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Report:

Immiscible melt morphologies and coagulation mechanisms, and how these couple with hydrodynamic forces and solid-liquid interface morphologies have been studied in-situ by X-radiographic video microscopy during solidification of 6 different Al-Bi(-Zn) monotectic alloys. Binary and tertiary alloy samples were prepared with constitutions of 6 and 8%wtBi, and 6%wtBi8%wtZn and 8%wtBi5%wtZn, respectively. In addition, some binary alloy samples were prepared also with inoculants in terms of 0.05%wt TiB_2 particle additions to the melt. The experiment has provided results that are crucial to the ESA MAP Monophas project, which is aiming at the development of a new Al-based monotectic alloy for demanding bearing applications.

From previous in-situ investigations (exp. code IN516), it had been established that solidification in Al-Bi monotectics could appear as far more intricate than anticipated by theory and existing state-of-the-art numerical modelling, implying the need for a deeper phenomenological understanding of the process prior to a proper modelling assessment of the interplay between the mechanisms involved. In particular, it was evident that the coupling of hydrodynamic fields with short range interactions between adjacent secondary phase droplets in the binodal region was decisive for the outcome of the process. An objective for MA199 was therefore to have a closer investigation into this coupling, and its impact on droplet coagulation in relation to various growth modes realised by a systematic variation of solidification parameters. As a part of this study also TiB_2 inoculated samples were used, not to study conventional grain refinement, but to investigate the impact of inoculation on the nucleation of the secondary liquid phase, which again could affect subesequent droplet coagulation and segregation.

The IN516 study also lead to the observation of a completely unforseen phenomenon in the tertiary alloys. In the Zn-enriched solute boundary layer ahead of the α-Al dendritic solidification front, Bi-droplets were found to dissolve, indicating the liquid-liquid surface tension to be vanishing at a critical Zn-concentration. Upon entery into the mushy region, Zn diffused rapidly into the solid (large partition + high diffusivity) and consequentially Bi-immiscibility re-established with fine, and well dispersed droplets as a result. The limited amount of beam time in IN516 did not allow for a firm conclusion regaring this observation, and consequentially, another objective in MA199 was to confirm the existence of this immiscible-miscible-immiscible liquid phase transition.

In the experiments a 17 KeV monochromatic energy was used together with a FReLoN 2000 detector (4-channel read out, 2×2 binning of the CCD), employing a medium resolution ~20 μm thick, transparent scintillator. All together this configuration provided nominal resolution of about 2.5 μm and a read-out dead time of about 150 ms. It was planned originally to employ a SensiCam detector rather than the FReLoN, but the former was not equipped with the necessary drivers for ring-buffer memory image acquisition. The multilayer monochromator provided adequate beam flux for the experiment. Yet, a degradation that had occurred with the multilayer, gave a 1.3 x 1.3 mm^2 incident intensity profile with two dark bands of full horizontal width and of about 0.25 mm and 0.1 mm vertically with ~ 50% intensity loss. Directional solidification conditions were imposed onto the samples in a custom built Bridgman furnace, employed in several earlier studies[1]. For this experiment, the sample thicknesses were about 150 μm. The solidification processes were controlled by adjustments of furnace temperatures, furnace inter spacing and sample pulling velocities, with imposed thermal gradients, G, from 2.0 to 90 K/mm, yielding global cooling rates, dT/dt, from 0.016 to 4.9 K/s.

In total 80 solidification sequences were collected with the binary and tertiary immiscible alloys. The systematic study in the binaries has provided unprecedented data to the solidification community, and in particular for our numerical modelling partners in the Monophas-project, with several unforseen aspects concerning solidification fundamentals in monotectics. First of all, in pure Al-Bi monotectics, it is clear that there is a severe nucleation problem for the secondary liquid droplets in the immiscibility gap. Irrespective of the solidification parameters, all Bi-droplet nucleation was found to occur at the monotecitc reaction, corresponding to nucleation undercoolings for the miscible-immiscible transition of about 70 and 110 K for Al-6%wtBi and Al-8%wtBi, respectively. Secondly, with $G \geq 4$ K/mm, the thermocapillary forces on nucleated droplets are superceeding gravtiy and Stokes friction, leading to Marangoni motion of the droplets parallel with G, despite the Bi-density being about 4 times that of the surrounding Al-rich melt. Thermocapillarity transports the droplets above the binodal temperature where they dissolve, causing thermo-solutally unstable density layering in terms of a local Bi-supersaturated liquid, which settles with gravity. This gives rise to mesoscopic convection with rolls scaling with the length of the immiscibility gap, i.e. typical roll radius ~ $\Delta T_{gap}/G$. In addition it was found that suppression of the Bi-droplet nucleation often caused the monotectic reaction itself to be slightly constitutionally undercooled, leading to cellular- or coarse dendritic-like α-Al interface perturbations. Under such circimstances, microscopic convection rolls, with diameters corresponding to the interface perturbations, arise just ahead of the solidification front, and superimpose on the mesoscopic flow field. Drolpet coagulation was found to be initiated and predominant in the shear flow between adjacent microscopic rolls, yet it has been found from the experimental data that besides the hydrodnamically driven coagulation, at least three other droplet-droplet interaction mechanisms are contributing to the overall Bi-coagulation. Several other important discoveries were made with the binaries; droplet engulfment and pushing at the α-Al front, where the observations with planar fronts are quite contradictary to established models for solid-particle pushing and engulfment, but still fully logic due to the local droplet-droplet interactions that applies to these systems[2]. With the grain refined samples it was found that TiB_2-inoculation also casued nucleation of Bi-droplets in the immiscibility gap. Droplets nucleated on the solid particles where not adequately supported by thermocapillary forces, and were always found to settle leading to serious agglomoration of large Bi-colonies at the solidification front. In consequence inoculation is therefore detrimental for obtaining a well disperesed product for bearing applications, but due to the intricate coagulation mechanisms found, it would also be problematic to derive a suitable casting procedure for the non-grain refined binaries. It was also found that for any casting process, Bi-coarsening in the interdendritic/intercellular or grain boundary regions subsequent to primary solidification is a serious challenge.

In the teritiary alloys we were able to confirm the existence of the miscible-immiscible-miscible trasnsition observed in the IN516 study. It was not possible with these alloys to have droplets nucleated freely in the melt- just as previously Bi was found to form at the sample surfaces. At present we presume that the difference in wetting conditions between the Al-Bi and the Al-Bi-Zn samples most likely can be ascirbed to chemical differences in the surface oxides formed on the two samples, and closer investiagations into this matter is on its way. Anyhow, it is now clear that with some adjustments to established casting procedures it may be possible to take advantage of the Zn-driven Bi-droplet dissolution, to arrive at a cast material with a uniform, fine-dispersed Bi-droplet distribution. There will, however, still be several challenges that must be solved. Ideally Bi-dissolution should be made to occur sufficiently ahead of the primary solidification front for the droplets to diffuse completely into a homogeneous melt. It is also not clear yet if reestablsihement of Bi immiscibility and subsequent local droplet interactions provides enough time for the mean droplets to grow to the ideal sizes (~2-5 μm).

At present work is being undertaken with quantitiative analiyisis of the video sequences, extratcing data such as spatio temporal droplet size distributions, droplet veolcity fields and solid-liquid interface coordinates. It is expected that the MA199 data contains sufficient material for 2-3 prominent publications on fundamentals of monotecitc solidification.

[1] RH Mathiesen, K Ramsøskar, L Arnberg, T Weitkamp, C Rau and A Snigirev. *Met. Mater. Trans* **B**33 (2002); 613.
[2] G Tegze, T Pusztai, L Gránásy. *Mat. Sci. Eng.* **A**413-414 (2005); 418.