oxide additions, form different phases in the slag. There are two types of chromium-oxide-based phases that are generally found in a chromium slag, i.e., chromium-oxide-based spinels, which are solid solutions, and calcium chromites, which are stoichiometric compounds.[8] Chromium-oxide-based spinels contain Cr_2O_3, Al_2O_3, FeO, MgO and MnO, while calcium chromites contain only CaO and Cr_2O_3. Chromium oxide spinels precipitate in the liquid slag[9] and affect the slag's properties. The slag stiffens and becomes inactive, thus preventing the reduction of oxides and attributing to the loss of alloying elements. When spinels are formed, the activity of the chromium decreases because of the strong bonding in the spinel, especially in the $MgCr_2O_4$.[10]

Reductive agents such as aluminum, carbon, ferrosilicon and even calcium carbide are introduced into the slag in order to minimize the chromium losses.[4,5,9,11–15] In the case of the decarburization of the melt a typical stainless-steel slag can contain from $w = 30$ % to 40 % Cr_2O_3.[15] The aim of this work is to study the phase composition of chromium-rich slags and the composition of chromium-oxide-based phases in order to establish the basic conditions for further studies of the thermodynamic equilibrium mechanism of the chromium distribution between the steel and the slag.

2 EXPERIMENTAL

Slag samples were taken with a special spoon during the steel processing in the EAF. One sample was taken after the ferrochrome addition and the oxygen blowing and another after the ferrosilicon addition. The samples were left to cool; smaller pieces were cut away and put into the mass for metallographic investigation. They were grinded and polished and then carbon was evaporated onto the surface to provide electrical conductivity for the electron microscope. Other pieces of the same slag samples were crushed in a steel mortar, then in a steel ball mill, and finally in an agate mortar to achieve the final fine powder that is needed for the X-ray diffraction. The slag samples underwent light microscopy (LM), (Microphot FXA, Nikon), electron microscopy and electron-dispersive spectroscopy (EDS) analysis (SEM-EDS, JEOL – JSM6500F) and X-ray diffractometry (XRD, Panalytical XPert Pro PW3040/60).

3 RESULTS AND DISCUSSION

Slag samples, before and after the ferrosilicon addition, were taken from high and low basicity slag.

The basicity is defined as:

$$B=\frac{\%\mathrm{CaO}}{\%\mathrm{SiO}_2} \tag{2}$$

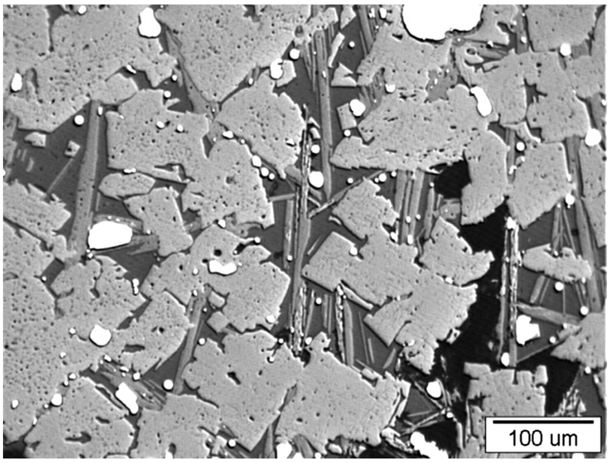

Figure 2: Microstructure of slag with chromites, and calcium chromites ($B = 2$, before FeSi addition)

Slika 2: Mikrostruktura žlindre s kromitnimi spineli in kalcijevimi kromiti ($B = 2$, pred dodatkom FeSi)

The samples with high basicity before the ferrosilicon addition contain both calcium chromites and spinels, whereas the low-basicity samples after ferrosilicon contain only spinels. The formation of spinels is preferred over the formation of calcium chromites.[16] The spinels are particles that precipitate at processing temperatures from liquid slag, and the equations for precipitation are:[17,18]

$$\mathrm{MgO}_{(S)} + \mathrm{Cr_2O}_{3(S)} = \mathrm{MgO}\cdot\mathrm{Cr_2O}_{3(S)}$$
$$\Delta G_3^0 = -30\ 221 - 19.945T\ (\mathrm{J}) \tag{3}$$

$$\mathrm{FeO}_{(S)} + \mathrm{Cr_2O}_{3(S)} = \mathrm{FeO}\cdot\mathrm{Cr_2O}_{3(S)}$$
$$\Delta G_4^0 = -37\ 706 + 3.846T\ (\mathrm{J}) \tag{4}$$

$$\mathrm{MgO}_{(S)} + \mathrm{Al_2O}_{3(S)} = \mathrm{MgO}\cdot\mathrm{Al_2O}_{3(S)}$$
$$\Delta G_5^0 = -20\ 740 - 11.57T\ (\mathrm{J}) \tag{5}$$

The precipitated spinels are solid solution of all the oxides mentioned above. The analyzed samples can be divided into two groups, i.e., those with high basicity and those with low basicity. The low-basicity samples contain only chromites and no calcium chromites. The spinels are of various sizes, from 10 μm to 100 μm, as shown in **Figure 1**. The high-basicity slags (**Figure 2**), on the other hand, contain large spinels that can reach

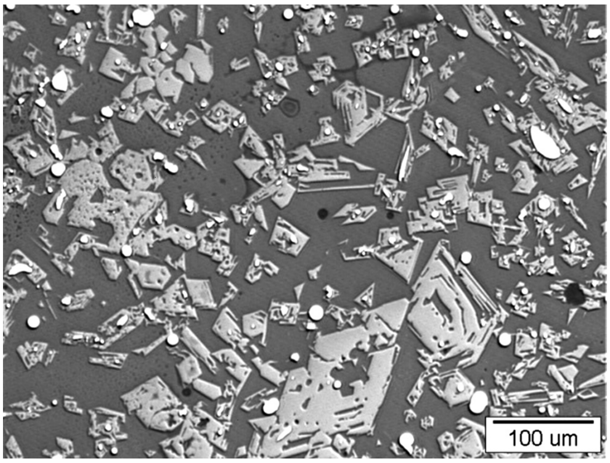

Figure 1: Microstructure of slag with chromite spinels ($B = 0.8$, after FeSi addition)

Slika 1: Mikrostruktura žlindre s kromitnimi spineli ($B = 0,8$, po dodatku FeSi)

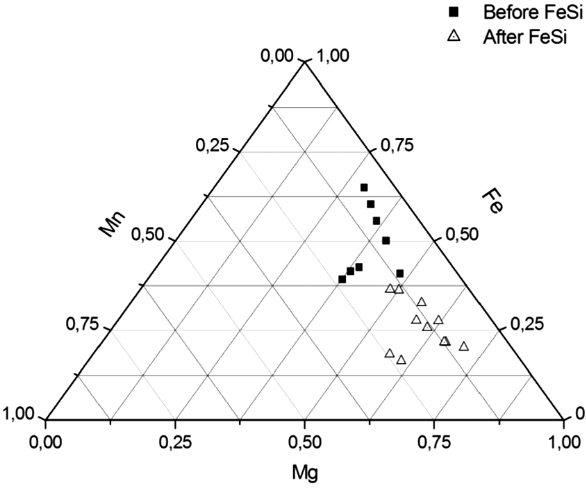

Figure 3: Ternary diagram of Mn-Fe-Mg in spinels (mole fraction) before and after FeSi addition

Slika 3: Ternarni diagram Mn-Fe-Mg v spinelih (molski delež) pred dodatkom FeSi in po njem

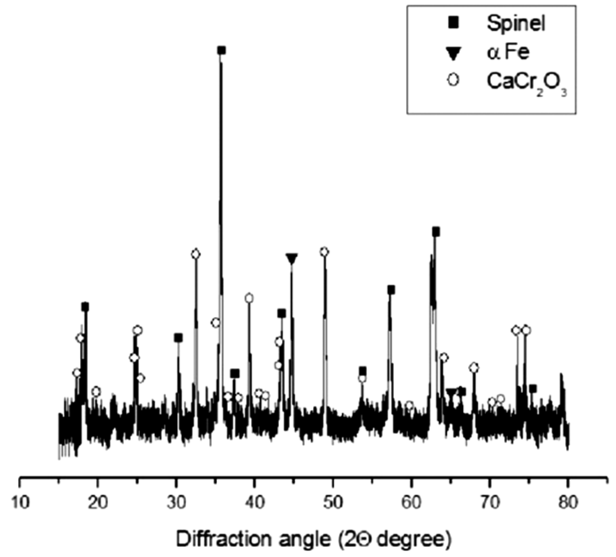

Figure 4: XRD spectrum of a slag sample before the FeSi addition
Slika 4: XRD-spekter vzorca žlindre pred dodatkom FeSi

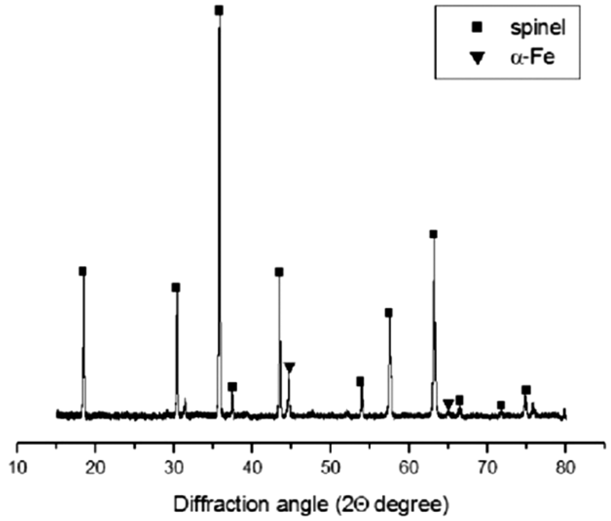

Figure 5: XRD spectrum of a slag sample after FeSi addition
Slika 5: XRD-spekter vzorca žlindre po dodatku FeSi

sizes above 100 µm in diameter. The main difference, however, is the presence of needle-shaped calcium chromites. The EDS analysis of the slag samples showed that the chemical composition of the spinels changes during the processing. After the ferrosilicon addition, the content of FeO in the spinels is lowered, as can be seen in **Figure 3**.

Iron oxide is the most easily reduced of all the oxides in the spinels and is therefore the most impacted by the addition of FeSi. Magnesium oxide, on the other hand, is very stable in the spinel phase and is not reduced, its content is also increased by refractory degradation.[19,20] FeSi is mainly added in order to reduce the chromium content in the slag, but a significant part is used to reduce the iron oxides. The diagram in **Figure 3** shows that FeSi does not reduce the manganese from the spinels very effectively. The composition of spinels follows the parallel Mn concentration lines in the ternary diagrams, showing only slight deviations.

The XRD spectrum of the slag before the FeSi addition at high basicity (**Figure 4**) shows the presence of spinels, calcium chromites and alpha iron.

After the FeSi addition at low basicites there are no calcium chromites present, only spinels and alpha iron, as can be seen in **Figure 5**. There are no more calcium chromites present.

Alpha iron is the presence of metal droplets that form due to the entrapment of the melt during the steelmaking process, either because of mixing during the arc melting and oxygen blowing or during the reduction of the oxides to the metal state. The XRD spectra confirm the observations under both SEM and LM. In fact, the SEM EDS analysis of the metal droplets revealed that they contained mostly iron and chromium, hence the ferrite phase, the composition spanning from $w(\mathrm{Cr}) = 10\ \%$ up to 20 %.

The examinations of the slags revealed that although all of the slags contained calcium chromites before the FeSi additions, none of the samples after the FeSi additions did. The tendency of calcium oxide to form phases with silicon oxides is clearly greater than that of forming them with chromium oxides.

4 CONCLUSION

Chromium slags contain two types of chromium-based oxides: calcium chromites and chromite spinels.

The composition of the chromites changes during the processing; the addition of ferrosilicon (FeSi) significantly decreases the Fe content in the spinels.

The magnesium contents in spinels increases during the steelmaking process, both due to the relative increase of the content (FeO and Cr_2O_3 reduction) during ferrosilicon injection and due to MgO dissolution from the refractory.

Calcium chromites form only in slags with high basicity, when the silicon content in the slag is low; the slag is saturated with CaO.

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5 REFERENCES

[1] F. Tehovnik, B. Arzenšek, B. Arh, D. Skobir, B. Pirnar, B. Žužek, Microstructure Evolution in SAF 2507 Super Duplex Stainless Steel, Mater. Tehnol., 45 (**2011**) 4, 339–345

[2] S. Sun, P. Uguccioni, M. Bryant, M. Ackroyd, Chromium control in the EAF during stainless steelmaking, Proc. of the 55th Electric Furnace Chicago, 1997, 297–302

[3] F. Tehovnik, B. Žužek, B. Arh, J. Burja, B. Podgornik, Hot Rolling Of The Superaustenitic Stainless Steel AISI 904L, Mater. Tehnol., 48 (**2014**) 1, 137–140

[4] B. Arh, F. Tehovnik, The Oxidation and Reduction of Chromium, Metalurgija, 50 (**2011**), 179–182

[5] B. Arh, F. Tehovnik, The Oxidation And Reduction of Chromium During the Elaboration of Stainless Steels in an Electric Arc Furnace, Mater. Tehnol., 41 (**2007**) 5, 203–211

[6] Y. Xiao, L. Holappa, M. A. Reuter, Oxidation State and Activities of Chromium Oxides in $CaO-SiO_2-CrO_x$ Slag System, Met. and Mater. Trans. B, 33 (**2002**), 595–603

[7] K. Morita, N. Sano, Activity Of Chromium Oxide in $CaO-SiO_2$ Based Slags At 1873 K, Proc. of the VII International Conference on Molten Slags Fluxes and Salts, Johannesbourg, 2004, 113–118)

[8] J. H. Park, I. H. Jung, S. B. Lee, Phase Diagram Study for the CaO-SiO2-Cr2O3-5 mass.%MgO-10 mass.%MnO System, Met. Mater. Int., 15 (**2009**), 677–681

[9] S. Mostafaee, A Study of EAF High-Chromium Stainless Steelmaking Slags Characteristics and Foamability, PhD. Thesis, Stockholm, 2011

[10] G. J. Albertsson, Investigations of Stabilization of Cr in Spinel Phase in Chromium-Containing Slags, Licentiate Thesis, Stockholm, 2011

[11] N. Sano, Reduction Of Chromium Oxide In Stainless Steel Slags, Proc. of 10th Int. Ferroalloys Congr. INFACON X Transformation through Technol., Cape Town, 2004, 670–677

[12] E. Shibata, S. Egawa, T. Nakamura, Reduction Behavior of Chromium Oxide in Molten Slag Using Aluminum, Ferrosilicon and Graphite, SIJ Int., 42 (**2002**), 609–613

[13] J. Björkvall, S. Ångström, L. Kallin, Reduction Of Chromium Oxide Containing Slags Using CaC_2, Proc. of the VII Int. Conf. Molten Slags Fluxes Salts, Johannesbourg, 2004, 663–670

[14] X. Hu, H. Wang, L. Teng, S. Seetharaman, Direct Chromium Alloying by Chromite Ore with the Presence of Metallic Iron, J. Min. Metall. Sect. B Metall., 49 (**2013**), 207–215

[15] R. I. L. Guthrie, M. Isac, Z. Lin, A Fluid Dynamics Simulation Of Chromium Recovery From Aod Slags During Reduction With Ferrosilicon Additions, Proc. of the VII Int. Conf. Molten Slags Fluxes Salts, Johannesbourg, 2004, 465–472

[16] H. Cabrera-Real et al., Effect of MgO and CaO/SiO_2 on the Immobilization of Chromium in Synthetic Slags, J. Mater. Cycles Waste Manag., 14 (**2012**), 317–324

[17] M. Hino, K. Higuchi, T. Nagasaka, S. Ban-Ya, Phase Equilibria and Activities of the Constituents in FeO·Cr2O3- MgO·Cr2O3 Spinel Solid Solution Saturated with Cr203, ISIJ Int., 34 (**1994**), 739–745

[18] S. Jo, B. O. Song, S. Kim, Thermodynamics on the Formation of Spinel ($MgO \cdot Al_2O_3$) Inclusion in Liquid Iron Containing Chromium, Met. and Mater. Trans. B, 33 (**2002**), 703–709

[19] M. Guo, S. Parada, S. Smets, P. T. Jones, J. Van Dyck, B. Blanpain, P. Wollants, Laboratory Study of the Interaction Mechanisms Between Magnesia-Chromite Refractories and Al_2O_3-rich VOD slags, Proc. of the VII Int. Conf. Molten Slags Fluxes Salts, Johannesbourg, 2004, 327–336

[20] M. Guo, P. T. Jones, S. Parada, E. Boydens, J. Van Dyck, B. Blanpain, P. Wollants, Degradation Mechanisms of Magnesia-Chromite Refractories by High-Alumina Stainless Steel Slags under Vacuum Conditions, J. Eur. Ceram. Soc., 26 (**2006**), 3831–3843