

MICROSTRUCTURAL CHANGES IN FREEZE LININGS DURING ZINC FUMING PROCESSES

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Introduction

A freeze lining is a solidified layer of slag which adheres to a cooled furnace wall. This technique of furnace protection can be used in pyrometallurgical processes where degradation of refractory material occurs, for example in zinc fuming processes. Due to volatilisation of ZnO and PbO and the addition of new slag batches, the furnace lining must withstand changes in bath composition and atmosphere.

Research on freeze linings in zinc fuming processes and with Zn rich slags exists already¹⁻⁴ but dynamic bath compositions were not yet considered. Campforts *et al.*^{5,6} described microstructures in freeze linings based on a subdivision in zones with different growth morphologies and scales. Fallah-Mehrjardi *et al.*⁷ continued the microstructural investigation of freeze linings and stated that under some conditions an additional subliquidus boundary zone can form.

In this research the purpose is to investigate the effect of the change from an Al₂O₃-CaO-FeO-SiO₂ slag to an Al₂O₃-CaO-FeO-PbO-SiO₂-ZnO slag on a freeze lining. With microstructural analysis it is shown how the freeze lining composition is modified.

Methodology

A similar cooled probe setup was used as in earlier freeze lining research². Air (20 m³/h) is used as cooling agent. The bath temperature is measured by a thermocouple 50 mm below the probe. Two other thermocouples measure the temperature in the freeze lining 15 mm above the probe bottom, at distances of 7 mm and 17 mm (measured before the experiment) from the probe wall. Starting material (3000 g, Table 1) is molten at 1250°C in an Al₂O₃ crucible. To limit the oxidation of FeO to Fe₂O₃ and to prevent crust formation, 100 l/h N₂ gas is blown above the crucible and cokes (30 g, size: 3 mm) are placed on the bath surface. Once the slag is molten, the crucible is rotated (25 rpm) and the probe is placed 30 mm

deep in the slag. A freeze lining is formed during 90 min. Next, without removing the probe, ZnO and PbO are added to obtain the final bath composition (Table 1). The probe stays again submerged for 90 min. Afterwards, the probe is removed quickly and quenched in water. The bath is sampled at the start and end of the experiment. A cross section of the freeze lining is prepared for analysis with an electron microprobe. The slag samples are milled and glass beads are made for XRF analysis.

Table 1: Targeted slag composition

(wt%)	total Fe	SiO ₂	CaO	Al ₂ O ₃	ZnO	PbO
initial bath	25.80	39.40	24.71	0.56	0	0
final bath	23.2	35.46	22.29	0.5	8	2

Results and discussion

Table 2 shows the XRF results of the bath samples. The target compositions are well approached, except for the Al₂O₃ content due to the dissolution of Al₂O₃ from the crucible and protective thermocouple sheaths during the experiment.

Table 2: Obtained compositions (measured by XRF analysis on glass beads)

(wt%)	total Fe	SiO ₂	CaO	Al ₂ O ₃	ZnO	PbO
initial bath	25.1	39.5	24.1	4.2	0	0
final bath	22.8	34.4	21.4	6.4	6.9	1.6

Figure 1 shows all temperature data. During the first 90 min the bath temperature and temperature in the freeze lining slightly increase after they stabilised from the immersion. During the PbO and ZnO addition (between 90 and 99 min) the bath temperature decreases due to the addition of cold material. During the second part of the experiment, the temperature close to the probe stays rather constant, but that 17 mm from the probe increases by 50°C. The temperature changes after 160 min are probably caused by the removal of a crust on the bath surface.

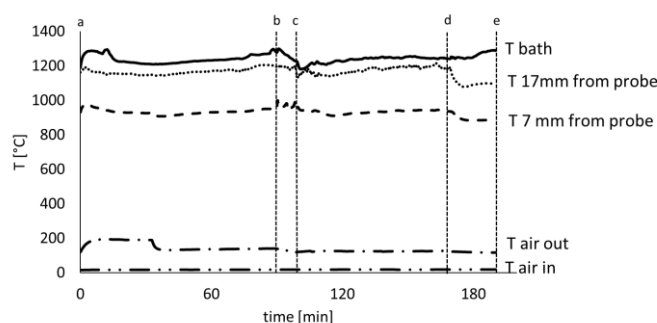


Figure 1: Temperatures during the experiment; a: 0 min, start immersion b-c: 90 min-99 min, PbO and ZnO addition d: 160 min, crust removal e: 190 min, end immersion

Six zones are distinguished in the cross section (Figure 2). Zone 1 is a glassy layer containing small crystals. Zone 2 consists of a mixed glassy and microcrystalline layer, while zone 3 is a closed crystalline layer. Zone 4 and 5 both contain an open crystalline structure and can thus also be seen as a whole. In zone 5 however, the amount of crystals is limited and Pb and Zn were measured in certain phases. The composition of liquid in zone 4 resembles the original slag whereas the composition of liquid in zone 5 matches with the final slag. Zone 6 contains the bath material with some crystals. Most crystals in the freeze lining are olivine, melilite and spinel.

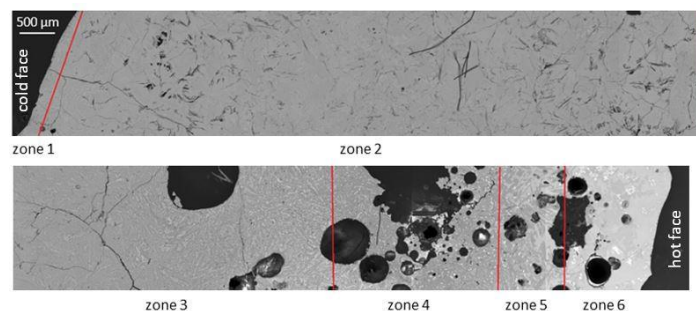


Figure 2: cross section of the freeze lining

To determine how the freeze lining is altered, the microstructures in zones 4, 5 and 6 (Figure 3), and the normalised elemental analyses (Table 3) are given. Quenched liquid, melilite and spinel phases are observed. In zone 4 and closer to the probe no Zn or Pb was measured, while in zone 5 and 6 the quenched liquid contains Zn and Pb and spinel crystals contain Zn. The measured concentrations are however lower than in the final slag. Only the two outer zones are altered. Zone 1, 2, 3 and 4 stay unaffected.

The modification has two possible causes: decay of the exterior zones formed from the initial slag, which are rebuilt from the final slag, or the diffusion of elements into the existing freeze lining. It is expected that the modifications are an effect of diffusion, since the Zn and Pb concentration is lower than in the final slag. This would mean that in a Zn fuming furnace the freeze lining thickness will not change significantly by changing bath compositions. To validate this theory a comparison between the observed freeze lining and those formed solely from the initial and from the final slag, will be added in future work.

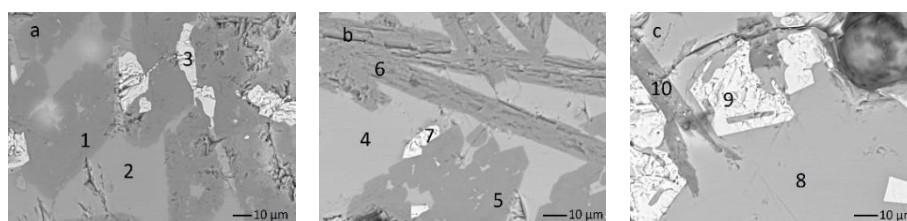


Figure 3: microstructures of zone 4 (a), zone 5 (b) and zone 6 (c)

Table 3: Normalised measured compositions (wt%) of the phases in Figure 3

Point	Si	Fe	Ca	Al	Zn	Pb	O	Phase
1	23.8	11.7	23.9	0.1	0	0	40.4	melilite
2	18.4	26.0	13.0	3.1	0	0	39.5	quenched liquid
3	0.7	70.0	1.6	2.4	0	0	25.4	spinel
4	19.1	21.7	13.6	2.9	2.2	1.2	39.4	quenched liquid
5	24.9	9.5	24.5	0	0.1	0	41.0	melilite
6	25.0	9.2	24.7	0	0.1	0	41.0	melilite
7	1.7	63.6	1.2	3.7	1.8	0	28.0	spinel
8	19.3	17.5	15.7	2.3	4.2	2.4	38.7	quenched liquid
9	0.2	68.3	0.3	2.0	4.5	0.2	24.5	spinel
10	25.2	3.9	28.5	0.1	0.5	0.1	41.7	melilite

Conclusion

In this experiment the effects of a changing bath composition by ZnO and PbO additions on a freeze lining were investigated. Zn and Pb are only observed in the two outer zones of the freeze lining: an open crystalline layer and the bath material with some formed crystals. The zones closer to the probe are unaffected by the bath composition change. Zn is mainly found in the amorphous phase and the spinel crystals while Pb is only found in the amorphous phase. It is expected that the changes are caused by diffusion.

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