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Report:

The understanding and control of grain nucleation during the liquid-solid phase transformation of aluminum alloys is a challenging problem, which plays an important role in the tailoring of solidified materials and their properties during processing. A significant improvement in the mechanical properties of aluminum can be achieved by the addition of micron size TiB_2 particles, which can act as a substrate for heterogeneous nucleation and significantly reduces the average grain size. This process, known as grain-refinement, has been studied extensively both theoretically and experimentally, but there is still no consensus on the physical mechanism involved. The main reason for this is a lack of in-situ experimental data on the nucleation and growth of individual grains within the melt at high temperatures. In order to get better insight in the nucleation and growth process of individual aluminium grains in the bulk of the material in-situ X-ray diffraction experiments were performed.

The X-ray diffraction measurements were performed using the three dimensional X-ray diffraction microscope (3DXRD) at beam line ID11 in transmission geometry. A monochromatic X-ray beam with an energy of 70 keV (wavelength of 0.177 $Å^{-1}$) and a beam size of 200×200 μm^2 illuminated the 5 mm diameter of the sample (with a height of 10 mm) that was mounted in a glassy carbon container within the vacuum furnace. A continuous sample rotation of 1^o around around the vertical axis (perpendicular to the beam) gives rise to a diffraction pattern on the two-dimensional detector that is placed behind the sample. This pattern gives direct information on both the liquid and solid phases during the solidification process.

Figure 1 shows the diffraction pattern of an aluminium alloy with solute titanium and added TiB_2 particles at three stages during continuous cooling. In the liquid phase two broad rings indicate the maxima in the liquid structure factor resulting from short-range order of the aluminium atoms. In the mixed phase the intensity of the broad rings is reduced, and a limited number of diffraction spots from the solid grains is observed at the diffraction angles corresponding to reflections of the face-centred cubic lattice structure of aluminium. In the solid phase the broad rings of the liquid phase are absent and the diffraction spots show an

increase in number and intensity. According to standard diffraction theory the number of spots detected is proportional to the number of illuminated grains and the intensity of each spot is proportional to the volume of the grain from which it originates. By repeated acquisition of images, the nucleation and growth of individual grains were studied with a typical time resolution of 8 s.

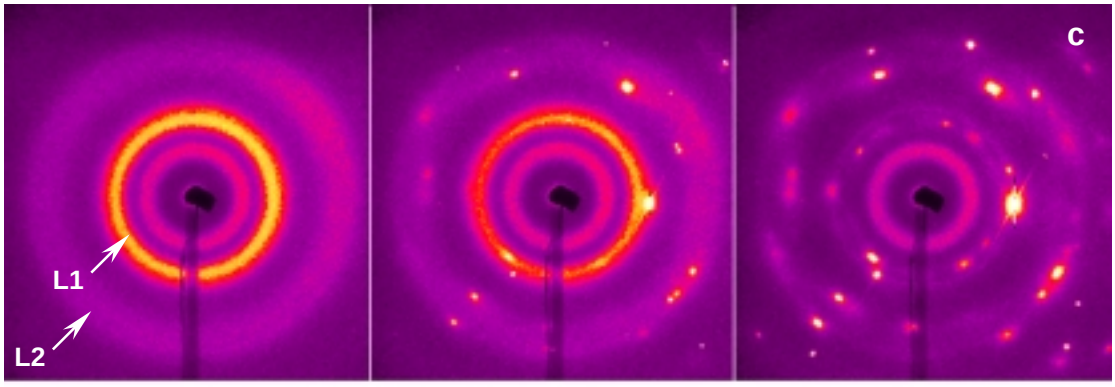

Fig. 1. *X-ray diffraction patterns of an aluminium alloy with solute titanium (0.1 wt.%) and added TiB_2 particles (0.1 wt.%) at different stages of the solidification process. The data were collected during cooling from 973 K at a rate of 1 K/min. (a) In the liquid phase the two broad outer rings are due to the first (L1) and second (L2) maximum in the liquid structure factor. (b) In the mixed phase additional bright spots are Bragg reflections from nucleated grains at the scattering angles of the aluminium lattice structure. (c) In the solid phase the diffraction spots have increased in number and intensity while the diffuse scattering of the liquid phase has vanished. The diffuse innermost ring arises from the quartz windows of the vacuum furnace.*

The aluminium alloys were kept for 30 min at 973 K (about 40 K above the melting temperature of aluminium) in order to form a homogeneous liquid phase, and were subsequently cooled at a rate of 1 and 10 K/min. By counting the number of diffraction spots as a function of time, the evolution of the number of aluminium grains in reflection was obtained. From all reflections on the detector only the grains that nucleated in the illuminated sample volume were considered and the grains that grew into it were discarded. The corresponding solid phase fraction was determined from the scaled intensity at the first ring in the diffraction pattern of the liquid phase. When the final number of reflecting grains is compared for the different alloys, significantly more are found for the alloy containing both solute titanium and added microscopic TiB_2 particles. This clearly confirms that grain refinement is only effective when both solute titanium and added microscopic TiB_2 particles are present in the aluminium alloy. Further, our measurements demonstrate that the nucleation process is limited to the initial stage of the solidification and is complete at a solid phase fraction of about 20% for all samples.

The growth behaviour of individual aluminium grains during solidification was determined by monitoring the intensity of the diffraction spots continuously. The individual growth curves for the alloys containing solute titanium with and without added TiB_2 particles show a close resemblance to the behaviour of the solid fraction. The observed growth behaviour of the individual grains is controlled by the diffusion of solute titanium and the release of latent heat. As titanium has a strong affinity for the solid phase, its concentration in the melt decreases as the solidification proceeds. In the first stage of the growth the individual growth curves closely overlap with the model prediction for diffusion-controlled growth of non-interacting grains.

Prior to the main transformation, weak reflections of a metastable $TiAl_3$ phase were detected. This observation finally pinpoints the highly debated mechanism responsible for enhanced grain nucleation. Detailed understanding of the enhanced grain nucleation in liquid metals is the key to control the widely used process of grain refinement.

Publications resulting from the experiment:

[1] N. Iqbal et al., Materials Research Society Proceedings, Volume 840, (2005), p. Q7.12.1-7.
[2] N. Iqbal et al., to be published in Journal of Non-Crystalline Solids.
[3] N. Iqbal et al., submitted to Acta Materialia