Quantitative analysis by *in situ* synchrotron X-ray radiography of the evolution of the mushy zone in a fixed temperature gradient

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ABSTRACT

This paper deals with a series of experiments dedicated to the analysis of the time evolution of a mushy zone in a fixed temperature gradient, carried out on the BM05 beamline at the European Synchrotron Radiation Facility (ESRF) on Al–Cu alloy. Because most of phenomena involved in this evolution are dynamic, *in situ* and real time investigation is essential for conducting a thorough analysis as a function of time. Synchrotron X-ray radiography is a non-invasive visualization technique, perfectly suited to such a study since it is able to reveal the microstructural changes of the mushy zone during the holding stage. In addition, we extended our analysis by performing advanced image processing of synchrotron X-ray radiographs to characterize the solute distribution in the liquid phase. These measurements gave us crucial information for understanding the competition between the diffusion processes in the bulk and the mushy zone. Moreover, combining these data with mass balance equations at the two boundaries of the mushy zone enables us to demonstrate the major role of solute diffusion in the dynamics of the mushy zone, from the early instants to the final state of the holding stage.

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1. Introduction

In a context of nuclear safety, the melting of the core and the subsequent flow down of the molten materials (a mixture called corium) onto the concrete basement is one of the most severe reactor accidents that can occur [1]. When molten corium makes contact with the cold concrete basement, a mushy zone (partially solid–liquid region) can form against a cold wall, assuming dendritic directional solidification [2]. Owing to the significant residual power dissipation in the materials ($\sim 1\,\mathrm{MW/m^3}$), the temperature field reaches a quasi-steady state and thus does not significantly evolve over a long period (months), with a temperature gradient of the order of $10^2\,\mathrm{K/mm}$. The subsequent time evolution of the mushy zone constitutes a key issue because it impacts the heat flux distribution through the various structures of the reactor, with the important question of the lifetime of the concrete wall which is the last barrier of protection. Besides the nuclear interest of this topic, the evolution of a mushy zone

towards a solid crust can also occur in a wide variety of processes, such as the solidification of sea ice or lava lakes [3].

For the time being, the complexity of the topic (multiphase and multi-component phenomena, at different time and spatial scales) prevents any global approach which can take into account all the phenomena. To the best of our knowledge, very few models have been proposed to explain certain phenomenological aspects of the process [4,5], with oversimplified approaches. In addition, there is no validation of these models due to the lack of dedicated experiments in well-defined and controlled conditions. In this work, we aim to investigate experimentally the evolution of a mushy zone for a binary alloy in a fixed temperature gradient, when the cooling phase that is at the origin of the mushy zone is suddenly stopped and all other experimental control parameters are maintained constant. During this phase, which will be termed the *holding stage* in this paper, the mushy zone undergoes a slow evolution which is governed mainly by the complex interaction of various diffusion-controlled phenomena inside and at the boundaries of the two-phase region. A first diffusion-controlled phenomenon to mention is the Ostwald ripening or coarsening process, which is related to the reduction of the interfacial energy of the primary phase. In alloys, the coarsening process proceeds by the diffusion of mass from regions with high interface curvature to

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those of lower interface curvature, which results in a more globular microstructure with a larger size scale [6,7]. Secondly, in the presence of a temperature gradient, a solute gradient exists in the liquid phase of the mushy zone and the solute diffuses from the cold side to the hot side of the mushy zone in the vertical liquid channels. This causes a slow solidification of the bottom part of the mushy zone, as shown by Nguyen-Thi et al. [8]. This solute diffusion is also responsible for the migration of liquid inclusions through a solid by temperature gradient zone melting (TGZM) [8,9] which helps in the purification of the solid as shown by Pfann et al. in the case of metals [10]. Thirdly, Combeau et al. [4] recently showed that, in the presence of a gradient of liquid fraction, a non-zero net flux of solute induced by diffusion exists in the direction of the gradient of the liquid fraction, even with a fixed solute gradient in the liquid phase like in the case of a mushy zone created by directional solidification where the liquid fraction decreases from the top to the bottom. In that case, there is a net flux of solute towards the upper part of the mushy zone, which tends to locally decrease the amount of solute in the liquid phase. According to the phase diagram, this yields to solidification within the mushy zone, in particular in the upper part of the interdendritic channels, where the liquid fraction gradient is the highest.

In a recent paper [11] we have clearly identified by using *in situ* synchrotron X-ray radiography at the ESRF the successive steps in the evolution of a mushy zone during the holding stage. Those preliminary results are in qualitative agreement with the numerical model developed by Gewecke and Schulze [5], describing the evolution of a mushy zone formed during the solidification of a binary alloy cooled from below in a finite height tank, taking into consideration only the solute diffusion and neglecting the latent heat.

In the present work, in addition to qualitative observations of the microstructural changes, we extend our analysis of the time evolution of the mushy zone by performing advanced image processing of synchrotron X-ray radiographs to quantitatively characterize the solute distribution in the liquid phase, within the mushy zone and in the liquid bulk, for the whole duration of the experiment. In a second step, these measurements were injected in the solute balance equation at the solid crust interface to calculate its evolution as a function of time and compared with experimental observations.

2. Experimental details

2.1. Experiments

Due to the complexity of the subject and the technical difficulties of handling melting-solidification experiments of alloys with very high melting temperatures such as Corium (about 2000 °C), we choose to work with a model Al–Cu binary alloy. In addition to having a much lower melting temperature than corium, this alloy has the great advantage of being well characterized in terms of physical and chemical parameters. The sample size was 37 mm long, 5 mm wide and 0.2 mm thick and was sandwiched between two graphite foils and two molybdenum diaphragms, held together with two molybdenum clips and fixed to a sample holder [12-14]. The whole assembly was inserted into a vertical Bridgman furnace and a series of four experiments (labeled E1–E4) on the same sample was carried out at the ESRF (European Synchrotron Radiation Facility) in Grenoble, France, on beamline BM05. The typical duration of an experiment was in the range 1–6 h, including the solidification and the holding stages (Table 1). The first experiment E1 was mainly used to adjust the heater temperatures (initial and final values), as well as the initial solid–liquid interface position. Consequently, even if the general features of the process were similar to the subsequent

experiments, quantitative analysis was performed only for the three last experiments (E2–E4), for which thorough analysis at every stage of the process could be performed. For the solute measurements, they were only possible for the last experiment E4 for reasons explained in Section 2.3.

2.2. In situ characterization by synchrotron X-ray radiography

The mushy zone evolution was observed using *in situ* synchrotron X-ray radiography [14], which has become an important tool in solidification science due to its non-destructive nature and its ability to visualize the microstructure in real time. The main surface of the sample (37 mm × 5 mm) was set perpendicular to the incident monochromatic X-ray beam at 13.5 keV. A Fast Readout–Low Noise (FReLoN) CCD camera developed at the ESRF [15] was used as the detector and the camera optics were chosen so as to visualize the solidified mushy zone plus some of the liquid bulk (field of view $= 5.3 \times 8.3$ mm^2) with sufficient spatial resolution (pixel size 7.46 µm × 7.46 µm) to reveal the microstructural features. Images of the solid–liquid zone were recorded at a maximum frequency of about 0.3 Hz and it was thus possible to display videos (image sequences) of the mushy zone evolution.

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2.3. Image processing for solute measurement

The as-recorded radiographs always presented several spurious artifacts due to the non-uniform profile of the X-ray beam, monochromator defects or surface defects on the crucible. Therefore, an image processing was applied before performing solute measurements. In a first step, it is critical to compensate for the intensity reduction over time of the synchrotron X-ray beam, due to the long duration of these experiments. For this purpose, a small area with no sample was kept in the field of view, which allowed us to record the variations in the direct beam intensity. This information was then used to perform a flat field correction for each radiograph. In a second step, the image quality of each radiograph was improved by dividing it by a reference image, recorded when most of the sample was liquid and assumed at a nearly uniform composition [13]. This assumption was checked by measuring the grey level profile in the liquid phase along the sample on the reference image at the beginning of the experiment. The result of the image processing is an enhanced contrast and defect-free image as shown in Fig. 1a, with a much improved visibility of features. The variation of solute amount in the images is then deduced from the brightness distribution (grey level) using a conversion of the pixel value based on the Beer–Lambert law as described by Buffet et al. [16]. Fig. 1b shows the solute distribution in the whole sample at an arbitrary time ($t = 607$ s) during the holding stage. To improve the legibility, grey levels were converted to false colors and one can see in this image that the liquid concentration varied from nearly 5 wt% Cu (in the upper part of the sample) to 9 wt% Cu (deep at the bottom of the two liquid channels in the mushy zone). The validity of this solute measurement technique was proven in several previous papers for various type of solidification experiments such as columnar growth [16–18] and equiaxed growth [19]. According to those previous measurements, the minimum distinguishable concentration variation by our procedure is estimated to about 0.1 wt% Cu. Since this conversion procedure involves physical parameters of the medium crossed by the X-ray beam, it must be performed separately for each phase (liquid and solid). In this paper, solute measurements were carried out only in the liquid phase.

As the sample was melted and solidified several times, it could have led to macrosegregation of the solute in the liquid. In order to calibrate the solute measurements carried out on the basis of