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PRECIPITATION OF METALLIC CHROMIUM DURING RAPID COOLING OF Cr_2O_3 SLAGS

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The slag systems of $CaO-SiO_2-Cr_2O_3$ and $Al_2O_3-CaO-MgO-SiO_2-Cr_2O_3$ were analyzed. These slag systems occur in the production of stainless steel and are important from the process metallurgy point of view. Synthetic slag samples with different chromium oxide content were prepared and melted. The melted slag samples where then rapidly cooled on large steel plates, so that the high temperature microstructure was preserved. The samples were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The precipitation of different chromium oxide phases was studied, but most importantly the precipitation of metallic chromium was observed. These findings help us interpret industrial slag samples.

Key words: stainless steel oxidation, steelmaking slag, chromium oxide, cooling, microstructure

INTRODUCTION

Chromium is one of the main alloying elements in stainless steel grades, due to the corrosion resistant oxides and creep resistant steels, due to high temperature carbides [1]. Chromium losses occur during the production of the stainless steel melt, especially during decarburization phase in the electric arc furnace (EAF) [2,3]. The main reaction for decarburization of the Fe-Cr-C system can be described by equation 1:

$$2Cr + 3CO_{(g)} = Cr_2O_{3(s)} + 3C \tag{1}$$

The equilibrium lines on Figure 1 show equilibrium lines for the reaction 1 for different C-Cr concentrations and at temperatures from 1 550 to 1 800 °C. Thermodynamic data was taken from Sigworth and HSC8 [4]. The highest losses occur during decarburization at lower temperatures. Due to the exothermic nature of the decarburization reaction, the melt temperature increases significantly during processing, therefore the oxidation cannot begin at very high temperatures; otherwise the melt must be cooled down by additional charging. Because of the lower starting temperatures chromium losses are inevitable (unavoidable).

Therefore, oxide systems that describe the slag during steelmaking are important for understanding and optimization of the steelmaking process. The phase composition of slags is greatly influenced by the slag basicity. At steelmaking temperatures 2+ and 3+ chromium oxides are present. They can be described as CrO and Cr_2O_3. CrO is soluble in slags, while Cr_2O_3 has negligible solubility in the slag matrix [5–7].

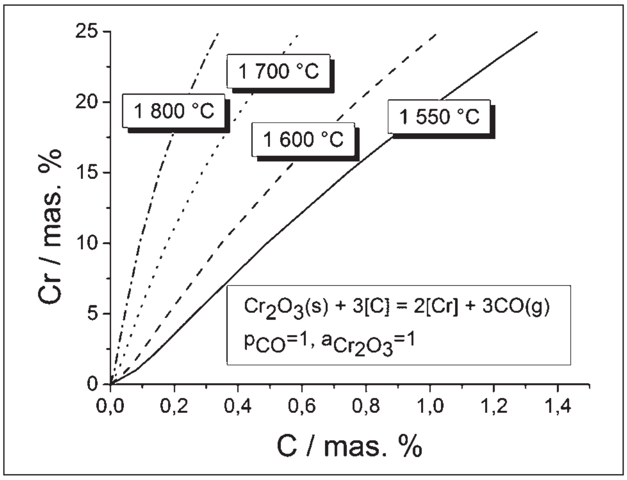

Figure 1 Equilibrium lines for Cr an C concentrations at different temperatures

MATERIALS AND METHOD

The compositions of melted samples with different Cr_2O_3 concentration and slag basicity are shown in Table 1.

Slag basicity was calculated using equation 2 [8]:

$$B = \frac{\text{mas. \% CaO} + \text{mas. \% MgO}}{\text{mas. \% SiO}_2 + \text{mas. \% Al}_2\text{O}_3} \tag{2}$$

The melting was done in an arc-melter with graphite electrodes. The melted specimens were rapidly cooled by placing them on a steel plate. The samples were prepared for electron microscopy (SEM-EDS, JEOL – JSM6500F) by grinding and polishing, carbon was additionally evaporated on the sample surface, to ensure conductivity. The samples for XRD analysis (XRD, Panalytical XPert Pro PW3040/60) were mechanically milled into fine powder.

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Table 1 **Sample name, basicity and composition in mas. %**

name	B	Al_2O_3	SiO_2	CaO	Cr_2O_3	FeO	MgO
A105	0,5	0,0	62,7	32,0	1,0	0	0,0
A205	0,5	0,0	62,7	32,0	2,0	0	0,0
A505	0,5	0,0	60,8	32,0	5,0	0	0,0
A805	0,5	0,0	58,8	30,0	8,0	0	0,0
A2005	0,5	0,0	51,0	26,0	20,0	0	0,0
A110	1,0	0,0	49,0	50,0	1,0	0	0,0
A210	1,0	0,0	49,0	50,0	2,0	0	0,0
A510	1,0	0,0	47,0	48,0	5,0	0	0,0
A810	1,0	0,0	45,1	46,0	8,0	0	0,0
A2010	1,0	0,0	39,2	40,0	20,0	0	0,0
A115	1,5	0,0	39,2	58,0	1,0	0	0,0
A215	1,5	0,0	39,2	58,0	2,0	0	0,0
A515	1,6	0,0	37,2	58,0	5,0	0	0,0
A815	1,6	0,0	35,3	56,0	8,0	0	0,0
A2015	1,5	0,0	31,4	48,0	20,0	0	0,0
B105	0,5	22,4	40,6	32,7	1,0	0,80	0,4
B205	0,5	22,1	40,0	32,0	1,9	1,12	0,8
B505	0,5	21,3	37,9	30,0	4,8	2,09	1,9
B805	0,6	20,4	35,8	28,0	7,7	3,06	3,0
B2005	0,6	17,0	27,5	20,1	19,2	6,96	7,6
B110	1,0	16,8	30,5	49,0	0,9	0,67	0,4
B210	1,0	16,7	30,0	48,0	1,9	1,00	0,8
B510	1,1	16,2	28,6	45,1	4,7	1,95	1,9
B810	1,1	15,6	27,1	42,0	7,7	2,97	3,0
B2010	1,1	13,6	21,3	30,1	19,2	6,89	7,6
B115	1,5	13,8	24,9	58,0	1,0	0,61	0,4
B215	1,6	13,3	23,8	58,0	1,9	0,93	0,8
B515	1,6	13,1	23,0	54,0	4,8	1,92	1,9
B815	1,5	12,9	22,2	50,0	7,7	2,91	3,0
B2015	1,5	11,5	17,6	36,1	19,2	6,85	7,6

RESULTS AND DISCUSSION

The slag samples contained different oxide phases. The slag microstructure consists of the slag matrix and two chromium oxide based phases, the chromite spinel phase and the calcium chromite phase, similarly to the industrial samples [9]. The analysis of the samples showed the precipitation of chromium rich oxide phases depends on Cr_2O_3 concentrations and on slag basicity as shown in Figure 2. The diagram in Figure 2 was constructed from the results of both SEM and XRD analysis (Figures 3-6). At higher slag basicity, the chromium oxide phase precipitation occurs at lower concentrations (5 % Cr_2O_3) than in low basicity slags. This is because high temperatures, low oxygen partial pressure and low slag basicity increase the CrO/Cr_2O_3 ratio values [2,7,8,10–14]. Slag basicity is one of the main factors influencing the solubility of chromium oxides in steel slag through the control of CrO/Cr_2O_3 ratio. Because Cr_2O_3 has almost no solubility in slags it precipitates from the liquid slag at steelmaking temperatures as solid particles, to therefore increased slag basicity promotes higher chromium oxide activity.

The chromium oxides form oxide phases with Al_2O_3, CaO, FeO, MgO, and MnO [15–17]. The two chromium rich phases in steelmaking slags are calcium chromite and chromite spinel [9]. The spinel phase present in samples is predominantly $MgOCr_2O_3$ type, as they are the most stable chromite spinel, as confirmed by theory and industrial investigation [16,18,19]. While the spinel phase is always present when the solubility of chromium oxides is exceeded, the calcium chromite only precipitates at high basicity (B=1,5). Mostafaee et al. [9] observed that spinel precipitation occurs at 1,8 mas. % Cr_2O_3 when the slag basicity is 1,5.

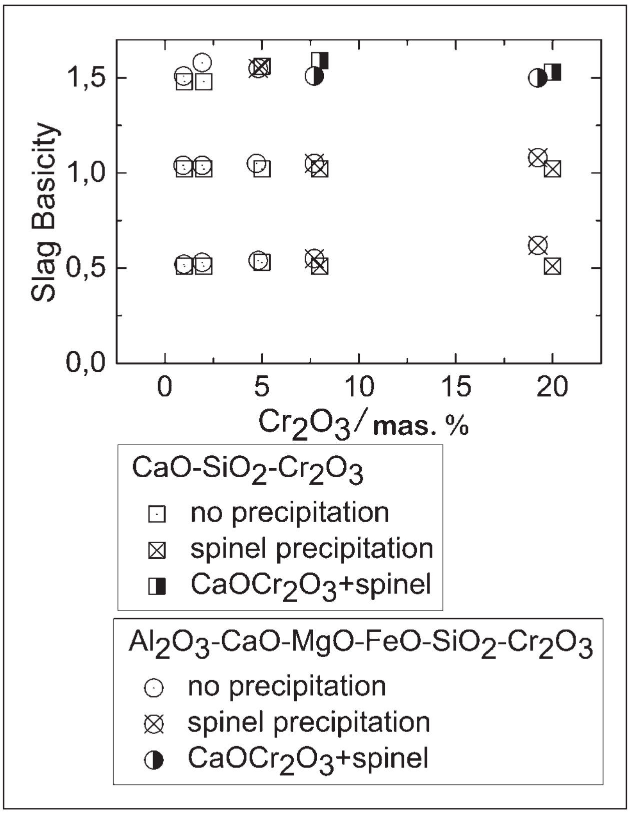

Figure 2 Precipitation of chromium oxide phases at different Cr_2O_3 concentrations and slag basicity

The spinel solidifies through dendrite formation and ideally forms a cubic shaped crystal, while the calcium chromite forms needles. The Figures 3 and 4 show the presence of small metallic particles that occur in the presence of the spinel and $CaOCr_2O_3$ phase. In the case

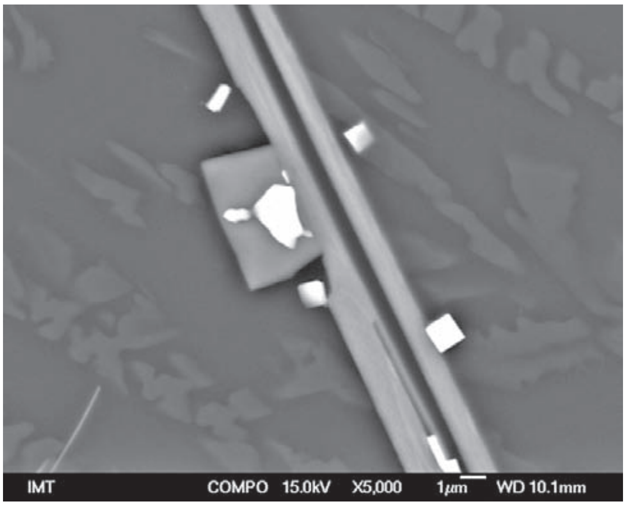

Figure 3 Calcium chromite needle with attached spinel and metallic chromium (sample A2015)

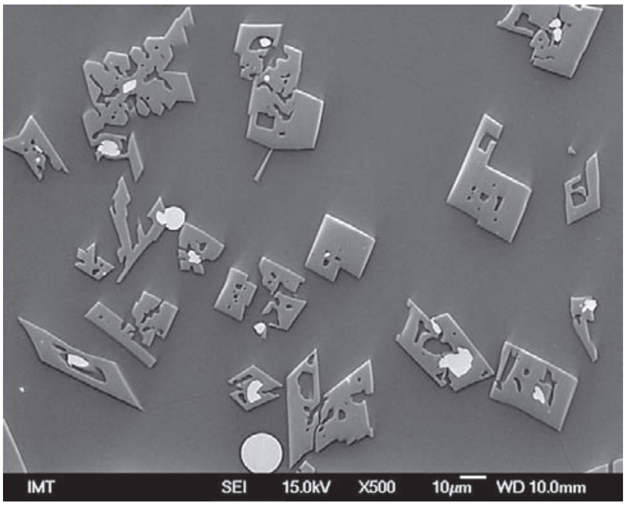

Figure 4 Chromite spinel grains and metallic Fe-Cr particles (sample B2010)

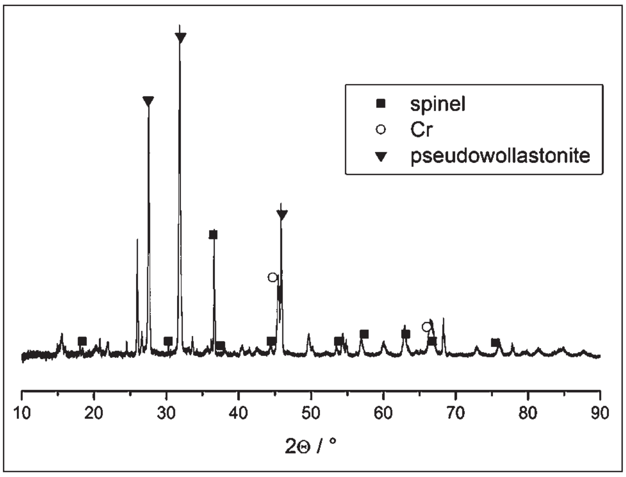

Figure 5 XRD diagram showing the presence of chromite spinel and metallic Cr particles and pseuowollastonite (sample A810)

of the chromite spinel phase the metallic particles are found within the spinel and are of irregular shape. In the case of the calcium chromite phase the metallic particles are of rectangular shape and always found directly next to the calcium chromite, never within.

The X-ray diffraction (XRD) analysis in Figures 5 and 6 confirmed the presence of spinel, metallic phase (either Cr or Fe-Cr) and calcium chromites. Some of the matrix also crystallized into pseuowollastonite ($CaSiO_3$) and larnite (Ca_2SiO_4).

In the slag samples that contained iron oxide the metallic particles contained iron and chromium, while the metallic particle occurrence can be explained by two possible mechanisms one is the reduction of the chromium oxides by the carbon based electrode, and the other is by precipitation of chromium oxides from the slag matrix. CrO is stable only at high temperatures and decomposes to Cr in Cr_2O_3 during cooling [20]. Because the high temperature soluble CrO becomes unstable during the cooling of the slag, it decomposes into the insoluble Cr_2O_3, in the form of a spinel or calcium chromite, and Cr in the form of metallic particles, which is especially true for low basicity slags that contain high CrO concentrations [7]. Various authors state that the solubility of CrO in $CaO-SiO_2$ slags is high, but the Cr_2O_3 is insoluble [2,5,21].

CONCLUSIONS

During the solidification of the synthetic slag the solubility of chromium oxides is exceeded, therefore chromium oxide rich phases and metallic chromium precipitate.

The slag melting experiments showed, that the solubility of chromium oxides in slags is exceeded at 8 mas. % Cr_2O_3 at slag basicity of 0,5 and 1, but at slag basicity of 1,5 the solubility is exceeded at 5 mas. %. The decreased solubility of chromium oxides in higher basicity slags is the result of the decreased CrO/Cr_2O_3 ratio.

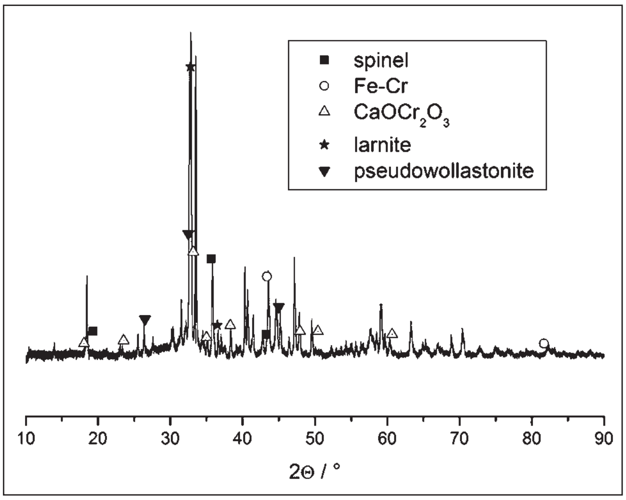

Figure 6 XRD diagram showing the presence of chromite spinel and metallic Fe-Cr particles, larnite and pseuowollastonite (sample B815)

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