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Effect of MnO on Mineral Composition of CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 System

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Abstract

The chromium leaching from stainless steel slag highly depends on the occurrence of chromium. The effect of MnO on the mineral composition of stainless steel slag was investigated through CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 synthetic slags. The experiments were performed in a conductive furnace, and the samples collected during tests were analyzed using X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) equipped Energy Dispersive Spectroscopy (EDS). The results show that the addition of MnO significantly reduces the solidus temperature of oxide systems from 1204˚C to 950˚C, promotes the spinel precipitation and increases the size of spinel crystals. The fraction of chromium contained in non-spinel mineral phases decreases and the amount of larnite dissolved into spinel phase slightly reduces with the content of MnO increasing. In addition, the amorphous phase forms when the content of MnO is up to 6 wt%. Hence, the addition of MnO is beneficial to suppress chromium leaching from slag.

Keywords

Mineral Phase, MnO, Leaching, Chromium, Spinel, Stainless Steel Slag

1. Introduction

Huge amount of stainless steel slags are produced annually during stainless steel-making, leading to important economical and ecological issues regarding their afterlife. Since chromium is one of the major constituents of the stainless steel and more easily oxidized to Cr_2O_3 than iron, the final slag contains a certain content of chromium [1]. It is well known that hexavalent chromium is toxic [2] and it is possible that chromium leaches out from stainless steel slag. Thus, utilization of stainless steel slags is highly restricted.

The leachability of chromium mainly depends on the occurrence of chromium in slags. Numerous mineralogical species present in steelmaking slags are soluble in aqueous media, for example, merwinite, periclase, dicalcium silicate and lime, but other phases viz. wustite, spinel and glass are considered as resistant to dissolution [3] [4] [5] [6]. Therefore, the part of chromium enclosed in soluble mineral phases could leach out as long as the slag is in aqueous condition. On the other hand, the leaching of chromium can be suppressed by means of adjusting the mineral composition of slag system. Mineralogical phases are significantly affected by slags composition and heat treatment method.

In order to understand the effect of MnO on the mineral composition of stainless slag, $CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3$ system, experiments are carried out to prepare synthetic slag samples under a certain cooling procedure. Some analysis methods are employed, including X-ray powder diffraction (XRD), scanning electron microscopy (SEM) equipped an energy dispersive spectrometer (EDS), as well as thermodynamic calculations with FactSage 6.2.

2. Experimental

Synthetic slags were prepared with analytical grade reagents (CaO, MgO, Al_2O_3, SiO_2, Cr_2O_3, and MnO). The composition of synthetic slag is on the basic of industrial stainless steel slag produced by EAF, shown in **Table 1**. The compound powders were homogeneously mixed and placed in an Al_2O_3 crucible, which was placed in a graphite crucible inside an induction furnace. The cooling procedure adopted is as follows. Firstly, the mixtures were heated to 1600˚C slowly and kept for 30 min; secondly, the temperature drop down to 1450˚C and held on for 30 min; then the temperature continued to decline to 1300˚C and kept for 60 min; finally, temperature dropped down to 1250˚C and kept for 120 min. Then, the slags were left inside the furnace to cool down to room temperature naturally. The temperature was measured with an R-type thermocouple (Pt, 30% Rh-Pt, 6% Rh).

The mineralogy of the samples was determined with X-Ray Powder Diffraction analysis (XRD, M21x, MAC). Diffraction patterns were measured in a range of 10˚ - 90˚ in 0.02˚/step. Microstructural characterization of the slags was performed using scanning electron microscopy (SEM, Jeol 6480LV), equipped a Thermo Electron NSS energy dispersive spectrometer (EDS). Thermodynamic calculations were performed by FactSage 6.2 using the model of Scheil cooling target phase.

3. Experimental Result

The solidified microstructures of $CaO-MgO-SiO_2-Al_2O_3-Cr_2O_3$ systems with dif-

Table 1. Scheme composition of synthetic slag [wt%].

Test No.	CaO	SiO_2	MgO	Al_2O_3	Cr_2O_3	MnO
S1	45.00	32.00	8.00	6.00	6.00	0
S2	43.65	31.04	7.76	5.82	5.82	3.00
S3	42.30	30.08	7.52	5.64	5.64	6.00

ferent MnO contents are shown in **Figures 1-3**, and the SEM-eds quantitative analysis results are summarized in **Tables 2-4**. The sample without MnO consists of four mineral phases: merwinite ($Ca_3MgSi_2O_8$), Larnite (Ca_2SiO_4), spinel [$Mg(Cr,Al)_2O_4$], and melilite, where larnite, spinel, and melilite are solid solutions on the basic of SEM-eds analyses. The white particles marked "4" are chromium-enriched spinel, and the dark areas around Cr-spinel are also spinel, which are rich in alumina. Melilite is a solid solution, consisting of akermanite ($Ca_2MgSi_2O_7$) and gehlenite ($Ca_2Al_2SiO_7$) [7]. As shown in **Figure 2**, the solidified microstructure is constituted by merwinite, larnite, spinel and melilite. The slag with 6 wt% MnO is composed of spinel and matrix. All spinels are in angular shape and unevenly distributed in matrix, which reveals that the spinels have precipitated from liquid slag at 1600˚C.

Figure 4 shows the XRD patterns for the solidified samples with different MnO content. The peaks corresponding to merwinite, akermanite, gehlenite, chromite ($MgCr_2O_4$), and larnite appear in all samples. In addition, diopside [$Ca(Mg,Al)(Si,Al)_2O_6$] is identified in 6 wt% MnO slag, while it is not observed in SEM analysis.

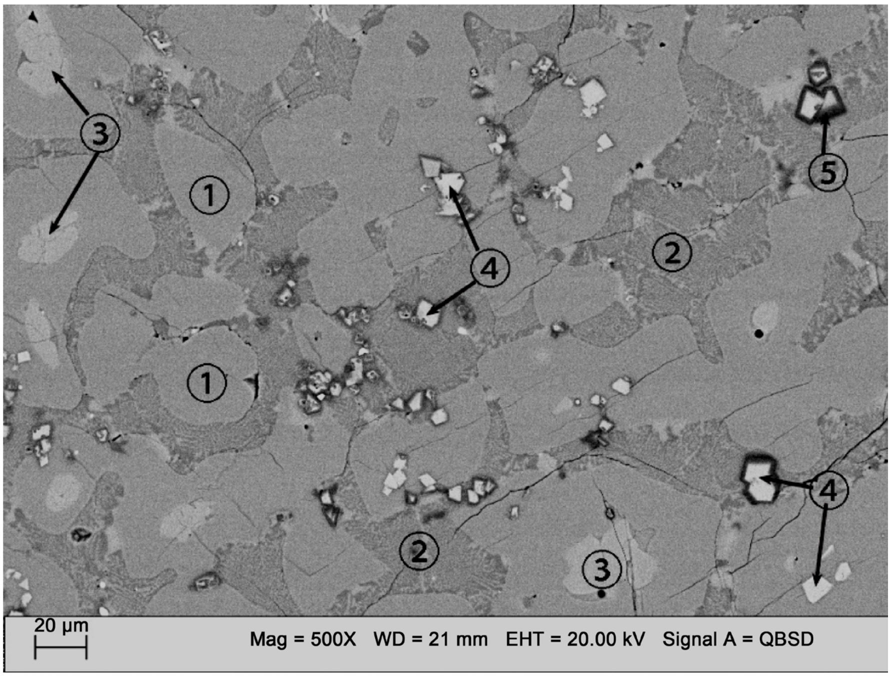

Figure 1. SEM graph of $CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3$ slag system without MnO addition.

Table 2. SEM-eds results of mineral phases in **Figure 1** [at%].

	O	Mg	Al	Si	Ca	Cr
①_Merwinite	52.22	7.84	0.42	16.66	22.77	0.09
②_Melilite	53.37	3.22	6.90	15.21	21.20	0
③_Larnite	52.08	3.89	1.20	16.83	25.9	0.10
④_Cr-spinel	53.12	15.71	7.15	0.26	0.49	23.27
⑤_Al-spinel	50.95	15.31	24.02	1.32	1.13	7.27

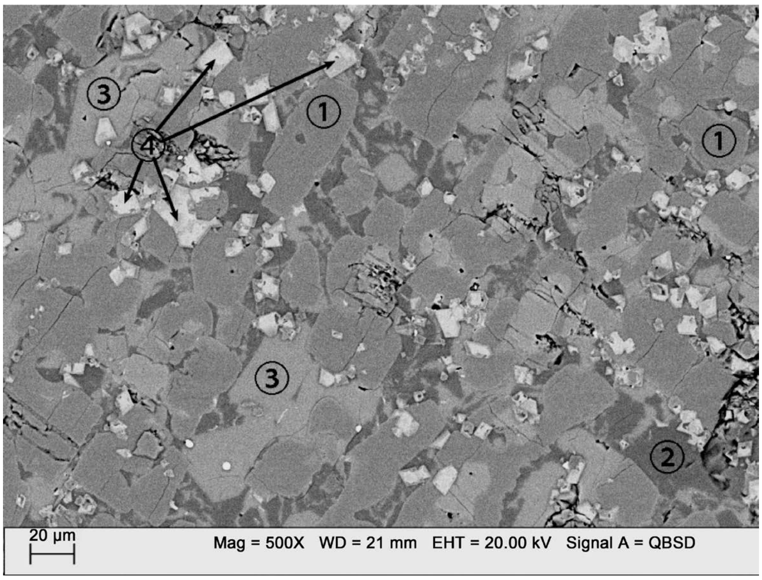

Figure 2. SEM graph of CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 slag system with 3% MnO.

Table 3. SEM-eds results of mineral phases in **Figure 2** [at%].

	O	Mg	Al	Si	Ca	Cr	Mn
①_Merwinite	54.18	7.14	0.30	16.09	21.86	0.10	0.33
②_Melilite	54.73	3.32	10.59	13.79	17.00	0	0.58
③_Larnite	55.85	1.82	0.25	15.76	26.15	0	0.18
④_Spinel	57.02	12.84	6.03	0.37	0.86	21.26	1.65

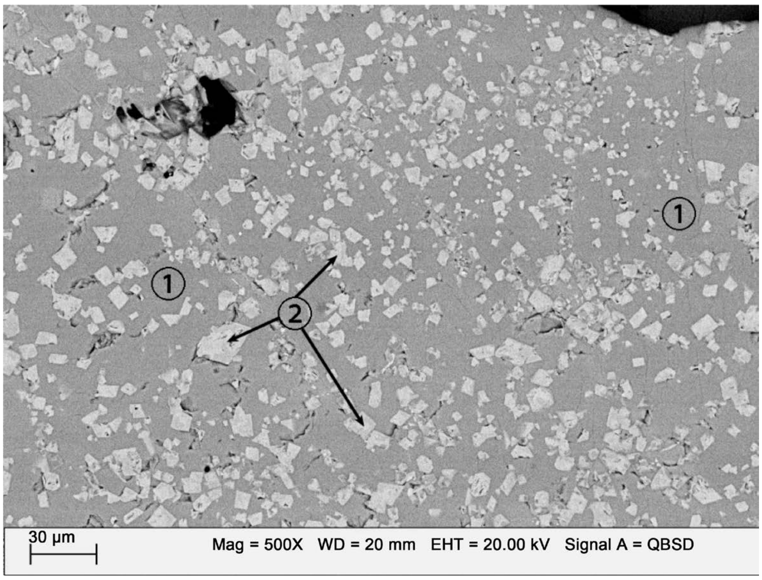

Figure 3. SEM graph of CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3 slag system with 6% MnO.

Table 4. SEM-eds results of mineral phases in **Figure 3** [at%].

	O	Mg	Al	Si	Ca	Cr	Mn
①_Matrix	53.81	7.03	0.42	16.28	21.81	0.04	0.61
②_Spinel	54.81	11.96	7.54	0.63	0.77	21.38	2.93

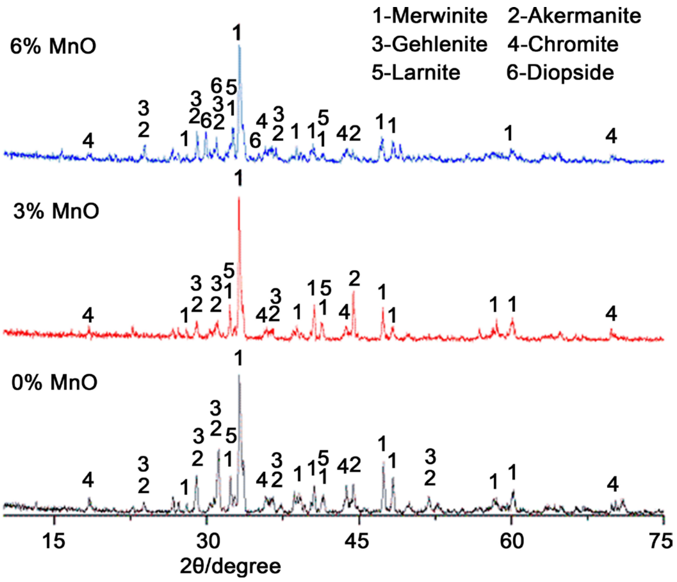

Figure 4. XRD patterns of the CaO-SiO$_2$-MgO-Al$_2$O$_3$-Cr$_2$O$_3$ systems with different MnO contents.

4. Discussion

The mass fractions of liquid and mineral phases of the CaO-MgO-SiO$_2$-Al$_2$O$_3$-Cr$_2$O$_3$ systems are shown in **Figure 5**, as functions of temperature and MnO content. The solidification processes of these slags calculated using FactSage 6.2 can be summarized as follows and a new phase underlined is calculated to precipitate at each step.

(1) Sample without MnO

Liquid + Chromite + Larnite (1600˚C) → Liquid + Chromite + Larnite + Merwinite (~1427˚C) → Liquid + Chromite + Larnite + Merwinite + Melilite (~1406˚C) → Solid mixture (~1204˚C);

(2) Sample with 3 wt% MnO

Liquid + Chromite + Larnite (1600˚C) → Liquid + Chromite + Larnite+ Merwinite (~1420˚C) → Liquid + Chromite + Larnite + Merwinite + Melilite (~1370˚C) → Liquid + Chromite + Larnite + Merwinite + Melilite + Mn_2SiO_4 (~1010˚C) → Solid mixture (~970˚C);

(3) Sample with 6 wt% MnO

Liquid + Chromite + Larnite (1600˚C) → Liquid + Chromite + Larnite + Merwinite (~1400˚C) → Liquid + Chromite + Larnite + Merwinite + spinel (~1380˚C) → Liquid + Chromite + Larnite + Merwinite + spinel + Melilite (~1300˚C) → Liquid + Chromite + Larnite + Merwinite + spinel + Melilite + Mn_2SiO_4 (~1000˚C) → Solid mixture (~950˚C).

According to the thermodynamic calculations, for all slag systems, $MgCr_2O_4$ phase primarily precipitates. This is in good agreement with the experimental results through SEM. The addition of MnO significantly reduces solidus temperature due to lower melt point of MnO. For example, the solidification temperature decreases from 1204˚C to 950˚C when the content of MnO in oxide systems increases from 0 wt% up to 6 wt%. This can explain the precipitation of amorphous phase in the system with 6 wt% MnO. The lower solidus temperature is expected for a better kinetic condition.

By comparing the SEM micrographs of the slags with different MnO contents, it is apparently found that the amount of spinel markedly increases with the

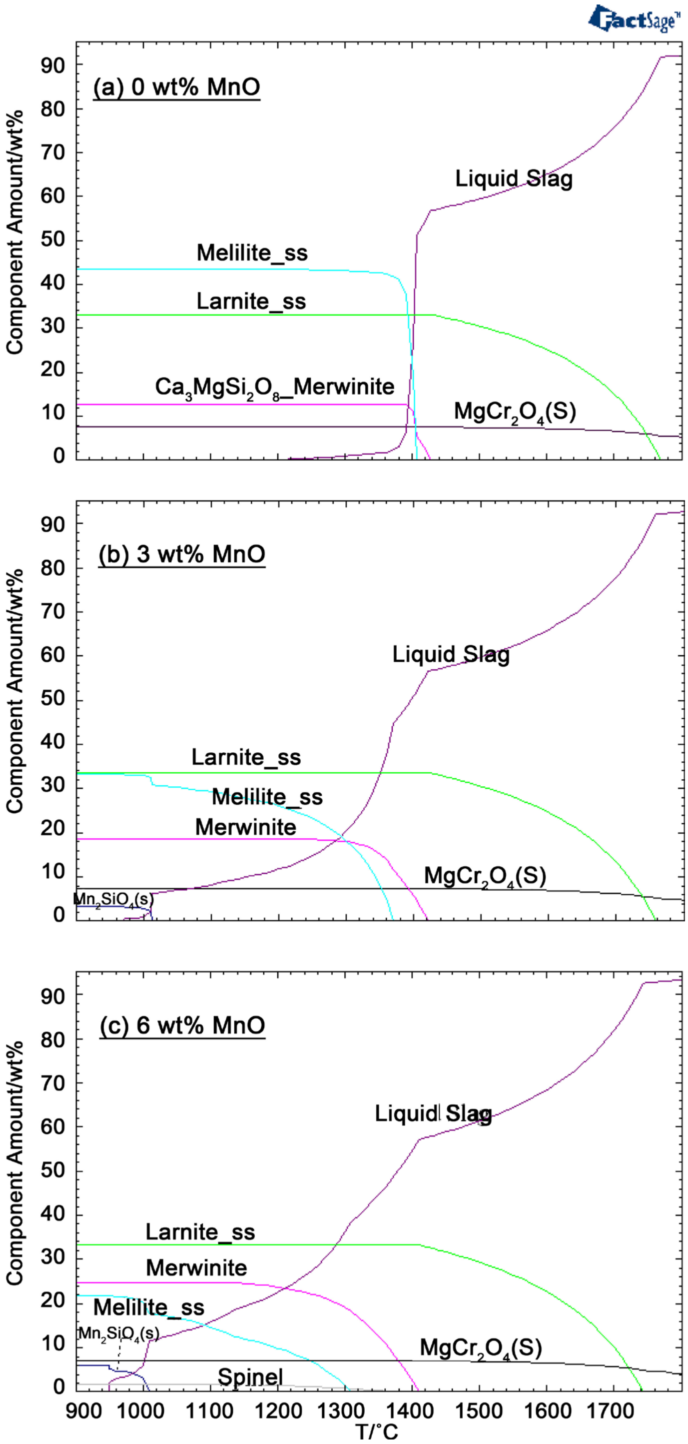

Figure 5. Calculated mass fraction of liquid and solid compounds in the CaO-MgO-SiO_2-Al_2O_3-Cr_2O_3-MnO system with different MnO contens. Larnite, melilite and spinel are solid solutions. Larnite is composed of Ca_2SiO_4 and Mg_2SiO_4, and spinel consists of $MgCr_2O_4$ and $MgAl_2O_4$.

content of MnO increasing. Moreover, the Mn content contained in spinel also significantly increases up to 2.93 at%. This can be explained by solid solution formed through isomorphous replacement. The investigation by L. Zhao [8] reported that Mn could dissolute into $MgCr_2O_4$ to form spinel through replacing the site of Mg in lattice. In addition, the size of spinel is bigger when the content of MnO is higher due to better mass transfer conditions.

As mentioned in introduction section, the leaching of chromium from slag limits the utilization in other fields. The leachability of chromium mainly depends on the occurrence of chromium in slags. Magnesium chromite ($MgCr_2O_4$) is considered as save mineral due to the strong bonding of chromium in the spinel and significant stability towards oxidation and dissolution [9], while merwinite and larnite are unexpected because of being soluble in aqueous media [3] [10]. In fact, for most basic slags, merwinite is present as main mineral phase and it is possible that a small fraction of chromium is enclosed into merwinite. Therefore, this part of chromium might leach out as long as merwinite dissolves into water. Additionally, the investigation by Samada *et al.* [11] shows that larnite (Ca_2SiO_4) can form solid solution with magnesium chromite ($MgCr_2O_4$), and the results found the dissolution of larnite weakens the stability of $MgCr_2O_4$.

As shown in **Tables 2-4**, chromium is mainly present as spinel solid solution. On the basic of comparison of SEM-eds analyses, the amount of chromium existing in larnite phases reduces with the addition of MnO, while the increase of MnO content does not show great influence on the amount of chromium contained in merwinite. On the other hand, the amount of calcium dissolved into $MgCr_2O_4$ reduces slightly with the content of MnO increasing. It is not ignored that the amorphous phase is formed in oxide system with 6 wt% MnO. Amorphous phase is expected to suppress the leaching of chromium [12]. Furthermore, the content of chromium impurity enclosed in matrix is low down to 0.04 at%. Therefore, the addition of MnO fluxes could suppress the leaching of chromium from slag through adjusting the slag mineral composition.

5. Conclusion

The effect of MnO on the mineral composition of $CaO-SiO_2-MgO-Al_2O_3-Cr_2O_3$ synthetic system during cooling process from 1600˚C was investigated using X-ray diffraction, SEM-eds, and commercial thermochemical software, FactSage 7.0. The addition of MnO significantly reduces the solidus temperature of oxide systems from 1204˚C to 950˚C and promotes the precipitation of spinel by means of isomorphous replacement. The fraction of chromium contained in non-spinel mineral phases decreases and the amount of larnite dissolved into spinel phase slightly reduces with the content of MnO increasing. In addition, the amorphous phase forms when the content of MnO is up to 6 wt%. Therefore, the addition of MnO is beneficial to suppress chromium leaching from slag.

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