Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 91 (2015) 34–40
Acta MATERIALIA
www.elsevier.com/locate/actamat

Resolidification of the mushy zone of multiphase and multicomponent alloys in a temperature gradient – Experiments and modeling

Andrea Löffler, Klemens Reuther, Hannes Engelhardt, Dongmei Liu and Markus Rettenmayr*

Otto Schott Institute of Materials Research, Friedrich Schiller University, Jena, Germany

Received 5 January 2015; revised 5 March 2015; accepted 12 March 2015
Available online 28 March 2015

Abstract—Resolidification of the mushy zone of multiphase and multicomponent alloys in a temperature gradient is investigated. Experiments of gradient annealing are conducted for a multiphase Cu-40 wt.%Al alloy and an Al-1 wt.%Mg-5 wt.%Si alloy with varying holding times, and the resulting microstructures are evaluated with respect to the evolution of phase fractions and concentration distributions. A numerical model that describes the macroscopic mass transport along the temperature gradient out of the mushy zone and that predicts the evolution of phase fractions and concentration distributions for multicomponent and multiphase alloys is put forward, and the calculation results are compared with the experimental observations. Full qualitative agreement is achieved between experiment and simulation. Effects in a resolidifying mushy zone of a multiphase alloy such as local solutal melting prior to resolidification that have so far not been documented in the literature are captured by the model.

Keywords: Solidification; CALPHAD; Multicomponent; Multiphase; Mushy zone dynamics

1. Introduction

Directional solidification experiments are generally initiated by directional melting in a temperature gradient, followed by a thermal stabilization phase that generates well-defined initial conditions in the form of a plane solid–liquid interface. During thermal stabilization, the sample is kept in the temperature gradient and will remain completely liquid in the heated zone and completely solid in the cooled zone. In between these regions, a mushy zone with a gradient in liquid fraction f_L will form initially. Local equilibration (dependent on the position in the temperature gradient) at the solid/liquid interfaces generates a concentration gradient in the melt, which in turn causes mass transport out of the mushy zone towards the hot regions of the sample. With increasing annealing time in the temperature gradient, the local fractions of solid and liquid change, the mushy zone resolidifies until it eventually is fully solid, with a plane front at the position of the liquidus temperature. The solute concentration distribution in the fully resolidified mushy zone follows the solidus concentrations of the respective phase diagram. The holding time that is required for complete resolidification may vary considerably and needs to be adjusted for different alloys and temperature gradients when performing directional solidification experiments [1–4].

On the microstructural scale, a number of processes that occur during thermal stabilization have been reported in the literature, most of them involving simultaneous melting and solidification, e.g., Temperature Gradient Zone Melting (TGZM) [1,5–8], Liquid Film Migration (LFM) [9,10], and coarsening [11]. Thermomigration [12] is generally neglected, but may in some cases play a certain role. During investigations in peritectic Al–Ni alloys, non-equilibrium phase transformations were observed in the vicinity of the peritectic temperature [13,14].

For predicting the evolution of concentrations and phase fractions on the macroscopic length scale (i.e., the entire length of the mushy zone) during mushy zone resolidification, an analytical model was proposed that is applicable to binary alloys that resolidify to a single solid solution phase [15]. The calculation results were verified experimentally for an Al–Cu alloy [16], and it was shown that mass transport by liquid diffusion is the governing physical process for mushy zone resolidification.

Until the present, the majority of experimental and theoretical investigations on mushy zone resolidification have been restricted to binary model alloys, usually in a concentration range that yields a single solid phase. For this case the phase fraction evolution and the formation of the concentration gradient are essentially understood, even though the microstructure evolution has not yet been modelled quantitatively. Reason is that various processes in the gradient (build-up of supersaturations during the heating

---

* Corresponding author at: Otto Schott Institute of Materials Research, Friedrich Schiller University, Löbdergraben 32, 07743 Jena, Germany. Tel.: +49 3641 947790; fax: +49 3641 947792; e-mail: M.Rettenmayr@uni-jena.de

http://dx.doi.org/10.1016/j.actamat.2015.03.030
1359-6462/

phase and reduction of the supersaturations, e.g., by LFM or nucleation of droplets, change of the imposed temperature gradient due to varying thermophysical constants, etc.) and their interaction have so far been regarded separately, but not with their full interactions. Comparatively little is known about multiphase and multicomponent alloys, even more so since in such experiments new phenomena and an even higher complexity are to be expected.

In the present work, the mushy zone resolidification in multiphase and multicomponent alloys is investigated. Temperature gradient annealing experiments with varying holding times are carried out in binary and ternary alloys that resolidify to more than one solid phase. While the investigated alloys are not technically *multi*phase and *multi*component, they are considered as representative for multiphase and multicomponent alloys, as the general principles are the same for alloys with three or more components and two or more phases [17]. Microstructural features that do not occur in the single phase case and have so far not been documented in the literature are illustrated. In the second part of this paper, a model is presented for predicting mushy zone resolidification in multiphase and multicomponent alloys. The evolution of concentrations and phase fractions along the resolidifying mushy zone is calculated by solving the mass transport equation coupled with the thermodynamic software package ChemApp that is based on the Calphad method, and the calculation results are compared with the observed microstructures.

2. Temperature gradient annealing experiments

Alloys with a nominal composition of Cu-40 wt.%Al and Al-5 wt.%Si-1 wt.%Mg, respectively, were prepared from the pure elements with >99.9% purity, cast into cylindrical rods of 7 mm diameter with an estimated cooling rate of 10 K/s and cut to samples with a length of 70 mm. A conical tip with an opening angle of 30° was manufactured at the lower end of each sample. The samples were inserted in an alumina tube, and their lower end was positioned in streaming water for cooling. A high frequency induction furnace was used to heat the upper end of the sample and to induce strong forced convection in the melt by the build-up of lateral temperature gradients. Longitudinal temperature gradients of up to 55 K/mm were achieved. For temperature control, a thermocouple was attached to the sample at a position below the lower end of the induction coil. The samples were heated with a heating rate of ca. 2 K/s at the position of the thermocouple. The final control temperature was adjusted to ensure that the mushy zone formed near the lower end of the induction coil. For this, the solidus temperatures were calculated using the thermochemical software package FactSage and the SGTE 2010 database.

The samples were held in the temperature gradient for 2 min, 30 min and 180 min (Cu-40 wt.%Al) or 5 min and 15 min (Al-5 wt.%Si-1 wt.%Mg), and then either quenched using the heat conduction in the steep temperature gradient by switching off the furnace (Al-5 wt.%Si-1 wt.%Mg and Cu-40 wt.%Al, 2 min) or cooled by gradually lowering the control temperature by 2 K/s (Cu-40 wt.%Al, 30 min and 180 min). The slower cooling was applied to minimize the formation of cracks that are induced in the resolidified section if the brittle intermetallics are quenched too fast. The samples were then ground longitudinally with SiC paper (up to 4000 grid) and polished with diamond spray (0.25 μm). The microstructures were examined by scanning electron microscopy (SEM) with backscattered electrons (BSE) and light microscopy (LM); the initial concentrations and phase compositions were determined by energy dispersive X-ray spectroscopy (EDX) measurements. The mean temperature gradients were determined by dividing the solidification interval that was taken from the phase diagram by the length of the mushy zone, as observed in the microstructures.

3. Microstructure observations

For the Cu-40 wt.%Al alloy, a mushy-zone is expected at temperatures between the peritectic temperature of the θ-Al_2Cu phase ($T_{p,\theta}$) at 595 °C and the liquidus temperature (T_L) at 686 °C, and a phase transformation $L + \varepsilon \rightarrow L + \eta$ is predicted at the peritectic temperature of the η-phase ($T_{p,\eta}$) at 624 °C. The microstructures of resolidified mushy-zones of the corresponding samples are shown in Fig. 1. The as-cast structure is on the left hand side, the quenched liquid is on the right hand side. In the sample that was quenched after 2 min holding time (Fig. 1a), three zones are found: at temperatures above $T_{p,\theta}$ and below T_L two zones with coarsened dendrites of both ε-phase and η-phase are found. In between, in the vicinity of the peritectic temperature, very fine dendrites are observed that are similar to those in the quenched liquid zone.

After 30 min holding time (Fig. 1b), no more dendritic morphologies are visible in the former mushy zone, and instead two zones are observed: in the section between T_L and $T_{p,\eta}$, a phase with an Al concentration of ~25% that appears as light gray in the BSE contrast is prominent (ε-phase). Below $T_{p,\eta}$, this phase vanishes, and a phase with ~21% Al that appears in a darker gray shade (η-phase) is observed. Traces of residual liquid channels and droplets that resolidified to θ-Al_2Cu (dark phase) and η during quenching are visible in both sections. Their number and density increase towards higher temperatures. In the sample that was held in the temperature gradient for 3 h (Fig. 1c), no more traces of residual liquid are visible, and two regions with apparently pure ε and η-phase, respectively, are observed.

The length of the mushy zones in the Cu-40 wt.%Al samples (Fig. 1) is very sensitive to variations of the initial concentration. This is due to the slope of the liquidus line in the phase diagram that leads to a significantly longer extension of the mushy zone for somewhat higher concentrations. This becomes visible in the length of the ε-rich sections between $T_{p,\eta}$ and T_L of the 30 min sample (with an initial Al concentration that is somewhat lower than the nominal composition) and the 180 min sample (with an initial Al concentration that is somewhat higher than the nominal composition).

The microstructure of the Al-1 wt.%Mg-5 wt.%Si sample that was annealed for 5 min is shown in Fig. 2a. Two sections can be distinguished in the resolidified mushy-zone: at temperatures below T_L, a zone that consists mostly of Al solid solution phase (light gray phase) is observed. Inclusions with eutectic microstructure and elevated Mg and Si content with increasing volume fraction towards higher temperatures are visible. Their morphology indicates that they are residual liquid channels that solidified to a