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IN-SITU OBSERVATION OF ZnO CONTAINING Cu SLAG SOLIDIFICATION BY CONFOCAL LASER SCANNING MICROSCOPE

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Introduction

Copper slag is produced during pyrometallurgical production of copper. In general, the main components in the copper slags are Fe_xO and SiO_2 with an amount of 25 to 50 wt.% for each. The most common copper slag is the iron (Fe^{2+}) silicate crystal and glass containing dissolved accessory impurities, such as Al_2O_3, CaO, ZnO, PbO, Na_2O and MgO[1,2]. When molten slag is cooled slowly, it forms a dense crystalline product, whereas through rapid solidification i.e. water granulation, gives rise to an amorphous granulated slag.

The density and properties of the cooled slags typically depend on the formation and content of crystalline phases, and the morphology of the crystalline phases. It is known that slag solidification determine microstructure of the slag which affects its properties[3-4]. Rapid cooling by granulation aspires to produce a predominantly amorphous material that will find application in blended cements and as a precursor in inorganic polymers. Controlled cooling aspires to produce a microstructure with certain specific crystal growth that will find application as a high quality glass-ceramic aggregate. Therefore, it is essential to provide fundamental information related to the crystallization characteristics of the coper slag to enable control of its eventual structure and composition.

A CCT diagram is a useful guide for the design of hot processing methods of molten slags. A few methods have been reported to study the crystallization characteristics of molten slags, such as the differential thermal analysis method[5] single and double hot thermocouple technique[6,7] as well as confocal laser scanning microscopy technique[8,9]. In the current work, the crystallization of a primary phase in molten Cu

slag was observed in situ by CLSM method. The influence of crucible materials on Cu slag solidification was investigated initially. CCT diagram of the Cu slag was then constructed based on the experimental data, using Pt foil as crucible.

Material and methods

The water granulated Cu slag was taken from a metal recycling company in Belgium. The chemical composition of the slag sample was determined by XRF analysis. The fayalitic slag has a FeO content of 57 wt.% and SiO_2 of 26 wt.% and a ZnO, Al_2O_3 and CaO content of 6, 3 and 2 wt.% respectively. The Cr, Pb and Cu oxides are found in concentrations < 0.7wt.%. The mineralogical composition indicates an amorphous content of around 73 wt.%, together with the main crystalline phase of fayalite (24 wt.%) and balanced amount of spinel. The slag samples were ground to less than 80 µm.

The crystallization behavior of sample during cooling was done in an infrared (IR) heating chamber combined with a confocal scanning laser microscope (CSLM, Lasertec, 1LM21H-SVF17SP, Japan). Approximately 10 mg slag sample is heated by a 1.5 kW halogen lamp in a focal point of a gold plated ellipsoidal chamber while the sample is in the focal point. This infrared heating system can reach temperatures up to 1700 °C in a few minutes. The sample temperature is measured with a B-type thermocouple at the bottom of the platinum sample holder. The CLSM chamber was flushed three times with purified Ar before it was filled with 1 atm Ar. The slag sample was either heated in an Al_2O_3 crucible or a thin Pt foil at a rate of 200 °C/min to 1250 °C and dwelled for 2 minutes to homogenize its composition. After that, the slag was cooled down to 500 °C at a rate of 30 to 2400 °C/min. The images were monitored and recorded at the interval of 30 frames per second. The precipitation temperature of primary crystals can be determined from the images. After cooling, some slag samples were ground and polished to a mirror surface. The microchemistry and microstructure of the polished slag were analyzed by FEG EPMA-WDS (JEOL Hyperprobe JXA-8530F) at 15 kV and 20 nA.

Results

Continuous cooling in an Al_2O_3 crucible

When the slag sample was melted in an Al_2O_3 crucible, it was hard to focus the laser microscopy, therefore was impossible to take clear images and record the onset of crystallization during the melt cooling. Figure 1a shows a cross-sectioned Al_2O_3 crucible with the melted slag inside, cooled at 500 °C/min from 1250 to 500 °C. Due to the good wetting between Al_2O_3 and the molten slag, the liquid surface was

unstable and tended to move to the Al_2O_3 interface. Moreover, a heterogeneous cooling of the slag is expected due to the different slag thickness. According to Figure 1b, the dominate crystal is fayalite (Fe_2SiO_4), followed by some dispersed Al-Zn-Cr spinel particles, with the dark-grey glass phase present as a main mass. The fayalite grains are typical dendritic growth and subparallel orientation in space as well as not fully formed skeletal crystals.

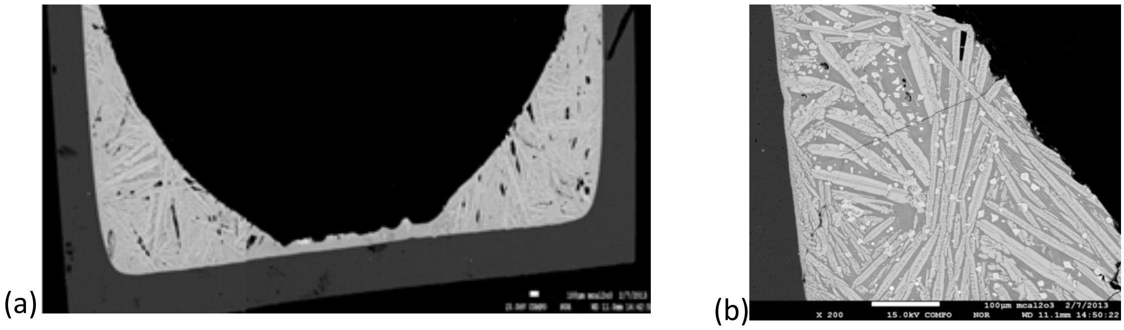

Figure 1: Overview of a cross-sectioned slag sample melted in an Al_2O_3 crucible (a) and detailed microstructure of the slag (b).

A detailed WDS elemental mapping of the slag is presented in Figure 2. The dendritic fayalite grains are rich in Fe and Si oxides, as well as a small amount of Zn and Mg oxides. Besides the Fe and Si oxides, the glass matrix contains high concentration of Al, Ca and Na. Next to the Al_2O_3 crucible interface, a dense and fine grain sized spinel layer was observed. The spinel contains mainly Al and Zn oxides. It is apparent that the Al_2O_3 crucible reacted with the slag and formed the spinel layer. Due to the unstable liquid slag and interfacial reaction as well as inhomogeneous temperature, it is concluded that Al_2O_3 crucible is not ideal for the high temperature experiments.

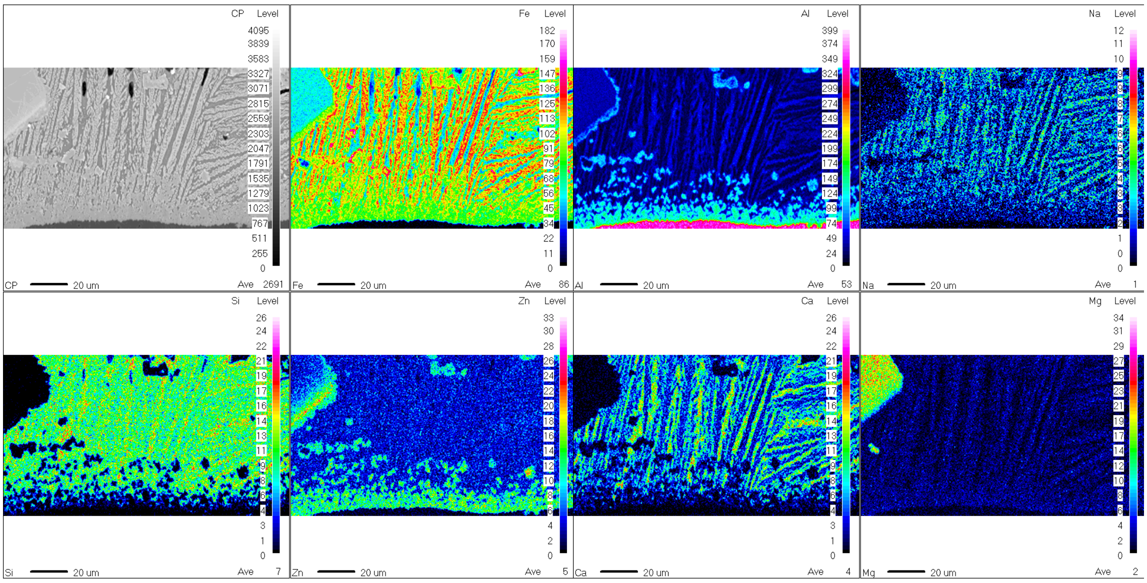

Figure 2: Elemental mapping of the slag melted in an Al_2O_3 crucible

Continuous cooling on a Pt foil

By using a Pt foil sample holder, it is able to observe the onset of crystallization in the melts through a single CSLM experiment at different cooling rates. The temperature profile applied in present study is shown in Figure 3a. The sample was heated to 1250 °C at 200 °C/min, which is around 200 °C higher than the corresponding solidus temperature. The sample was then quenched at 30 to 2400 °C/min to different temperatures in Ar.

(a)

(b)

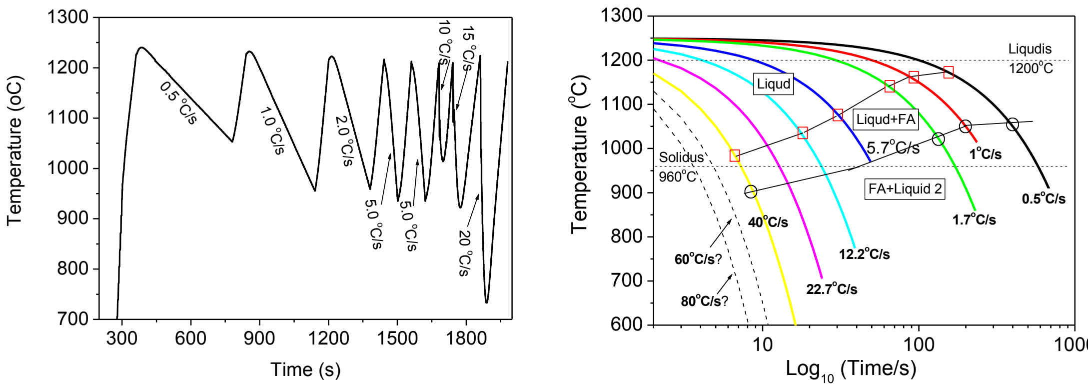

Figure 3: Temperature profile of a single CSLM experiment to obtain crystal onset temperature at cooling rate (a) and the obtained CCT diagram (b).

During the controlled cooling, the onset temperature was visually confirmed from the video images of the CLSM. The characteristic morphologies of precipitation and growth of the dendritic fayalite in the melt are presented in Figure 4, when continuously cooled at 255 °C/min. At 1250 °C, the liquid slag is in equilibrium with some Cr-rich spinel particles. With decreasing temperature, the dendritic fayalite started precipitating at 1106 °C and growth rapidly during cooling. It is found that the onset temperature is significantly influence by the cooling rate. As shown in Figure 3b, the higher the cooling rate of the slag, the lower the onset temperature of the fayalite formation. However, a cooling rate higher than 2400 °C/min is needed to obtain a full amorphous slag.

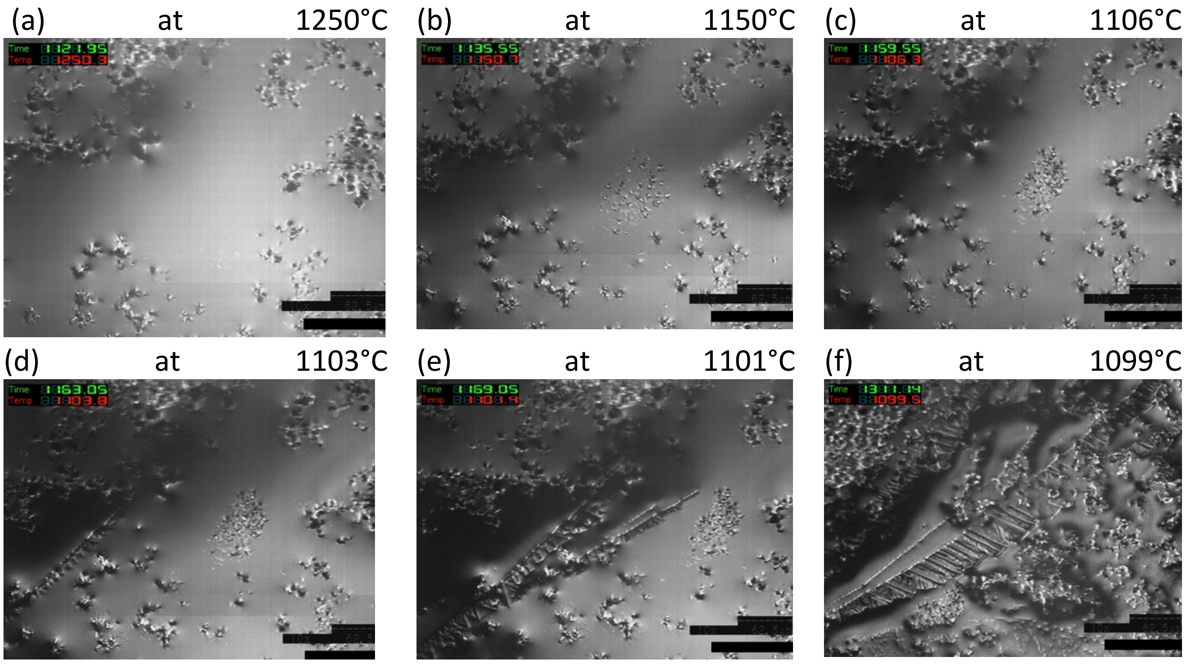

Figure 4: CLSM micrographs of crystallization of the Cu slag melt during continuous cooling at 255 °C/min.

Conclusions

The effect of crucible materials on the Cu slag solidification was investigated by the CSLM method. The Al_2O_3 crucible is not ideal for the high temperature experiments due to the moving liquid slag and the slag/Al_2O_3 reaction as well as inhomogeneous temperature distribution. On the other hand, the Pt foil is able to in-situ observe the slag solidification behavior at different cooling rates. The onset temperature is decreased continuously with the increased cooling rate. A cooling rate higher than 2400 °C/min is however needed to make a full amorphous slag.

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