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# FAYALITE SLAG MODIFIED STAINLESS STEEL AOD SLAG

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## Abstract

*The specific composition of AOD slag results in the  $2\text{CaO} \cdot \text{SiO}_2$  ( $\text{C}_2\text{S}$ ) phase formation, which transforms from  $\beta$  to  $\gamma$  structure upon cooling, resulting in large volume expansion and fines formation. An expensive boron treatment is currently used to stabilise the  $\beta$  polymorph at high temperature and prevent the slag disintegrate into powder. In this study, the addition of fayalite slag on AOD slag obtained from stainless steel production was evaluated through thermodynamic evaluation and lab experiments. The heat required to dissolve the fayalite was estimated and the required level of fayalite to stable an AOD slag was defined. Detailed microstructure analysis by EPMA clearly shows the distribution of Fe and Zn in the stabilised AOD slag.*

## Introduction

Slags are generated in all stages of stainless steel making process. AOD (Argon Oxygen Decarburisation) slag is the most important part of stainless steel slag by volume. It is well established that air-cooled AOD slag can disintegrate into fine particles due to its high basicity and the conversion of  $\beta$  to  $\gamma\text{-C}_2\text{S}$  during the cooling process<sup>1</sup>. The major mineral phase in a pulverised AOD slag is  $\gamma\text{-C}_2\text{S}$  phase if not properly treated. Therefore such slags cannot be used as construction aggregates.

It is known that there are several methods to avoid AOD slag disintegration. One of the most recognised way is to avoid the  $\beta$  to  $\gamma\text{-C}_2\text{S}$  transformation using either physical or chemical methods<sup>2,3</sup>. Physical stabilisation includes controlling the grain size, cooling rate and surrounding matrix to influence the  $\beta$  to  $\gamma$  transformation<sup>4</sup>. Chemical techniques are based on the incorporation of doping elements in the  $\text{C}_2\text{S}$  crystal. Numerous compounds for the stabilisation have been investigated, of which boron has the best stabilisation potential. It is proved that in industrial scale that 0.2 wt% of  $\text{B}_2\text{O}_3$  addition was sufficient to suppress the dusting of a slag with 51 wt%  $\text{CaO}$ , 33 wt%  $\text{SiO}_2$  and 11 wt%  $\text{MgO}$ <sup>4</sup>. However, the leaching of boron from slag can have a negative effect on the environment. By changing the chemical composition of AOD slag, the  $\text{C}_2\text{S}$  phase is not formed if proper amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  is added at high temperature. In the present study, a  $\text{SiO}_2$  rich source, named fayalite slag is introduced into synthetic AOD slag. The thermal stability of fayalite slag and its addition on AOD slag stability were investigated.

# Experiment

Table 1 lists the chemical composition of the fayalite slag (Metallo Chimique N.V.), measured by XRF technique. It is noted that the slag has only 2.22 wt% CaO, whereas SiO<sub>2</sub> content reaches 27.93 wt%. The other major oxides are FeO, ZnO and Al<sub>2</sub>O<sub>3</sub>. Chemical composition of industrial AOD slag is also summarised in Table 1. Basicity of the AOD slag can vary from 1.4 to 2.3. In this study, AOD slag with a basicity of 2.0 was synthesised in lab. Mixtures of analytical chemicals, such as CaCO<sub>3</sub> and other pure oxides were prepared by low energy mixing, followed by drying and sintering for 1 h in air, at 1620°C respectively. Prior to the AOD slag stabilisation, the thermal stability of fayalite slag in air was investigated. fayalite slag was heated at 900°C for 2 to 18 h, or 2 h at 1000°C. The heating and cooling rate are both 5°C/min. To reveal the role of fayalite addition, 10 or 25 wt% fayalite slag were mixed with the synthesised AOD slag and then heat treated at 1620°C for 1 h in air, with a heating and cooling rate of 5°C/min.

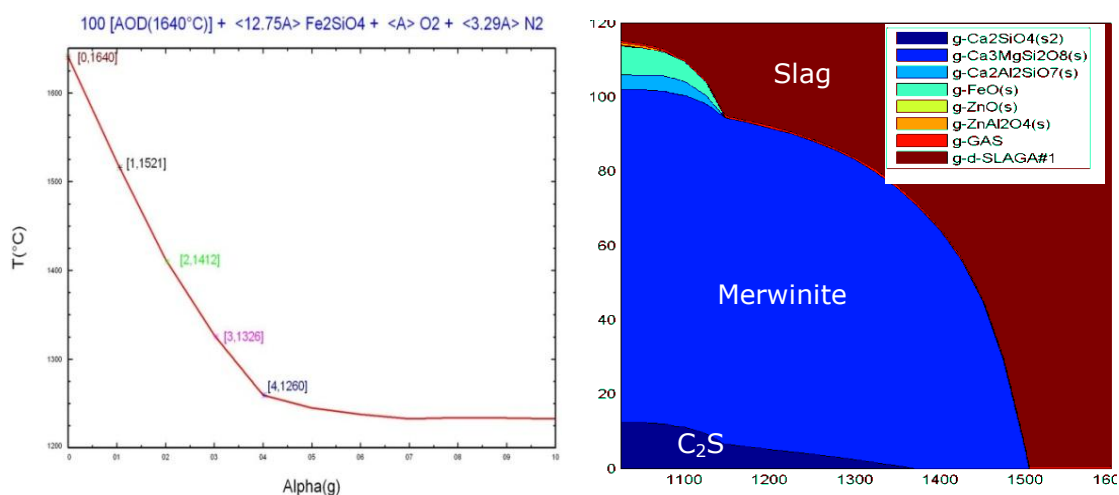
**Table 1:** Chemical composition of the fayalite slag characterised by XRF (in wt%)

Slag	Fe	ZnO	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	MgO	Cr <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	C/S
Fayalite	40.17	6.41	3.71	2.22	27.93	0.72	0.68	/	
Industrial AOD	/	/	1.1-1.4	47.8-61.5	27.2-35.3	4.6-11.4	1.10	5-7	1.4-2.3
AOD	/	/	1.28	59.57	29.78	8.19	/	/	2.0
AODF	/	/	1.22	56.04	28.15	7.71	/	6.0	2.0

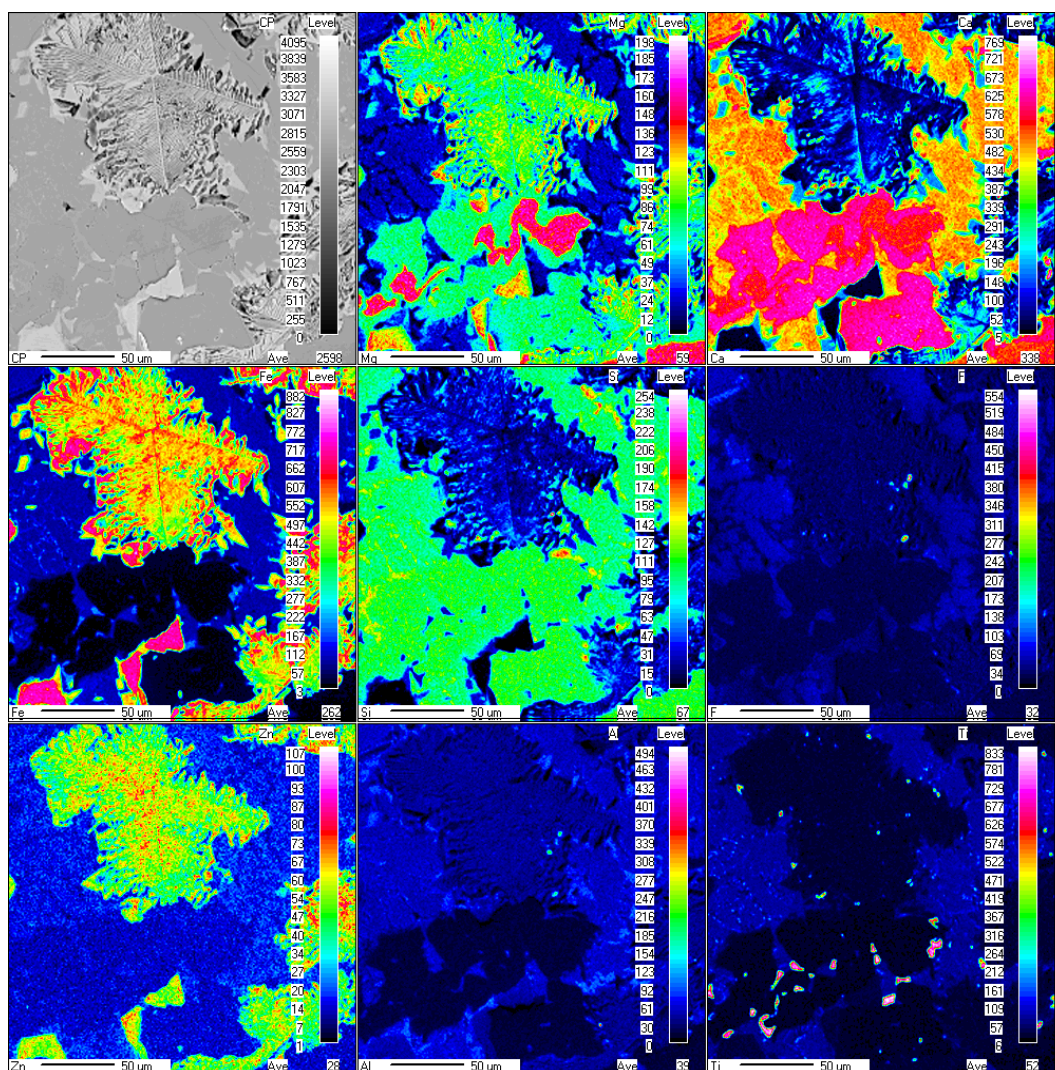
The thermodynamic calculations were performed by FactSage 6.2. The chemical composition was determined by X-Ray Fluorescence spectrometry (XRF, Philips PW 2400). The mineralogy of the samples was determined with X-Ray Powder Diffraction analysis (XRPD, D500 Siemens). Diffraction patterns were measured in a 2θ range of 10-70° using CuKα radiation of 40 kV and 40 mA, with a 0.01° step size and step time of 3 s. Qualitative analysis was performed with the “X’pert High Score plus” PANalytical software. Microstructural characterisation of the slag was performed using electron probe microanalysis (EPMA, JXA-8530F, JEOL Ltd.), equipped with five WDS-type detectors and an EDS-type detector.

# Results and discussion

FactSage calculations show that the oxidation of fayalite slag generates sufficient energy to dissolve the fayalite in to AOD slag. Figure 1 shows the decrease in temperature upon the addition of fayalite slag and air injection at room temperature to hot AOD slag (1640°C). The decrease in temperature is the combination of the energy required to heat up fayalite slag and the exothermic oxidation of fayalite in air. The final product is stable upon the addition of 25 wt% of fayalite slag. This corresponds with a value for alpha in the graph close to 2.5 and a temperature around 1350°C. 60 wt% of the slag is liquid at that temperature. Extra heat is required to get the other 40 wt% liquid as well.



**Figure 1:** Decrease in temperature upon addition of fayalite slag (room temperature) to AOD slag (a) and influence of 20 wt% fayalite slag addition on AOD slag (C/S=2.0) mineralogy (b)



**Figure 2:** Elemental mapping of the 25 wt% fayalite (with CaF<sub>2</sub>) modified AOD slag

The as-received fayalite slag has an amorphous matrix, which has a high concentration of  $\text{SiO}_2$  (43.5 wt%),  $\text{FeO}$  (31.7 wt%),  $\text{ZnO}$  (17.1 wt%) and  $\text{Al}_2\text{O}_3$  (5.7 wt%). 1-2 wt%  $\text{CaO}$  and  $\text{MgO}$  are also found in the matrix. The plate-like grains are fayalite, whereas the round grains are Fe rich oxides. Based on XRD analysis, the crystal phases in the slag are mainly fayalite and  $\text{Fe}_3\text{O}_4$  spinel. After heating the oxides powder for 1 h at  $1620^\circ\text{C}$ , the synthetic AOD consisted of fine powders. According to the Rietveld refinement, the slag contained 84.7 wt%  $\text{r-C}_2\text{S}$ , 8.0 wt%  $\text{MgO}$ , 3.4 wt% merwinite ( $\text{Ca}_3\text{MgSi}_2\text{O}_8$ ) and 3.9 wt% bredigite ( $\text{C}_{1.7}\text{Mg}_{0.3}\text{SiO}_4$ ). With an extra  $\text{CaF}_2$  input, the AOD slag still had  $\text{r-C}_2\text{S}$  matrix. Free  $\text{CaF}_2$  and some cupside phase were found in the AOD slag. 10 wt% fayalite addition is not able to stable the AOD slag, with nearly 60 wt%  $\text{r-C}_2\text{S}$  remained in the slag. With 25 wt% fayalite addition, the slag turned into an intact slag, with the major minerals of merwinite, bredigite and akermanite phases.

Figure 2 shows the EPMA-WDS map of the fayalite modified AOD slag. The slag contains  $\text{CaF}_2$  and 25 wt% fayalite slag and was heat treated for 1 h at  $1620^\circ\text{C}$ . The dendrite grains have a high concentration of Fe, Mg and Zn, whereas Ca and Si are only found in the matrix. Combined with the XRD analysis, it is clear that the dendrites are spinel phase.  $\text{ZnO}$  can be stabilised after the treatment. No fayalite is observed in all the treated slag.

## Conclusions

The fayalite slag reacts with  $\text{O}_2$  and form  $\text{Fe}_2\text{O}_3$ . Heat is generated along with this reaction. Addition of 25 wt% of the fayalite slag is sufficient to stable a high basity AOD slag ( $\text{C/S}=2$ ). With 10 wt% fayalite addition, the AOD slag still contains 60 wt%  $\text{r-C}_2\text{S}$  phase.  $\text{ZnO}$  from fayalite slag is incorporated in a Fe-Mg-Zn spinel phase in the stabilised AOD slag.

## References

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