KU LEUVEN

Proceedings of the
THIRD INTERNATIONAL

SLAG VALORISATION SYMPOSIUM

THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

19-20 March 2013
Leuven, Belgium

Editors Annelies Malfliet, Peter Tom Jones, Koen Binnemans, Özlem Cizer, Jan Fransaer, Pengcheng Yan, Yiannis Pontikes, Muxing Guo, Bart Blanpain

VISCOSITY AND THERMAL PROPERTIES OF SLAG IN THE PROCESS OF AUTOGENOUS SMELTING OF COPPER-ZINC CONCENTRATES

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Abstract

The temperature dependencies of slag viscosity in the process of autogenous smelting of copper-zinc concentrated products in Vanyukov furnaces at the Sredneuralsky Copper Smeltery JSC have been revealed. Values of viscous flow activation energy have been determined. Phase transition temperatures in the processes of slag heating and cooling have been measured. The influence of calcium oxide additives on viscosity and on the crystallised slag liquidus point has been evaluated. The results obtained may be used for slag composition improvement with the purpose to reduce copper losses and simplify material preparation to subsequent depletion operation.

Introduction

The smelting of copper-zinc concentrates in a Vanyukov furnace (VF) is accompanied by formation of a significant amount of slag. The study of its properties is among the powerful tools for the improvement of production facilities operation and high-priced metals saving. Viscosity and meltability of the slag are the most important properties for optimal selection of technological process modes. Monitoring the slag properties in the existing VF-assisted production process enables to estimate the limits of slag variations depending on composition and temperature. Increasing the calcium oxide content is one of the ways to control the slag properties, but this approach requires extra study.

Methods and Materials

The slag viscosity has been measured by means of a home-made oscillatory viscometer[1]. The relative error on the viscosity measurement was ±5%. Thermal behaviour of the slag has been examined using the thermoanalyser NETZSCH STA 449C Jupiter.

Test subjects were various slag blends forming in the process of oxidising melting of copper and zinc concentrated products in VF for copper production at the Sredneuralsky Copper Smeltery JSC. These specimens were picked out from the mixers. Slag compositions are shown in Table 1. Apart from the compounds mentioned below, the slag samples contain 0.21-0.27% Pb, 0.01-0.10% As and 0.06-0.09% Sb. Furthermore, the properties of the slag obtained by adding up to 13% of calcium oxide to industrial specimen have been studied.

Table 1: Chemical analysis of slag sample components

Sample	Content, wt%							
	Fe	SiO_2	Al_2O_3	CaO	Cu	Zn	S	MgO
1	38.0	33.2	3.7	3.2	0.80	4.55	1.0	1.0
2	35.5	33.5	4.2	3.1	0.70	4.92	1.0	1.1
3	34.9	33.8	4.0	3.1	0.62	5.05	0.8	1.2
4	36.8	33.0	4.3	3.2	0.71	3.64	0.9	1.4
5	37.9	30.3	3.6	2.8	0.97	3.74	1.1	1.1
6	36.2	31.9	3.9	2.4	0.71	3.82	0.9	1.1
7	36.5	31.5	3.9	2.5	0.77	3.89	0.9	1.1
8	36.7	31.3	4.0	2.6	0.76	3.47	1.0	1.1

Results

The Vanyukov process was developed for autogenuous smelting of sulphide concentrated products and is characterised by liquid slag and matte generation[2]. The microstructure of the crystallised slag of copper-zinc concentrates smelting in VF at the Sredneuralsky Copper Smeltery JSC is represented by iron silicate, magnetite, fine sulphide inclusions and matte particles[3]. In terms of phase composition and structure this microstructure is close to that of typical slag obtained by the same way in the process of autogenous smelting at the other copper-smelting plants[4].

The results of the molten samples viscosity measurement are within the range 0.23–0.48 Pa·s at 1300°C and 0.26–0.58 Pa·s at 1245°C (Figure 1). Slag # 5 shows divergent viscosity values as it achieves 1.30 Pa·s at 1245°C. This may be explained by a higher magnetite content (9.1%) and, probably, by a lower content of SiO_2 (30.5%). The temperature dependence of the viscosity η is represented in the form of the Arrhenius equation.

The temperatures of the slag crystallisation beginning have been determined from viscosity data as inflection points of $\ln\eta$ curves plotted against reciprocal temperature and viscous flow activation energy has been calculated from the slope of these curves in the area of melt homogeneity.

The estimated values of viscous flow activation energy and crystallisation temperatures of molten slag are within the ranges 21.8-81.8 kJ/mole and 1047-1235°C respectively. Viscosity characteristics of the slag under consideration are close to those of the slag obtained by VF processing at a Balkhash Copper Smelter[5].

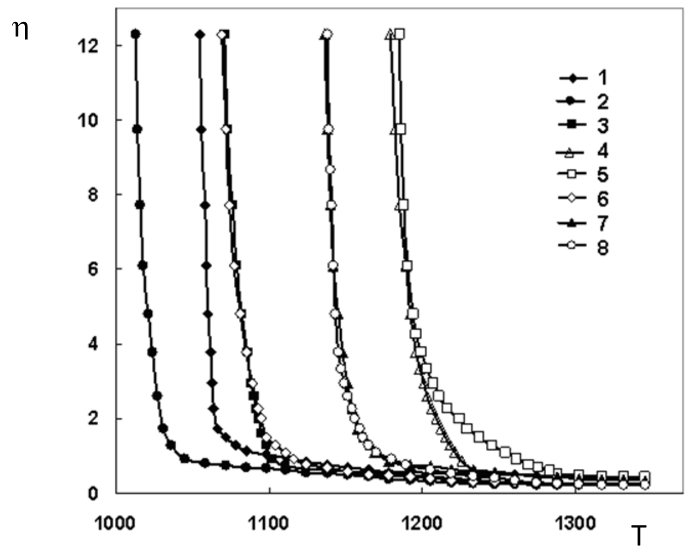

Figure 1: Apparent viscosity of the slag samples # 1-8 vs temperature

The growth of viscosity with increasing magnetite content in the slag is observed (Figure 2). Adding of 13% of calcium oxide to the slag # 8 decreases viscosity value of the latter down to 0.08 Pa·s at 1300°C. The slag samples with higher calcium oxide content are characterised by lower values of viscous flow activation energy (13.2-31.5 kJ/mole). It was shown by experiments that the melts with higher viscosity contain more copper. This observation may be attributed to imperfect separation of the liquid bath into matte and slag during the process of smelting. According to the results of viscosity measurement the minimal copper losses with the slag are expected for the following compositions: 35-36% Fe, 31-32% SiO_2, 7-8% CaO with Al_2O_3 and MgO content about 4.0% and 1.0%, respectively. Temperature conditions of the smelting process should provide homogeneity of the melt, i.e. should be at the level of 1240-1260°C.

Results of thermal analysis of slag # 1 indicate no sample mass loss when heating until 900°C. Further heating up to 1200°C results in minor sample mass decrease (by 1.8%)

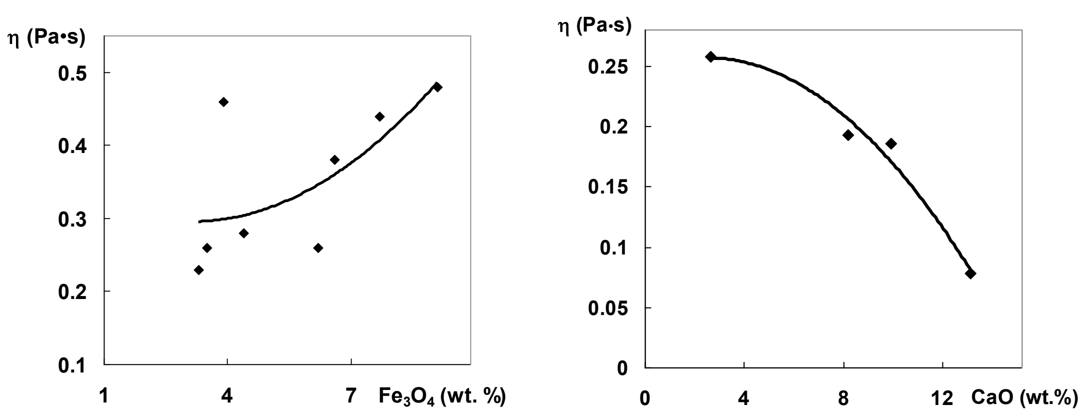

Figure 2: Slag viscosity change depending on Fe_3O_4 (left) and CaO (right) content, both measured at 1300°C

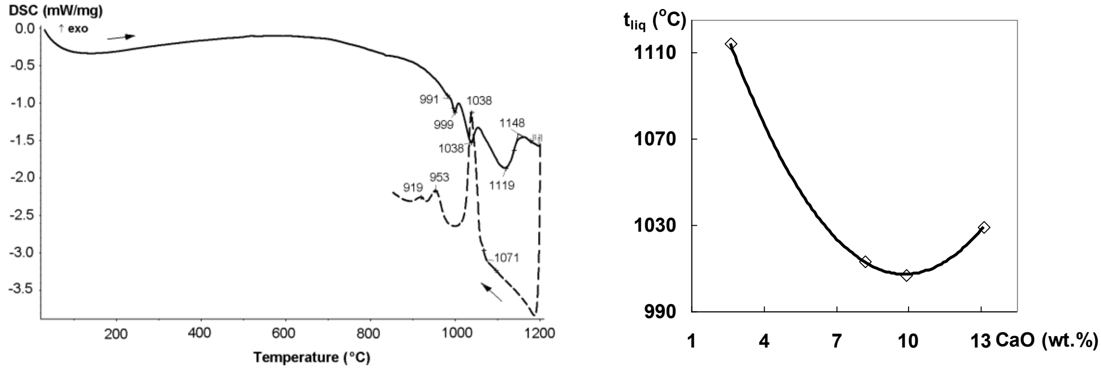

Figure 3: a) DSC heating (solid) and cooling (dotted) curves of the slag # 1. Sample weight is 22.53 mg; b) Liquidus temperature of the slag # 8 progressively diluted with CaO

caused by interaction of sulphide and oxide components of the slag. Multiple endothermic peaks with the onset at 991°C are observed in the heating curve (Figure 3a). The first thermal effect at 999°C corresponds to sulphide melting. Two other endothermic peaks appear at about 1038 and 1119°C due to the melting process of oxide components and may be considered as the indicators of solidus and liquidus of the slag. In the process of the sample cooling liquid phase crystallisation starts at 1071°C and is followed by overlapping peaks at 1038, 953 and 919°C.

General results of heating experiments for all the samples show that matte constituent melts between 915 and 991°C and liquidus temperature of the oxide phases lays within 1103-1119°C. Melting point of the oxide eutectic composition is close to 1040°C. Crystallisation range measured by cooling of the molten slag is 1017–1071°C. It was found that the slag tends to subcool by 71°C on an average. Adding of calcium oxide (up to 10%) to the slag of VF makes the samples melting temperature lower. Excessive increase of CaO content (over 10%) may result in a rise of the slag melting temperature (Figure 3b).

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