Effect of low oxygen partial pressure on the chromium partition in CaO-MgO-SiO_2-Cr_2O_3-Al_2O_3 synthetic slag at elevated temperatures

Galina Jelkina[1)*], *Lidong Teng*[1)], *Bo Björkman*[2)], *Seshadri Seetharaman* [1)]

1) *Division of Materials Process Science, Royal Institute of Technology (KTH), SE-100 44, Stockholm, Sweden.*

2) *Division of Extractive Metallurgy, Luleå University of Technology, SE-971 87 Luleå, Sweden.*

Abstract: The objective of the present work is to get an understanding of the impact of Al_2O_3 addition on the phase relationships in the CaO-MgO-SiO_2-Cr_2O_3 slags at low oxygen partial pressures, with a view to control the precipitation of Cr-spinel in the slag phase since Cr in the spinel phase is expected to have lower leaching levels. The equilibrium phases in CaO-MgO-SiO_2-Cr_2O_3-Al_2O_3 slag system in the range on 1673-1873 K have been investigated. The Cr_2O_3 content was fixed at 6wt% and MgO 8wt%. Al_2O_3 contents in the slag varied in the range of 3-12wt%. The basicity (CaO/SiO_2) of slag was set to 1.6. Gas/slag equilibrium technique was adopted to synthesize the slag at high temperature. The samples were heated to 1873 K and soaked at this temperature for 24h. The samples were then slow cooled to 1673 K and equilibrated for an additional 24h. The oxygen partial pressure was kept at 10^{-4} Pa. Gas mixture of CO/CO_2 was used to control the oxygen partial pressure. The samples were quenched in water. The chromium distribution and phase compositions in the quenched slag were studied using SEM-WDS and XRD techniques. FACTSAGE software was used for the phase equilibrium calculations. The size of spinel crystals increased drastically after slow cooling followed by annealing compared to samples being quenched after soaking at 1873 K. It was also found that low oxygen partial pressure has a strong impact on chromium partition. The amount of spinel phase increases with increased Al_2O_3 content.

Keywords: Phase equilibrium, chromium partition, spinel, scanning electron microscope (SEM), low oxygen partial pressure

1. Introduction

Metallurgical slag waste from stainless steel production process containing environmentally harmful elements, such as chromium, is a continuously growing problem. Leaching of chromium from the slag deposits is a major environmental problem that has to be solved. A number of mineralogical phases present in the slag matrix can dissolve chromium and lead to chromium leaching in water. Chromium in slag if not stabilized, could oxidize to the hexavalent state (Cr^{6+}), and thus leach out if exposed to acidic and oxygen rich environment[1, 2]. Utilization of chromium containing steelmaking slag is thus restricted.

Numerous mineralogical phases present in steelmaking slags are soluble in aqueous media, as for example, merwinite, periclase, dicalcium silicate and lime. Other phases present in the slags, viz. wüstite, spinel and glass are, on other hand, considered as resistant to dissolution. While the wüstite and glass formation were studied by earlier researchers [1-12], very little effort has been made towards an understanding of the precipitation of spinel phase in the slag. Mineralogical phases present in a slag system are highly dependent on slags composition and heat treatment history[2,3,4].

Mineralogical phases considered in the current work, are divided into spinel, monoxide solid solution and the silicate matrix phases. Mudersbach et al [13] suggested Al_2O_3 addition to decrease basicity of the slags and favor the formation of spinel during solidification. So-called “factor sp” developed by Mudersbach et al [13] empirically describes the expected chromium content based on slag composition:

factor sp = a * MgO + b * Al_2O_3 + c * FeOn – x * Cr2O3 [wt.%] (1)

The equation is based on the correlation between the spinel factor and measured chromium leaching levels. Adding relatively large amount of silica, for example quartz sand or waste glass, is another way to control the slag composition (basicity) and prevent slag disintegration [3-8].

Not much effort has been taken for the practical work for precipitation of spinel phase in the slag. Thus, it is of interest to find a method for spinel phase formation in slag that would be economically and practically applicable. The aim is to study the chromium partition in slag and to get an understanding of the phase relationships in the $CaO\text{-}MgO\text{-}SiO_2\text{-}Cr_2O_3$ slags with a view to control the precipitation of Cr-spinel in the slag phase by Al_2O_3 addition. In order to achieve this aim, the classical gas/slag equilibrium method was adopted in the present study with well-defined conditions such as oxygen pressures, slag basicities and heat treatment conditions.

Most part of the stainless steel is produced in AOD (Argon-Oxygen Decarburization) often combined with EAF (Electric Arc Furnace) processes. In the AOD process, the gas formed during the decarburization operation is continuously diluted by argon gas in order to decrease the partial pressure of P_{O2}. By this method, the carbon in the stainless steel can be removed efficiently without excessive chromium oxidation[14]. The partial oxygen pressures in the AOD and EAF processes after slag reduction are, in general, within the range of 10^{-4}-10^{-2} Pa. Very little experimental effort has been made towards an understanding of the precipitation of spinel phase in the slag at low oxygen partial pressures. Thus, the present work is intended for finding an approach for the optimum precipitation of the spinel crystals and their growth in the slag by means of controlled reaction gas atmosphere.

Slow cooling and soaking sequences as well as well-controlled oxygen partial pressures are applied in this work in order to keep the system close to equilibrium, so that the equilibrium phases could be studied. The chromium distribution and phase compositions were studied using SEM-WDS and XRD techniques in synthetic slags at a fixed MgO and Cr_2O_3 contents. The experimental results obtained from the present work are compared with the calculation results from FACTSAGE software[15].

2. Experimental

2.1 Materials and sample preparation

Phase equilibrium studies of a set of synthetic $CaO\text{-}MgO\text{-}SiO_2\text{-}Cr_2O_3\text{-}Al_2O_3$ slags, each containing 6wt% Cr_2O_3 and 8wt% MgO, with basicity (CaO/SiO_2) set to 1.6 were conducted. Al_2O_3 contents in the slag varied in the range of 3-12wt%. The chemicals used and their purity grades are given in the Table 1. The slag compositions studied are presented in Table 2. CaO, Al_2O_3 and MgO powders were calcined at 1273K (1000°C) in a muffle furnace for 12h in order to decompose any hydroxide and carbonate. SiO_2 and Cr_2O_3 powders were heat-treated at 383K (110°C) for 10 h in order to remove any moisture. After mixing the chemicals in appropriate proportions in an agate mortar, the powder mixtures were pressed into pellets of 15mm in diameter. The samples were placed in Pt crucibles, which were pressed out of platinum foil of thickness of 0.127mm and heat-treated at the required temperature in a gas mixture of CO/CO_2 gases to control the oxygen potential in the gas phase. The oxygen partial pressure was kept at 10^{-4} Pa. (technical grade, supplied by AGA, Stockholm). The samples were preserved in desiccators to prevent re-absorption of water and CO_2 from atmosphere.

2.2 Gas cleaning system

In view of the low oxygen partial pressures targeted in the present study, the gases used in the gas mixture were carefully purified before introducing into the reaction tube. The gas cleaning system consisted of a train of columns, present in the figure 1. Columns of silica gel, magnesium perchlorate and ascarite were used to remove the traces of H_2O and CO_2 from the commercial high purity grade gases. Columns of copper turnings were kept at 823K, to remove the residual O_2. The gases were mixed in a chamber filled with glass beads, before introducing the mixture into the reaction tube. The gas ratios used in the present study were pre-calculated using FACTSAGE software for attaining the required oxygen partial pressure. Bronkhorst High-Tech Flow-bus E600 mass flow meters were used to control the flow rates of the involved gases. A narrow gas inlet tube (5mm inner diameter) led the gas mixture directly into reaction zone just above the slag samples in order to minimize the error due to thermal segregation of the gases in the gas mixture.

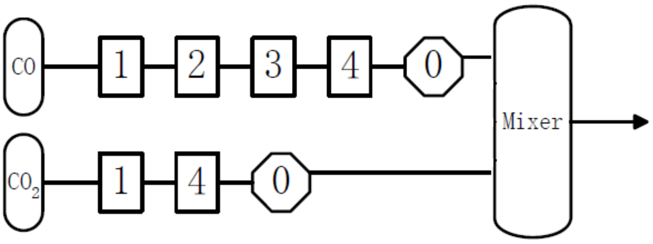

Figure 1: Schematic illustration of gas cleaning system: 0 – flowmeter; 1- silica gel; 2-magnesium percholorate; 3-ascarite; 4- copper turnings. Adopted from [3].

Table 1 Purity of the chemicals used

Chemical	Purity	Supplier
Pt-foil	99.99%	Alfa-Aesar, Germany
Cr_2O_3	99.8%	Sigma-Aldrich
SiO_2	99%(Reagent grade)	Sigma-Aldrich
MgO	99%	Sigma-Aldrich
CaO	99%	Sigma-Aldrich
Al_2O_3	99.8%	Sigma-Aldrich

Table 2 Chemical composition of the original slag samples

Sample No.	Composition (wt%)				
	Al_2O_3	CaO	SiO_2	MgO	Cr_2O_3
S1	3.0	51.1	31.9	8.0	6.0
S2	6.0	49.2	30.8	8.0	6.0
S3	8.0	48.0	30.0	8.0	6.0
S4	12.0	45.5	28.5	8.0	6.0

2.3 Principle of the experimental method

Classical gas/slag equilibrium technique was adopted in this work. The samples with targeted compositions were kept in Pt crucibles and were equilibrated with a gas mixture of CO/CO_2 gases to control the oxygen partial pressure. Oxygen partial pressure was kept at 10^{-4} Pa at the required temperature (1873K). The samples were then slow cooled to 1673 K and soaked at that temperature for 24h. The cooling rate was 2K/min.

2.4 Apparatus

Figure 2 shows the schematic arrangement of the furnace reaction tube. The furnace was equipped with $MoSi_2$ heating elements. The furnace was controlled by a Eurotherm PID controller equipped with PtRh30%/PtRh6% thermocouple as the sensor. The temperature deviation at the even temperature zone of the furnace that extended to about 80 mm at the centre of the reaction tube was found to be less than ±3K.

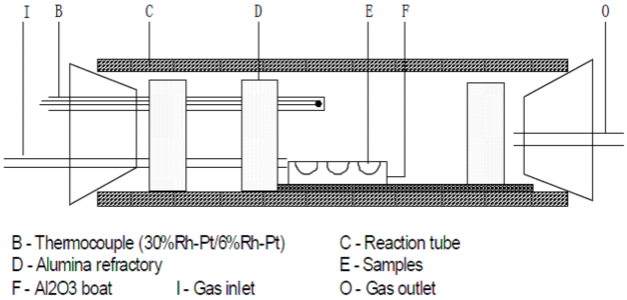

Figure 2 Schematic arrangement of the furnace reaction tube [3]

2.5 Procedure

The Pt crucibles containing the samples were positioned inside an alumina holder. Before the heating of the furnace, the alumina sample holder was pushed into the furnace and positioned in the even-temperature zone. The furnace was heated at a heating rate of 5K/min with a gas mixture of CO/CO_2 flowing through the reaction tube(technical grade, supplied by AGA, Stockholm). The gas flow rate was 100ml/min. After the targeted temperature was reached, the samples were equilibrated for 24h in a gas mixture of CO/CO_2 gases (corresponding to $p_{O2} = 10^{-4}$ Pa) as mentioned earlier. The samples were then slow-cooled at a cooling rate of 2K/min to 1673K and soaked for 24h at very low P_{O_2}. The samples were quenched by pulling them quickly to the water-cooled cold end of the reaction tube and then dropped into distilled water kept at room temperature. The samples were carefully dried and kept in desiccator. The quenched samples were taken out and analyzed using SEM-WDS and XRD techniques. For the XRD analysis SIEMENS D5000 X-Ray Diffractometer (K_α–Cu) was used. SEM analyses were carried out using a Hitachi S3700N SEM unit equipped with Bruker SDD–detector for WDS analysis. Selected experiments were repeated and the results were found to be reproducible. The results were compared with the results from previous study conducted in air atmosphere on the samples with the same compositions and the same heat treatment cycle.

3. Results and discussion

3.1 Thermodynamic calculations

The equilibrium phases of CaO-MgO-SiO_2 -Cr_2O_3-Al_2O_3 slag systems at 1673 K and oxygen partial pressure $P_{O_2}=10^{-4}$ Pa were calculated by FACTSAGE software (FACTSAGE 6.1), Thermfact Ltd (Montreal, Canada) and BTT-technologies (Aachen, Germany). Databases chosen were Fact53 and FToxid. Equilibrium phase amounts are presented in Table 3. Calculated results conducted for air atmosphere were the same as at low oxygen partial pressure. These calculation results will be compared with the current experimental results in the section of discussions.

Table 3 Amounts of equilibrium phases in mass percent at 1673 K and oxygen partial pressure $P_{O_2}=10^{-4}$ Pa, results from the thermodynamic calculations by FACTSAGE software. The calculated values for air atmosphere were totally equal.

Equilibrium phases	S1	S2	S3	S4
$Ca_2Al_2SiO_7$_gehlenite	5.7	13.1	17.0	26.3
$MgAl_2O_4$_spinel	1.2	1.6	2.3	3.1
(MgO)(Cr_2O_3)_chromite	7.6	7.6	7.6	7.6
$Ca_3MgSi_2O_8$_merwinite	49.5	48.6	46.9	45.1
a'-Ca_2SiO_4	35.9	29.1	26.2	17.9

Figure 3 shows the SEM image of the sample S1 with basicity 1.6, the Al_2O_3 content was 3 wt%. The sample was first equilibrated in CO/CO_2 gas mixture at $P_{O2}=10^{-4}$ Pa 1873 K for 24h, then slow cooled and soaked at 1673 K at $P_{O2}=10^{-4}$ Pa 1873 K for additional 24h. It was found that the sample had not melted completely, was pink in colour and opaque Smal spinel grains (7 µm) were found, see figure 3. The alumina rich matrix, was found to contain 6.43 mole% Al and 2.28 mole% Mg. Cr content in the matrix phases was less than 0.5 at%, according to WDS analysis see table 4. The spinel phase consisted of solid solution of Al_2O_3 CaO and MgO oxides.
In the Pt – crucible, chromium content according to WDS analysis is 0.0 at%.

Table 4 WDS analysis of the sample S1 (mole%)

	Cr	Mg	Al	Si	Ca	O
1 spinel	13.41	14.00	9.16	1.43	2.03	59.97
2 matrix	0.11	2.28	6.43	15.22	15.42	60.54
3 Ca_2SiO_4	0.44	3.70	0.15	15.35	23.99	56.37

Figure 4 shows SEM micrograph of the sample S2 with basicity 1.6, the alumina addition was 6 wt%. The sample was first equilibrated in CO/CO_2 gas mixture at $P_{O2}=10^{-4}$ Pa 1873 K for 24h, then slow cooled and soaked at 1673 K at $P_{O2}=10^{-4}$ Pa Pa for additional 24h. It was found that sample was not melted completely and was pink and opaque. Spinel grains, up to 10µm in diameter, can be observed, see figure 4. The matrix consisted of merwenite and dicalcium-silicates dendrites and amorphous Al_2O_3-rich matrix, Table 5 gives WDS analysis of the sample S2 (mole%). Cr content dissolved in the Pt-crusible of the sample S2 varied between 0.154-0.954 at% as a function of the distance from the slag/Pt-crucible surface. (Cr in Pt: 0.154, 0.454, 0.954 at%.)

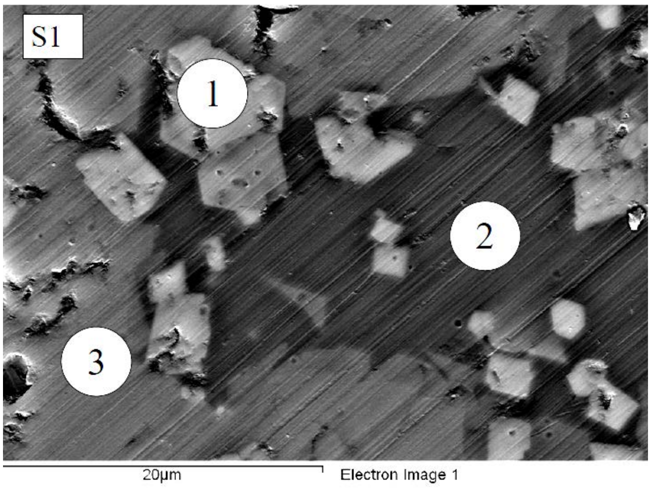

Figure 3 SEM image of the sample S1 with basicity 1.6, the Al_2O_3 content was 3 wt%. The sample was first equilibrated in CO/CO_2 gas mixture at $P_{O2}=10^{-4}$ Pa 1873 K for 24h, then slow cooled and soaked at 1673 K at $P_{O2}=10^{-4}$ Pa 1873 K for additional 24h. Spinel grains, up to 10µm in diameter, could be observed.

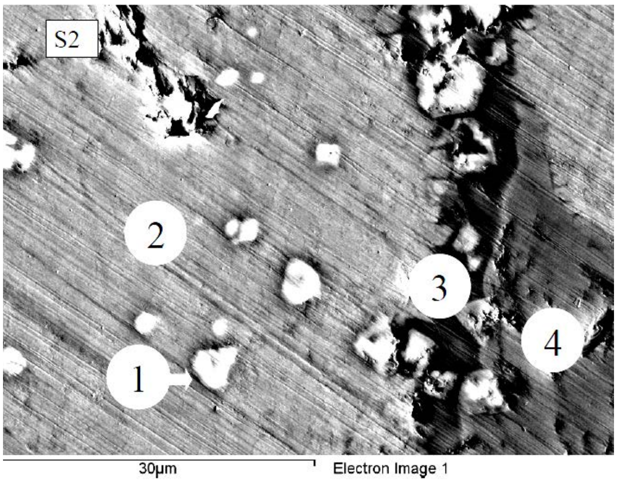

Figure 4 SEM micrograph of the sample S2 with basicity 1.6, the alumina addition was 6 wt%. The sample was first equilibrated in CO/CO2 gas mixture at $P_{O2}=10^{-4}$ Pa 1873 K for 24h, then slow cooled and soaked at 1673 K at $P_{O2}=10^{-4}$ Pa for additional 24h. Spinel grains, up to 10µm in diameter, could be observed.

Table 5 WDS analysis of the sample S2 (mole%)

	Cr	Mg	Al	Si	Ca	O
1 spinel	10.94	13.11	9.72	0.51	1.06	64.66
2 Ca2SiO4	0.03	1.55	0.13	13.76	22.99	61.54
3 matrix	0.19	1.89	5.35	12.38	15.62	64.57
4 merwinite	0.04	6.43	0.03	13.83	19.38	60.30

Figure 5 shows SEM micrograph of the sample S3 with basicity 1.6, Al_2O_3 content was 8 wt%. The sample was first equilibrated in CO/CO_2 gas mixture at $P_{O2}=10^{-4}$ Pa 1873 K for 24h, then slow cooled and soaked at 1673 K at $P_{O2}=10^{-4}$ Pa for additional 24h. It was found that sample had not melted completely and was pink in appearance and opaque. Spinel grains up to 5µm can be observed. The phases present are Ca_2SiO_4, merwinite, spinel; and Al_2O_3 rich matrix. Table 6 gives WDS analysis of the sample S3 (mole%). Phases thermodynamically stable at this temperature and composition (sample S3 basicity 1.6) according to FACTSAGE calculations are, see table 3; merwinite $Ca_3MgSi_2O_8$, spinel, and a-Ca_2SiO_4. Cr content dissolved in the Pt-crusible of the sample S3 varied between 0.00-0.188 at% as a function of the distance from the slag surface. (S3 Cr in Pt : 0.53, 0.188, 0.00)

Table 6 WDS analysis of the sample S3 (mole%)

	Cr	Mg	Al	Si	Ca	O
1 spinel	9.73	12.86	10.50	0.25	0.78	65.88
2 spinel	4.52	12.07	17.49	1.55	1.72	62.65
3 Ca_2SiO_4	0.03	1.60	0.15	12.94	21.50	63.78
4 merwinite	0.04	6.24	0.04	13.02	17.69	62.96
5 matrix	0.03	2.48	7.41	10.70	12.98	66.40

Figure 6 shows SEM micrograph of the sample S4 with basicity 1.6, the Al_2O_3 content was 12 wt%. The sample was first equilibrated in CO/CO_2 gas mixture at $P_{O2}=10^{-4}$ Pa 1873 K for 24h, then slow cooled and soaked at 1673 K at $P_{O2}=10^{-4}$ Pa for additional 24h. It was found that sample was not melted. The color of the sample was pink and opaque. According to SEM/WDS analysis, spinel grains 5 μm can be observed. Besides spinel phase, Ca_2SiO_4 and Al_2O_3 -rich amorphous matrix was found. Table7 gives WDS analysis of the sample S4 (mole%)

XRD analysis for the sample S4, see Figure 6, confirmed presence of spinel, and Ca_2SiO_4. Cr content dissolved in the Pt-crusible of the sample S4 varied between 0.166-0.764 at% as a function of the distance from the slag surface. (S4 Cr in Pt: 0.764, 0.349, 0.166)

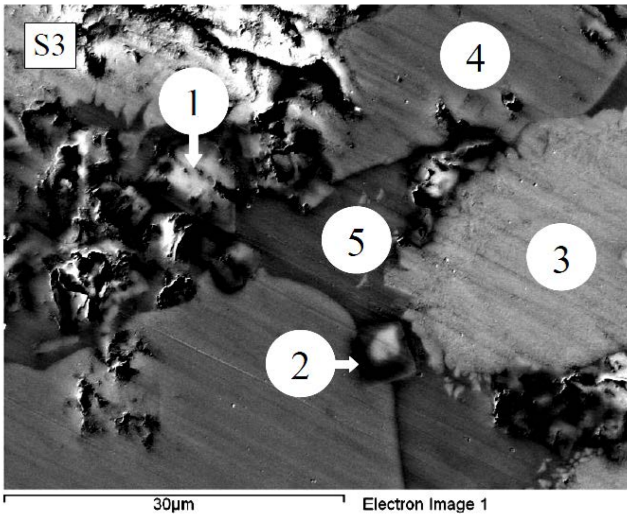

Figure 5 SEM micrograph of the sample S3 with basicity 1.6, the Al_2O_3 content was 8 wt%. The sample was first equilibrated in CO/CO_2 gas mixture at $P_{O2}=10^{-4}$ Pa 1873 K for 24h, then slow cooled and soaked at 1673 K at $P_{O2}=10^{-4}$ Pa for additional 24h. Fine up to 5μm spinel grains can be observed. The phases present are Ca_2SiO_4, merwinite, spinel; and Al_2O_3 rich matrix.

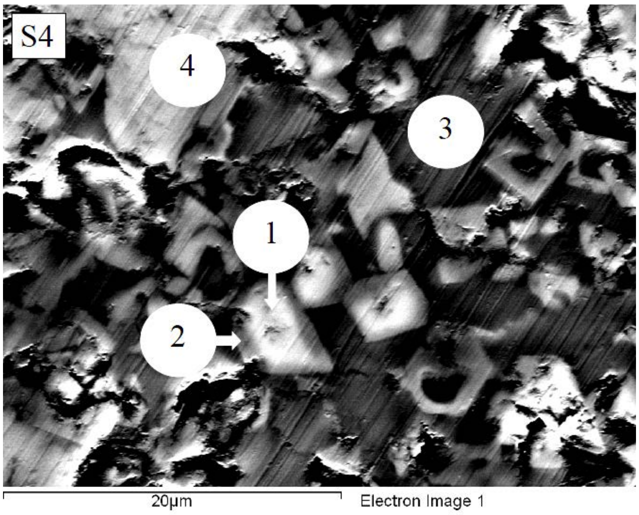

Figure 6 SEM micrograph of the sample S4 with basicity 1.6, the Al_2O_3 content was 12 wt%. The sample was first equilibrated in CO/CO_2 gas mixture at $P_{O2}=10^{-4}$ Pa 1873 K for 24h, then slow cooled and soaked at 1673 K at $P_{O2}=10^{-4}$ Pa for additional 24h. Spinel grains 5 μm can be observed.

Table 7 WDS analysis of the sample S4 (mole%)

	Cr	Mg	Al	Si	Ca	O
1 spinel	7.02	11.55	11.67	1.07	1.16	67.54
2 spinel	2.19	6.74	10.01	5.69	6.51	68.86
3 matrix	0.19	2.57	7.17	10.48	12.16	67.44
4 Ca_2SiO_4	0.02	1.38	0.26	13.12	22.08	63.13

Figure 7 shows the chromium partition in $CaO-SiO_2-MgO-Cr_2O_3-Al_2O_3$ synthetic slags. The results from current work are compared with previous study of the systems conducted in air atmosphere. While the chromium content in the matrix phases remains constant, regardless alumina content in the slag, the Cr in the spinel phase decreases as a function of Al_2O_3 addition. In the samples soaked in air, spinel phase contains Ca and Si as well as Al ions. In the samples soaked at $P_{O2}=10^{-4}$ Pa, Cr in spinel phase is gradually replaced by Al ions.

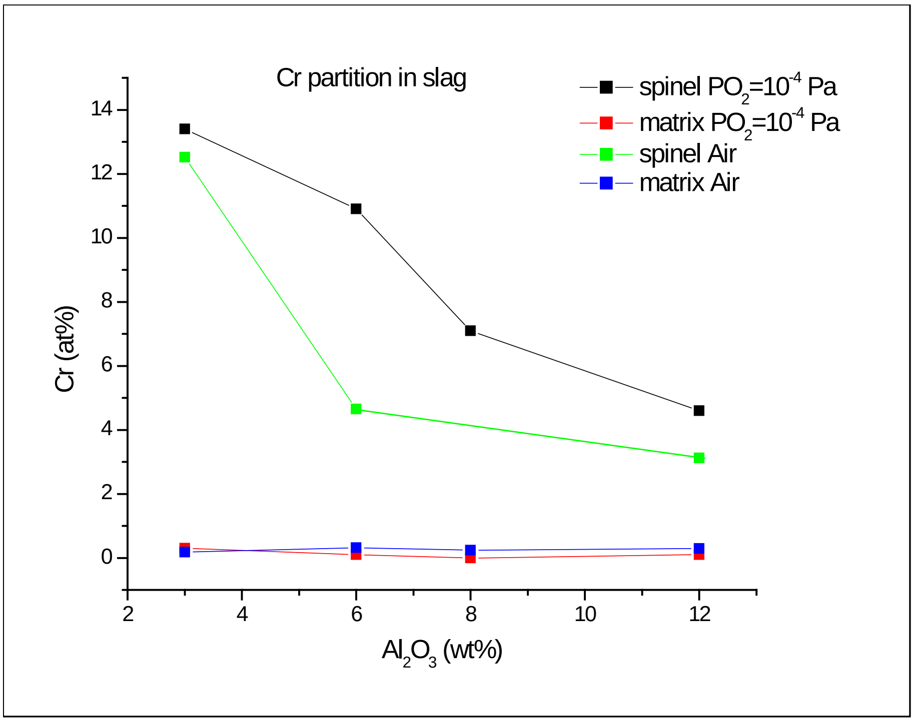

Figure 7 Cr partition in CaO-SiO$_2$-MgO-Cr$_2$O$_3$-Al$_2$O$_3$ synthetic slag. The results from current work are compared with previous study of the system conducted in air atmosphere.

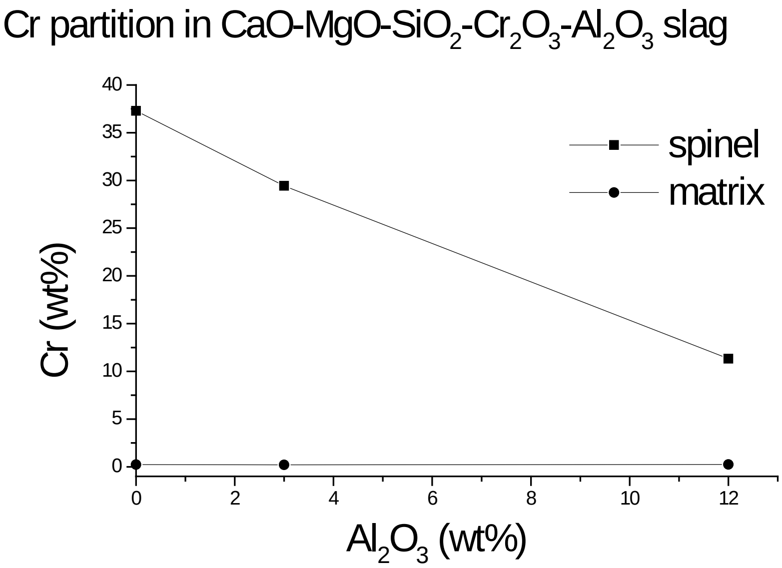

Figure 8 Cr partition in CaO-MgO-SiO$_2$-Cr$_2$O$_3$-Al$_2$O$_3$ slag system soaked at P_{O2}=10 $^{-4}$ Pa as a function of Al$_2$O$_3$ content.

Figures 9 and 10 show CaO-MgO-SiO$_2$-Cr$_2$O$_3$-Al$_2$O$_3$ slags soaked at P_{O2}=10 $^{-4}$ Pa and air respectively, with Al$_2$O$_3$ content in the rage of 3-12wt%. In contrast to results from the samples soaked in air, the spinel phase precipitated at P_{O2}=10 $^{-4}$ Pa has a regular polygonal crystal shape and not a disordered structure. Low oxygen partial pressure facilitates the crystal growth of the spinel phase in slag. High oxygen partial pressure enhances the solubility of Cr-oxide in the matrix phases at elevated temperatures.

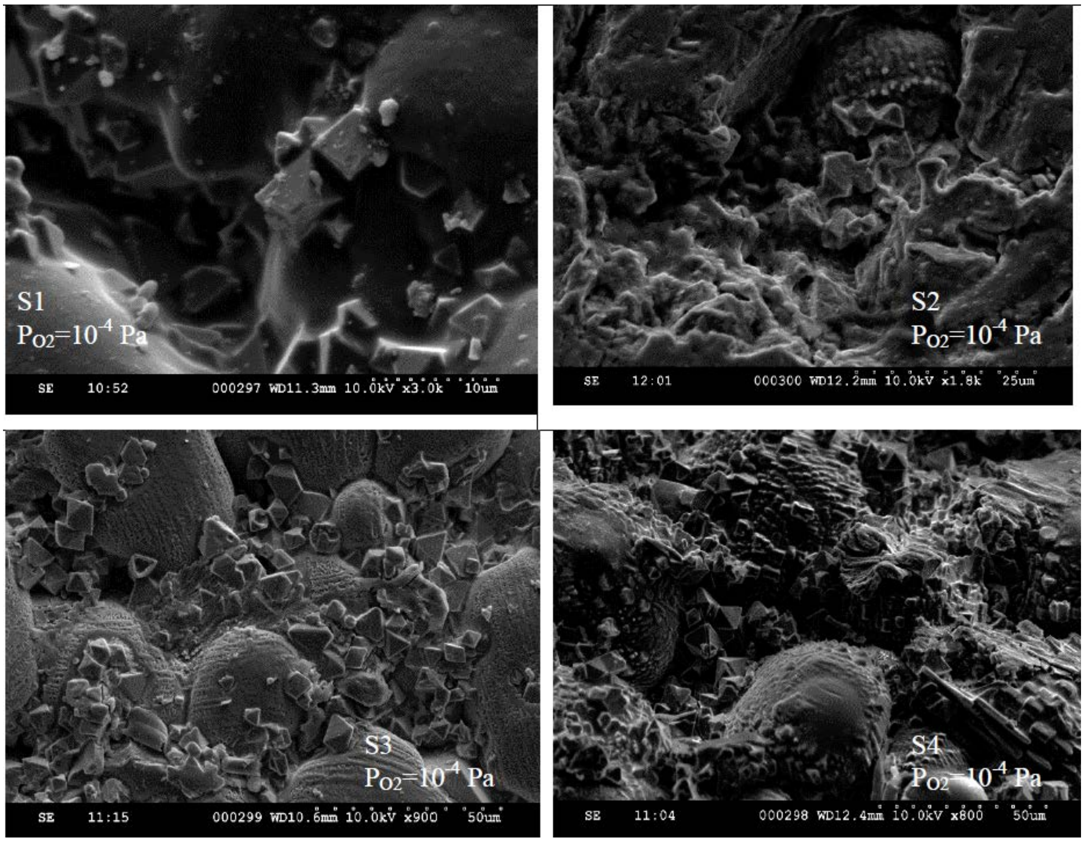

Figure 9 CaO-MgO-SiO_2-Cr_2O_3-Al_2O_3 slags soaked at P_{O2}=10 $^{-4}$ Pa, with Al_2O_3 content in the rage of 3-12wt%. Spinel phase precipitated at P_{O2}=10 $^{-4}$ Pa has a regular polygonal crystal shape.

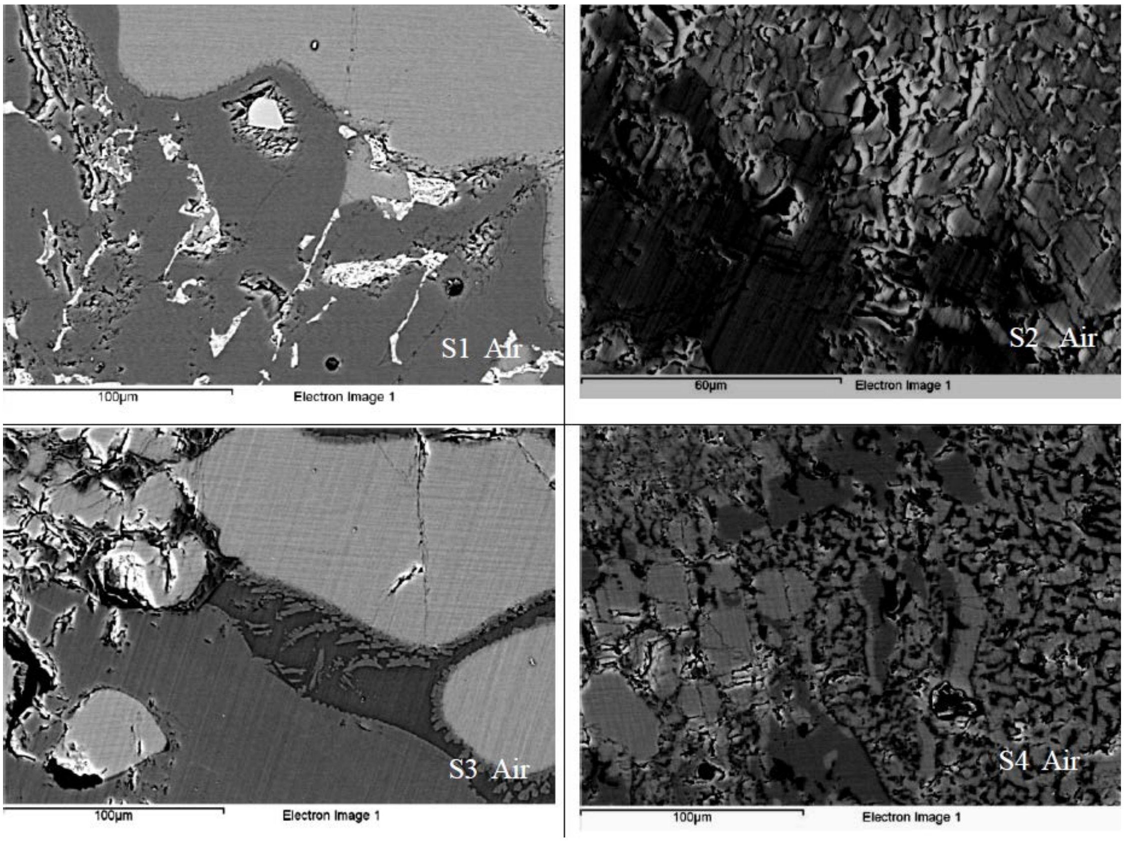

Figure 10 Samples soaked in air. The spinel phase, (white due to high Cr content in S1, and black due to high Al content in S4) has an irregular shape, (disordered structure). Besides irregular shape the spinel phase grown in air atmosphere has a lot of CaO and SiO_2 impurities.

Figure 11 shows the XRD analysis of the current slag systems soaked in air. Presence of Mg(Cr, Al)O_4 solid solution can be observed.

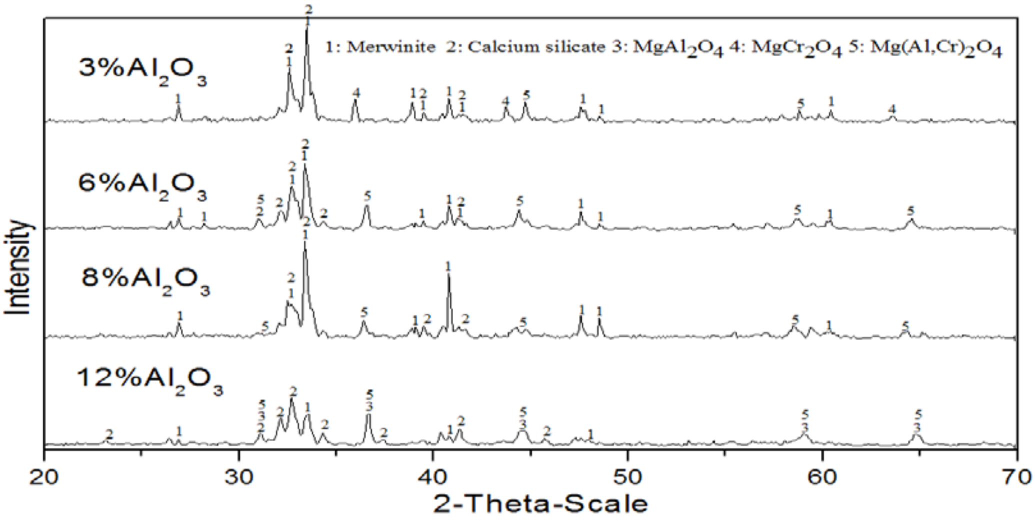

Figure 11 XRD analysis of the current slag system soaked in air. Presence of Mg(Cr, Al)O_4 solid solution can be observed.

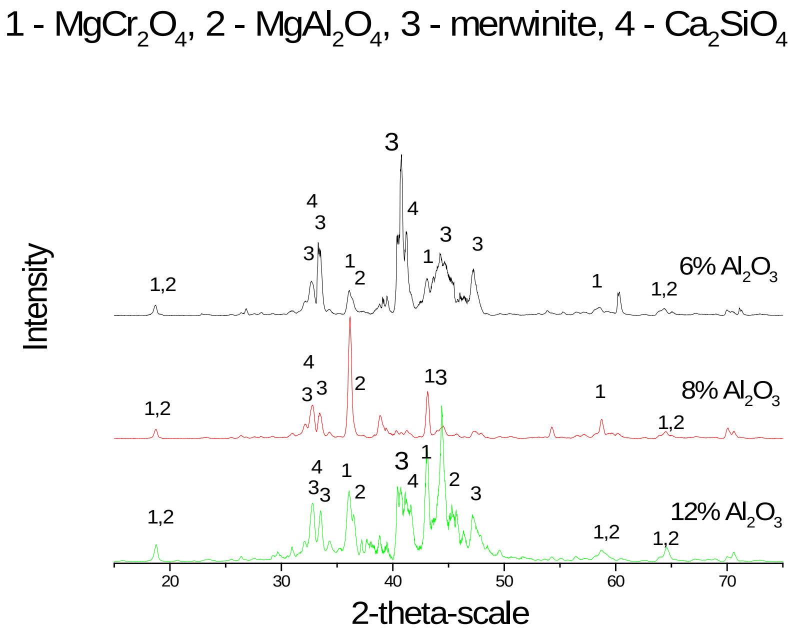

Figure 12 XRD analysis of the current slag system soaked at $P_{O2}=10^{-4}$ Pa. Presence of Mg(Cr, Al)O_4 solid solution is can be observed.

According to XRD analysis all the samples contained phases merwinite, dicalcium silicate and Mg(Al, Cr)O_4 spinel solid solution. Gehlenite phase was predicted by thermodynamic calculation, see table 3, however no gehlenite phase were confirmed either by XRD or SEM-WDS analyses.

It have been shown in earlier studies by current authors [16] that the purity of the spinel phase precipitated in air atmosphere was found to vary with slag basicity. Slags with basicities above 1.6 contained more Cr distributed in the water soluble matrix phases (merwinate, dicalcium silicate and periclase phases). In the current work, where the experiments were conducted at $P_{O2}=10^{-4}$ Pa for the slag systems with basicity (CaO/SiO_2) = 1.6, it was confirmed that very low oxygen partial pressure improves the spinel precipitation. Efficient spinel growth gives very low Cr content in the matrix. It was found that the grain size in all samples did not differ much. That can be due to the fact that none of the samples were melted completely (the samples were sintered). It was found that low P_{O2} has a strong impact on the liquidus temperature of the CaO-MgO-SiO_2-Cr_2O_3-Al_2O_3 slag system. The liquidus temperature increases as P_{O2} decreases. Diffusion through the solid phase can be rather slow compared to the liquid state. The rate of the crystal growth is described and controlled by kinetic laws. The driving force of spinel formation is however high due to undercooling. The crystal size of the spinel phase would be most probably increased if the holding time was increased. However, that would probably not give more volume fraction of spinel, since the Cr amount in the matrix would be already extremely low.

The color of the samples soaked in air was green and turned into pink after soaking at $P_{O2}=10^{-4}$ Pa. Pink is the color of $MgAl_2O_4$ spinel. The color change can be also due to the valence state change of Cr ions.

The possible explanation to why high P_{O2} would hinder the crystal growth of the spinel phase is that excessive oxygen creates point defects in the crystal structure. Parallels can be drawn with other crystals, such as quartz, the formation of which is impossible in the presence of foreign ions. Earlier results by current authors [16] show that spinel formation is inhibited at higher basicities, which can be explained by presence of CaO dissolved in the spinel phase. Current work confirms the presence of impurities (defects) in spinel phase in the samples soaked in air, hence irregular shape of the spinel phase, while the spinel with regular crystal grains are formed at very low oxygen partial pressure. The spinel phase from the samples soaked at very low P_{O2} consists of $MgAl_2O_4$-$CrMg_2O_4$ solid solution.

According to thermodynamic calculation, the spinel phase amount is constant, and does not change with temperature. The reason could be that the calculations are based on the assumption that the spinel phase precipitation is completed at higher temperature, and no crystal growth is taking place at lower temperature. The calculations do not consider the change of P_{O2} either.

4. Conclusions

The effect of alumina addition to CaO-MgO-SiO_2-Cr_2O_3 slag system at 1673 K (1400 ºC) has been studied. Gas/slag equilibrium technique was adopted to synthesize the slags and the equilibration experiments were conducted at very low oxygen partial pressure. The Cr_2O_3 and MgO content in the slag were fixed at 6 and 8wt% respectively. The slag basicity (CaO/SiO_2) was set to 1.6. The impurity content (Ca and Si ions) dissolved in the spinel phase is decreased drastically compared with the samples treated in air. Cr content is decreased in the matrix as a result of efficient spinel phase growth. Low P_{O2} improves the spinel precipitation. The amount of spinel phase (solid solution $MgAl_2O_4$-$MgCr_2O_4$) increases with alumina content, but do not affect the amount of chromium dissolved in the matrix phases. The chromium in the spinel phase is replaced by Al ions. Very low Cr content in the matrix phase is the results in efficient $MgCr_2O_4$ formation.

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References

[1] F. Engström: Mineralogical Influence of Different Cooling Conditions on Leaching Behaviour of Steelmaking Slag, Doctoral Thesis, Luleå University of Technology, 2010, ISSN: 1402-1544

[2] K. Pillay et al.: Ageing of chromium(III)-bearing slag and its relation to the atmospheric oxidation of solid chromium(III)-oxide in the presence of calcium oxide, Chemosphere 52 (2003) 1771–1779.

[3] Lijun Wang: Experimental and Modelling Studies of the Thermophysical and Thermochemical Properties of Some Slag Systems, Doctoral Thesis, Royal Institute of Technology, 2009

[4] Y. Samada: Prevention of Chromium Elution from Stainless Steel Slag into Seawater, ISIJ International, Vol. 51 (2011), No. 5, pp. 728–73.

[5] Gelfi, Cornacchia, Investigations on leaching behavior of EAF steel slags. University of Bresca, Italy, Euroslag 2010, Madrid.

[6] T. W. Parker and J. F. Ryder, “Investigations on ‘falling’ blast furnace slags”. Journal of the Iron and Steel Institute, 11, 21-51 (1942)

[7] M. Guo, P. Wollants, “EAF stainless steel refining - Part I: Observational study on chromium recovery in an eccentric bottom tapping furnace and a spout tapping furnace”. Steel Res. Int., 78 (2) (2007) 117-124.

[8] N. Sakamoto, “Effects of MgO based glass addition on the dusting of stainless steel slag (development of control process of stainless steel slag dusting-3)”. Current Advance in Materials and Processes, 14 (4) 939 (2001).

[9] Q. Yang et al: “Modification study of a steel slag to prevent the slag disintegration after metal recovery and to enhance slag utilisation”. In 8th International Conference on Molten Slags, Fluxes and Salts – MOLTEN 2009, 2009, Santiago, Chile.

[10] A. Monaco; W-K. Lu: The effect of cooling conditions on the mineralogical characterizations of steel slag, Proc Int Symp Res Conserv Environ Technol Metall Ind, 1994, 107-116

[11] P. A. Tanskanen, H. T. Makkonen, Design of Slag Mineralogy and Petrology, University of Oulu, Outocompu Finland, Global Slag Magazine, (5) (2007) 16-20.

[12] Wu Ren-Ping; Yu Yan: Influence of Cr_2O_3 on the Structure and Property of Mg-Al Spinel Synthesized by Waste Slag in Aluminium Factory, Chinese J. Struct. Chem. Vol.26, N.12, 1455-1460

[13] E. García-Ramos, A. Romero-Serrano, Immobilization of Chromium in Slags using MgO and Al_2O_3, Steel Research Int. 79 (2008) No. 5, pp 332-339.

[14] V. Arredondo-Torres; A. Romero-Serrano: Stabilization of $MgCr_2O_4$ spinel in slags of the SiO_2-CaO-MgO-Cr_2O_3 system, Revista de Metalurgia, 2006, 42 (6) 417-424

[15] FactSage software (FactSage 6.1), Thermfact Ltd (Montreal, Canada) and BTT-technologies (Aachen, Germany).

[16] G. Jelkina et al: Effect of the Heat Treatment on the Chromium Partition in CaO-MgO-SiO_2-Cr_2O_3 syntetic slags , Division of Materials Process Science, Royal Institute of Technology (KTH), SE-100 44, Stockholm, Sweden. (2011)