

## MICROSTRUCTURAL CHARACTERISATION OF CHROMIUM SLAGS

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Preliminary Note – Prethodno priopćenje

In this chromium slags that form during melting of chromium alloyed steels are examined. During melting and oxidation of these steel grades a considerable amount of chromium is lost, and gained back with slag reduction. Laboratory experiments were performed to study the mechanism of chromium oxide reduction by silicon. Slags chemistry and phase composition have a strong effect on the steelmaking process. Phase analysis revealed two types of chromium oxides, calcium chromites and chromite spinels dependent on chemistry and basicity of the slag.

*Key words:* steelmaking slag, chromium oxide, microstructure, chromium slag reduction

### INTRODUCTION

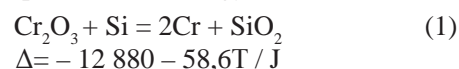
Chromium is an important alloying element, especially in stainless steel grades, with chromium contents above 10 wt% [1]. Chromium promotes the stability of ferrite in steel [2]. The phase ratio between  $\delta$ -Fe and  $\gamma$ -Fe in the microstructure of stainless steels can be predicted by using chromium equivalent (ferrite) and nickel equivalent (austenite) [3]. Chromium alloyed steel grades can suffer great losses of chromium during oxidation and melting of alloyed steel scrap. The most of chromium losses occur in the EAF. Chromium oxidation occurs during melting and to greater extent during blowing of oxygen into the melt aimed to remove carbon [4]. Chromium is normally added in the form of ferroalloy, ferrochrome that usually contains high amounts of carbon [5]. Because of its high affinity to oxygen, chromium reacts with oxygen to form chromium oxides.

The newly formed chromium oxides are then dissolved in the slag. When the point of saturation is reached, chromium oxides segregate from the liquid slag and form phases with other metal oxides, such as CaO, FeO, MnO and MgO.

Severe chromium losses in the melting stage may occur with the formation of stable FeO and MgO chromite spinels [6,7].

Studies report that FeO in slag increases the amount of spinel phase that form in slag and decreases the content of chromium oxides in calcium silicate liquid slag phase [6]. High chromium oxide contents increase the crusting of the slag, decrease its reactivity and impair the formation of foaming slag and slag reduction during the process of steelmaking [4,8]. Chromite spinels have high melting points and are therefore, generally, solid at

steelmaking temperatures. As the spinels are solid, the slag content of chromium oxides influences significantly the properties of the slag. The main problem however is the low recovery rate of chromium. Although chromium can in theory be reduced by aluminum, carbon, and silicon, reduction in practice poses many problems. The silicothermic reduction of chromium oxides and the effect of temperature free energy are [9]:



The chromium reduction increases the content of silicon in the steel melt [10]. The activity of silicon isn't sufficient at low silicon content, sometimes it has to be exceeded for sufficient reduction of chromium. Reduction of other less stable oxides besides chromium oxides, such as iron oxides is also problematic because of the consumption of the reducing agents [4]. Chromium reduction from slag requires long incubation periods that make the process time consuming and less suited for industrial steelmaking practice [4,8]. High stability of chromium spinels is the main obstacle in reduction of chromium which is also investigated to prevent of leaching chromium into the environment from waste chromium rich slags [6,11–14].

One way of avoiding severe chromium losses is to maintain a sufficient level of silicon in the oxidation stages. In theory the effectiveness of silicon decreases with the rising temperatures, but studies have shown [15] that the reduction is actually more effective at higher temperatures. This fact is attributed to the increased kinetics of the reaction for silicothermic reduction of chromium oxides.

### MATERIALS AND METHOD

Chromium slag samples were taken during steel industrial processing in the EAF and additional experi-

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ments were performed in a laboratory scale induction furnace (20 kg of steel). The industrial samples were taken after ferrochrome addition and oxygen blowing and after ferrosilicon (FeSi) addition. The laboratory samples were taken after the chromium alloyed steel was exposed to oxidizing conditions and after FeSi additions. The samples were embedded for metallographic observations. Samples were grinded and polished for the light optic microscope (Microphot FXA, Nikon) for examination and carbon was additionally evaporated on the surface to for the examination in electron microscope (SEM, Jeol – JSM6500F).

The chemical composition of the steel used in the laboratory experiments is given in Table 1.

Table 1 Chemical composition of steel / wt%

C	Si	Mn	Cr
0,21	0,32	0,60	11,10

The oxidation was performed by addition of iron oxide to the steel melt. The iron oxides formed a slag that oxidized chromium from the steel. As the content of chromium oxides rose, the slag stiffened and formed a “lid” in the melting crucible by slag content of chromium oxide close to 40 wt%. Then FeSi was added to the steel melt. When the FeSi had dissolved in the melt, a second slag sample was taken for metallographic analysis. The oxidized silicon formed a slag layer below the chromite slag and former (chromite based) slag “float-ed” on the “new” (SiO<sub>2</sub> based) slag.

## RESULTS AND DISCUSSION

The industrial chromium slag samples before reduction by FeSi contained both calcium chromites and chromite spinels as described previously [16]. The chromium slag also contains different types of metallic droplets with various chemical compositions due to their different origin. Some droplets formed by reduction of iron and chromium oxides, while others were entrapped steel melt. The reduction of oxides in the slag is present even before the reduction by FeSi. The size and iron content in analyzed metallic droplets is shown in Figure 1.

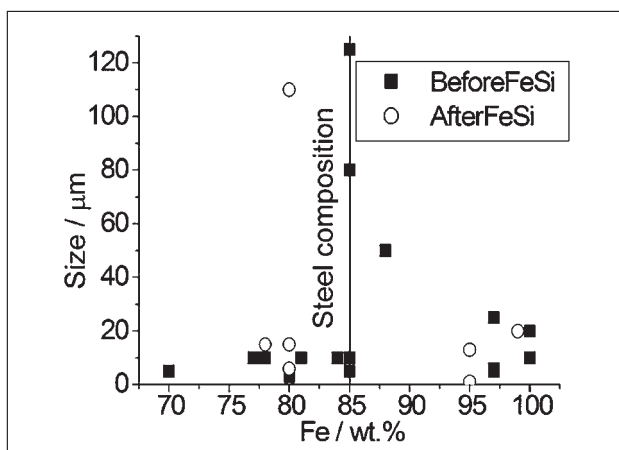


Figure 1 Size distribution and iron content in metallic droplets

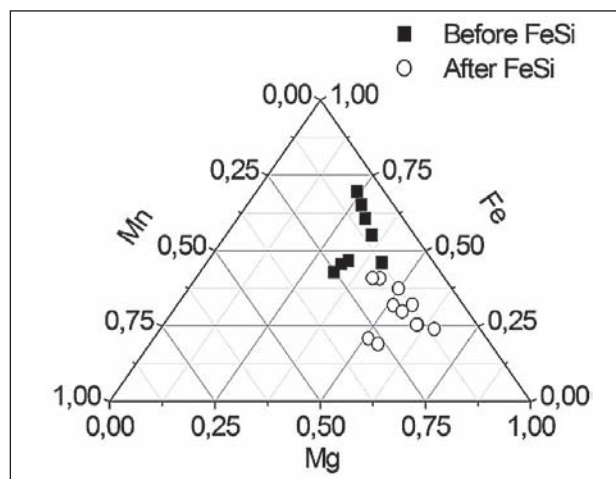


Figure 2 Ternary diagram of Mn-Fe-Mg in spinels (mole fraction) before and after FeSi addition

The FeSi addition greatly changes the slag chemical composition and also of chromite spinels as shown in Figure 2.

Before FeSi addition, the chromite spinels are large and solid at processing temperatures and calcium chromites are also present in the microstructure, as shown in Figure 3. The large gray angular particles are chromite spinels and the smaller needle shaped particles are calcium chromites.

The slag chemical analysis revealed an increased in MgO content. The increase of MgO before and after FeSi addition is presented in Figure 4. Since no dolomite or doloma lime were added the main source of magnesia is the furnace lining refractory degradation which has been described by several authors [17–20]. The evidence of the furnace refractory degradation is shown in Figure 5 with EDS analysis in Table 2, however, the increase of MgO content can not only be attributed to the refractory degradation, but also to the relative rise of MgO due to the reduction of some oxides in the slag, and therefore the mass reduction of the slag.

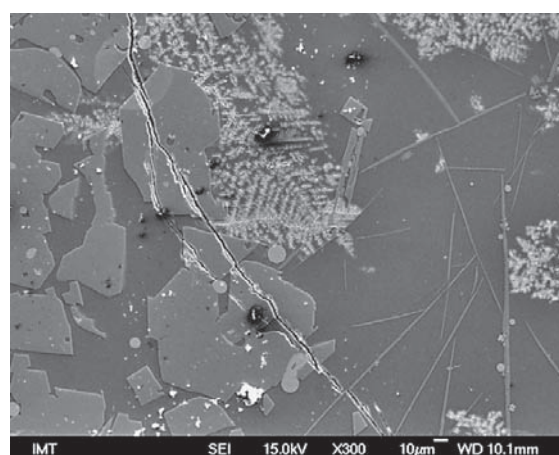


Figure 3 SEM micrograph of a slag sample before FeSi addition

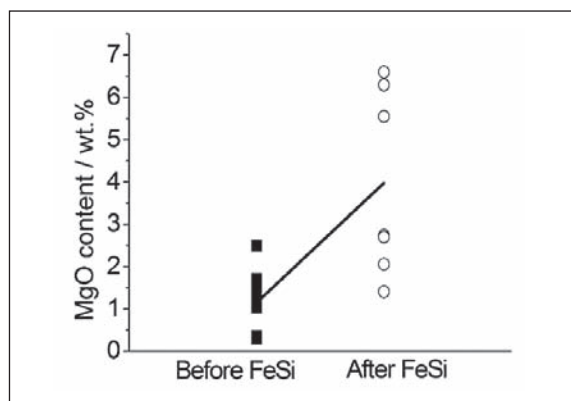


Figure 4 MgO content in slag

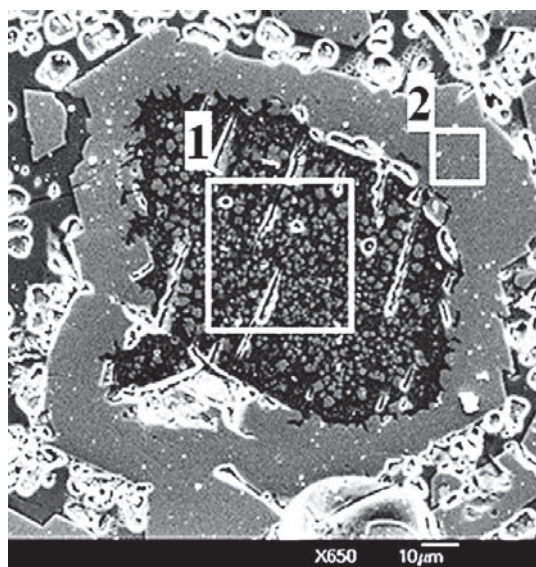


Figure 5 SEM micrograph and EDS analysis of a spinel particle forming around a piece of eroded magnesia refractory

Table 2 EDS analysis of Figure 5 (refractory particle entrapped in slag and a growing chromite spinel around it) / wt%

	O	Mg	Al	Si	Ca	Cr	Mn	Fe
1	42,8	27	0,8	0,4	1,2	18,6	2,6	6,6
2	40,6	4,5	2,4	0	1,2	44,5	2,4	4,4

After addition of FeSi the SiO<sub>2</sub> content in the slag rises significantly and the chromite spinels start to dissolve in the slag. The microstructure of the samples after FeSi additions contains chromite spinels with dendritic structure that is a clear indicator that some of the spinels were liquid at the processing temperatures. The microstructure of the slag sample after FeSi addition is shown in Figure 6.

During the laboratory experimental melting and oxidation of chromium alloyed steel, the added silicon had oxidized and formed a film of high silicon oxide slag on the steel melt surface and below the “old” chromite slag.

The new silicon oxide based slag had started to dissolve the old slag and enabled the reduction of chromium oxides from the old slag. Basically that means that chromium oxide rich spinel particles, solid at process-

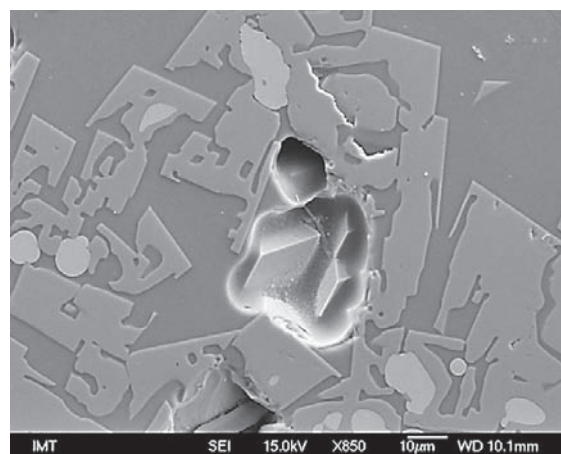


Figure 6 SEM micrograph of a slag sample after FeSi addition

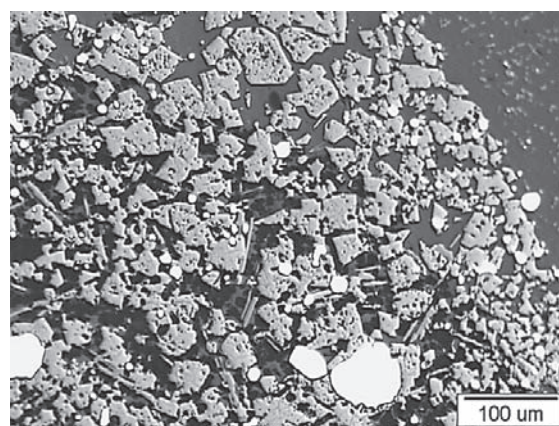


Figure 7 Slag microstructure from the FeSi reduction experiment

ing temperatures, were dissolved in silicon oxide rich slag and transported to the slag/melt interphase where chromium oxides were reduced by silicon dissolved in the steel, this mechanism was described by Durinck et al. [14]. Figure 7 shows the interphase between the chromite (solid) slag and the silicon oxide rich (liquid). The liquid SiO<sub>2</sub> based slag in the upper right corner in Figure 7 is slowly dissolving the solid chromite spinels (the lower left corner of Figure 7).

## CONCLUSIONS

The mechanism of chromium spinel reduction by silicon involves spinels dissolution in the slag. Chromium rich slags promote magnesia furnace lining refractory degradation. The eroded magnesia refractory particles are absorbed by chromite spinels. Iron oxides are the least stable oxides in the spinels and are in turn the first to be reduced, as indicated by the presence of iron rich metallic droplets.

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**Note:** Responsible person for English translation T. Šušteršič, Medvode, Slovenia