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MgO modification of slag from stainless steelmaking

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Slag from stainless steelmaking is known to disintegrate, which is an environmental problem and prevents the cooled slag from being utilized. This disintegration is due to the transformation from the β to the γ polymorph of di-calcium silicate. The transformation is accompanied by an increase in volume of about 11% and a total disintegration of the slag. AOD slag from stainless steelmaking was re-melted in a laboratory induction furnace, together with olivine and calcinated dolomite, to investigate the prevention of disintegration by increased MgO content of the slag with small changes in CaO to SiO_2 ratio. The modified slag was examined with X-ray diffraction and scanning electron microscopy. The trials showed that an increased MgO content can change the mineral composition towards formation of more Merwinite and Bredigite, which prevents disintegration of the slag.

Keywords: slag, disintegration, di-calcium silicate

Introduction

The phenomenon of the dusting of slag from stainless steelmaking is due to the disintegration of di-calcium silicate ($2CaO{\cdot}SiO_2$). The disintegration comes from the transformation from the metastable, monoclinic β polymorph of di-calcium silicate to the orthorhombic γ polymorph. The transformation is accompanied by an 11% increase in volume, which causes the disintegration. This phenomenon is well known and has been studied especially within cement manufacturing. The common method to avoid the disintegration is to chemically stabilize the β polymorph. This can be done by addition of e.g. boron oxide (B_2O_3). Seki *et al.*[1] have reported that only a 0.5 weight per cent addition of borate to the molten slag will prevent dusting. The natural occurrence of β di-calcium silicate has been reported to contain significant amounts of phosphorous[2], which can also be used to stabilize the β polymorph[3].

The dusting of slag is a working environment problem due to the formation of very fine particles that are very easily scattered at the slag pits. The disintegration also prevents the cooled slag from being utilized as e.g. aggregates for construction purposes. The γ polymorph has also very weak hydraulic properties and the slag can therefore not be utilized as a hydraulic binder.

The objective of this study was to investigate stabilization of stainless steel slag by increasing the MgO content of the slag. By increasing the MgO content it would be possible to form Merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$) and/or Bredigite, which has a composition between $7CaO{\cdot}MgO{\cdot}4SiO_2$ and $5CaO{\cdot}MgO{\cdot}3SiO_2$ according to Moseley and Glasser[4].

Experimental work

Melting trials

Converter slag (AOD) from stainless steel production was ground together with olivine (mainly Mg_2SiO_4) and burned dolomite (mainly (Ca,Mg)O with some $(Ca,Mg)CO_3$). Eight mixtures were prepared, with a total quantity of 200 g material in each mix. The used proportions are shown in Table I.

The material was melted in graphite crucibles with an induction furnace. The used maximum effect of the furnace was 20 kW and the melting time varied between 20 and 25 minutes. Nitrogen was used as a protective gas during melting. The maximum temperature was approximately 1600 to 1650°C. The cooling of the material was performed in the crucible by turning off the effect of the furnace. The slag was visually verified to be liquid before turning off the furnace. The temperature was measured above the slag surface in the crucible during the cooling. As the sample amount is very small compared to the crucible and furnace system, there should not be any large temperature gradients in the samples during cooling.

Characterization

The materials from the trials were ground and the chemical analysis was determined with X-ray fluorescence (sample prepared through fusion with LiB_4).

The mineralogical composition of the modified slag was determined with X-ray diffraction (XRD). XRD data was recorded with a Siemens D5000 powder diffractometer using CuKα radiation. The measurements were performed with diffraction angles between 25–75° (2θ) and step size 0.01° and time per step 1.5 seconds.

A central part of the characterization was performed with a Philips XL 30 scanning electron microscope (SEM) equipped with a LaB_6 emission source and an Oxford Ge X-ray detector with a super atmospheric thin window (ATW), used for energy dispersive X-ray analysis (EDX). The samples were sputtered with gold. Slag samples from trials nos. 1, 2, 3, 4 and 6 were thoroughly examined with SEM.

Results

Re-melting trials

The cooling rate was initially about 60ºC per minute, but

Table I
Proportions in weight per cent of raw material used in trial no. 1 to 8

Trial no.	1	2	3	4	5	6	7	8
AOD slag	78	76	75	90	92	91	74	100
Olivine	12	14	15	10	8	9	16	0
Dolomite	10	10	10	0	0	0	10	0

decreased after 15 minutes to less than 20ºC per minute (cf. Figure 1). The time of cooling down to 400°C was approximately 70 minutes. The modified slag in trial no. 1 and the remelted AOD slag in trial 8 disintegrated completely during cooling. The modified slag in trials nos. 2 and 5 disintegrated partially. Four of the modified slag materials did not disintegrate (trials nos. 3, 4, 6 and 7).

Characterization

The chemical analyses are summarized in Table II. The chemical analysis values were normalized in such a way that the sum of CaO, SiO_2 and MgO become 100 per cent. These values were plotted in the phase diagram of the CaO-MgO-SiO_2 system (from Levin *et al.*[5]) and are presented in Figure 2.

The main mineral composition in all trials, according to the mineral characterization with XRD, was Merwinite ($3CaO\cdot MgO\cdot 2SiO_2$) and Cuspedine ($3CaO\cdot 2SiO_2\cdot CaF_2$). Periclase (MgO) was also detected in some samples.

The SEM examination confirmed the occurrence of a calcium oxide/magnesia silicate, which was the predominant mineral in all samples. Periclase and Cuspedine could also be detected. Quantitative spot analyses, where only Ca, Si, Mg and O were detected, was plotted in the CaO-MgO-SiO_2 system (from Levin *et al.*[5]). The plot is presented in Figure 3. Three groups of spot analyses can be detected. The largest group, no. 1 in Figure 3, has an average composition of 53.9 weight per cent CaO, 32.4 weight per cent SiO_2 and 13.7 weight per cent MgO and consists of spot analyses from all examined slag samples. Groups nos. 2 and 3 consist only of spot analyses from trials nos. 1 and 2 and have a varying composition between 60.0 to 68.6 weight per cent CaO, 29.7 to 32.3 weight per cent SiO_2 and 1.2 to 7.7 weight per cent MgO. Figures 4 and 5 are an example of some SEM images of slag from trial no. 6.

The SEM examination also detected small areas of calcium silicate with less aluminium and magnesium. The aluminium content varies in these areas from 0.11 to 1.49 atomic per cent and the magnesium content from 0.14 to 8.36 atomic per cent. The average SiO_2 content was 28.3 atomic per cent and the average CaO content was 66.1 atomic per cent in these areas.

Discussion

The average composition of the spot analyses in the

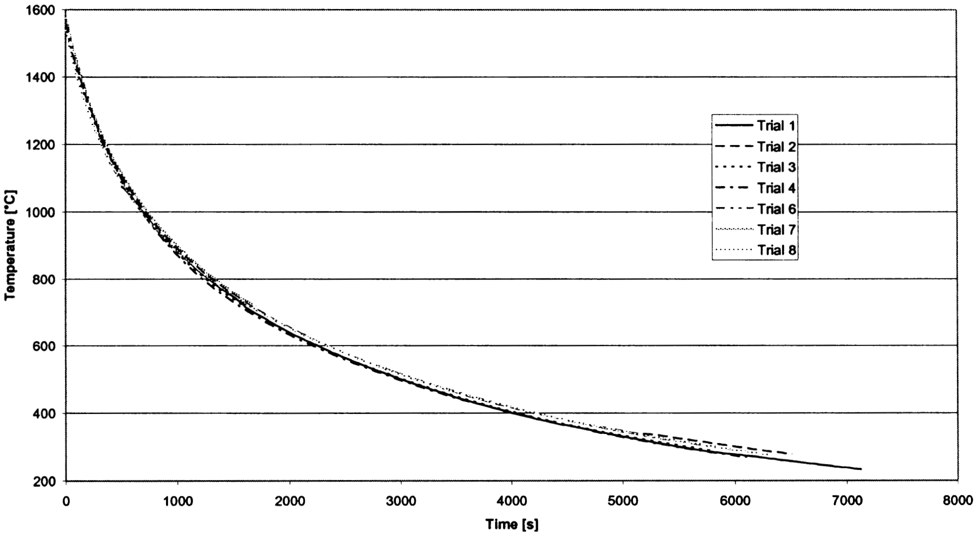


Figure 1. Cooling curves, trials 1–8

Table II
Chemical analysis in weight per cent

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8
CaO	51.1	50.4	49.5	52.5	54.3	53.1	49.3	57.8
SiO_2	30.2	31.0	30.5	32.7	32.8	32.7	31.0	31.2
MgO	14.1	14.4	15.9	10.8	9.8	10.3	15.6	7.6
Al_2O_3	1.7	1.7	1.6	1.6	1.4	1.5	1.6	1.5
Fe tot	1.6	1.5	1.3	1.1	0.6	1.2	1.4	0.6
Cr_2O_3	0.5	0.4	0.4	0.5	0.4	0.5	0.4	0.7
TiO_2	0.4	0.4	0.4	0.5	0.4	0.5	0.4	0.5
MnO	0.3	0.2	0.3	0.3	0.2	0.3	0.2	0.3

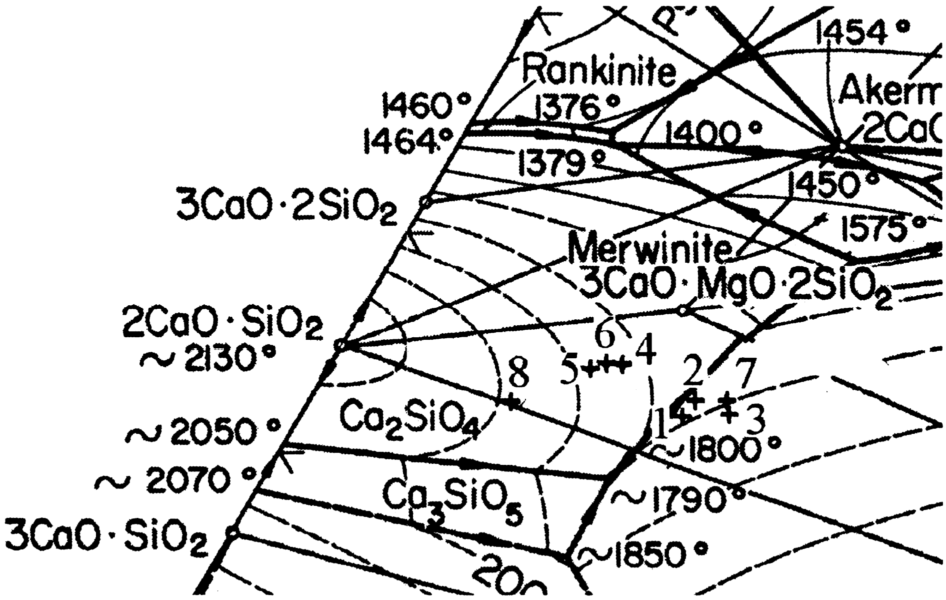


Figure 2. Chemical composition of the slag plotted in the ternary system CaO-SiO_2-MgO

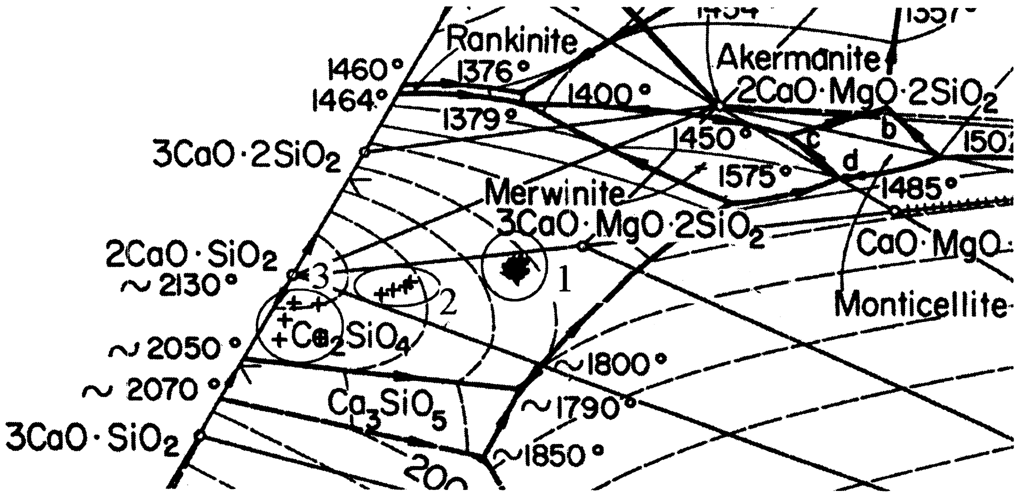


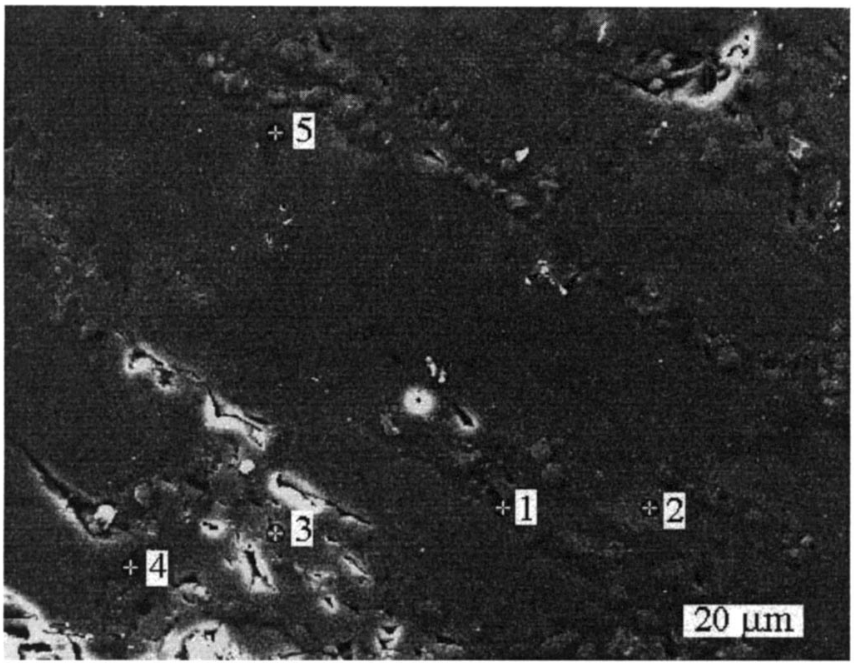
Figure 3. Spot analysis plotted in the ternary system CaO-SiO_2-MgO

groupings in Figure 3 is in between the mineral composition of Merwinite and Bredigite. According to the pseudo binary phase diagram between $2CaO{\cdot}SiO_2$ and $3CaO{\cdot}MgO{\cdot}2SiO_2$ of Moseley and Glasser[4] (cf. Figure 6) there should not exist any solid solution of Bredigite in Merwinite. It is therefore reasonable to claim that the most common material in the modified slag was a mixture of minerals Bredigite and Merwinite. According to the phase diagram in Figure 6, Merwinite should occur first during cooling. Therefore the formation of larger Merwinite crystals could be preferential. This could be the reason why Merwinite is clearly seen and Bredigite is not seen in the XRD analysis. But neither of these minerals disintegrates during cooling.

The formation of Cuspedine is due to the addition of fluorspar to the slag in the AOD process. Cuspedine will not disintegrate during cooling. Periclase was found in the samples. According to the phase diagram of Moseley and Glasser[4] MgO coexists with the high temperature polymorph -$\alpha 2CaO{\cdot}SiO_2$ and Merwinite, but the occurrence of Periclase is most likely due to undissolved MgO. The occurrence of calcium silicates with less aluminium and magnesium content can be the result of solid solution of Al and Mg in di-calcium silicate.

These trials have shown that, with a composition closer to Merwinite and further from di-calcium silicate, it is more likely that the slag will be stabilized. In all of the stabilized slags the mineral mixture of Bredigite and Merwinite is dominant, which is shown in Figure 5.

An implementation of the method to stabilize slag with an increased MgO content will also affect the refining process. The liquidus temperature of the slag will decrease with an increasing MgO content. This can improve metallurgical properties such as viscosity. The sulphur capacity of the slag will probably be more or less unaffected with minor MgO adjustments. The dissolution of magnesia from the refractory will eventually decrease with an increased MgO content in the slag, but minor additions of magnesia will not dramatically affect the metallurgical properties of the slag. A final slag product from MgO stabilization should be stored for 3–6 months to avoid volume instability due to hydration of free lime and or periclase.



Spot	O	Mg	Si	Ca	Al	F
1	41.48	1.53	17.26	39.47	0.27	Trace
2	50.18	6.95	15.92	26.95	n.d.	n.d.
3	38.14	0.88	18.15	42.68	0.15	Trace
4	46.52	10.01	11.93	29.76	1.79	Trace
5	49.07	7.05	16.40	27.48	n.d.	n.d.

(n.d. = not detected)

Figure 4. SEM image of sample from trial no. 6—spot analyses in atomic per cent

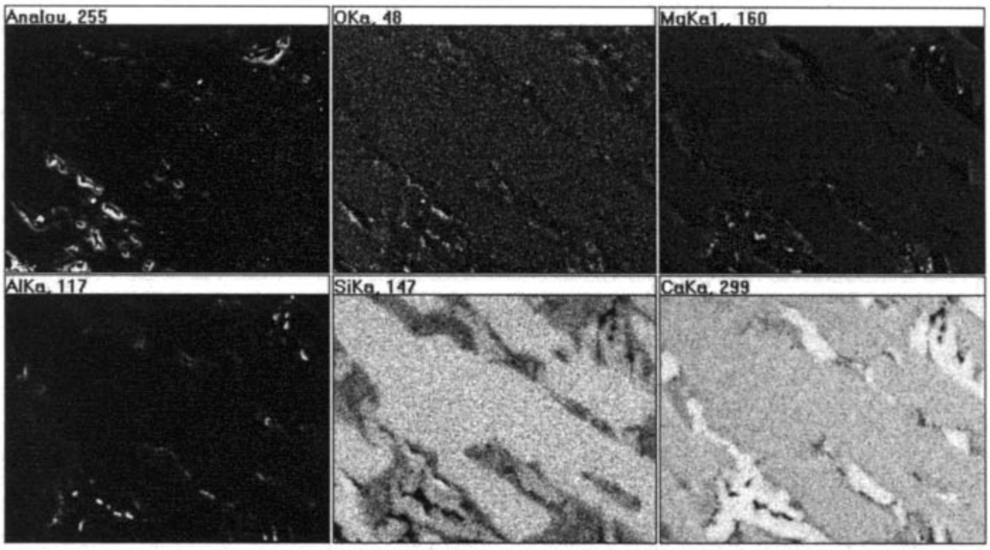


Figure 5. SEM image of sample from trial no. 6—qualitative mapping (same area as in Figure 4)

Conclusion

The performed trials have shown that it is possible to prevent disintegration of di-calcium silicate in slag from stainless steelmaking by increasing the MgO content of the slag. According to the XRD examination, Merwinite was the main Ca-Mg silicate, but the spot analyses from the SEM examination of the samples indicate a mineral mixture of Bredigite and Merwinite.

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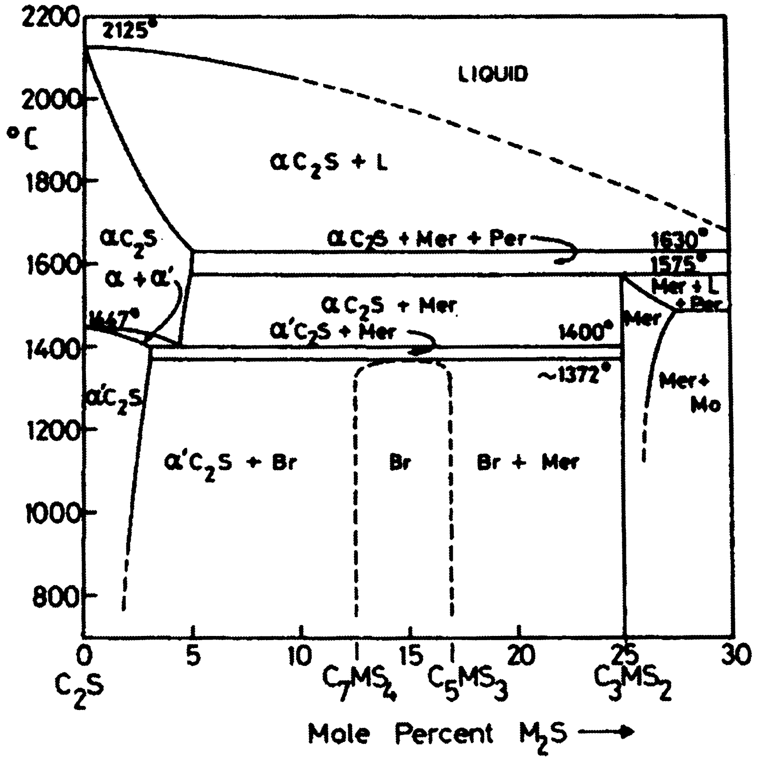

Figure 6. The pseudo binary system $2CaO{\cdot}SiO_2$—$3CaO{\cdot}MgO{\cdot}2SiO_2$ according to Moseley and Glasser[4]

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