ESRF	**Experiment title:** Microtomographic determination of the nearest-neighbor size-correlation function in polycrystalline Al(Ga)	**Experiment number:** ME-470
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Shifts: 9	**Local contact(s):** Dr. Lukas Helfen	*Received at ESRF:*

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Report:

The goal of experiment ME-470 was to perform a tomographic reconstruction of the microstructure of a sample of polycrystalline Al by allowing Ga to diffuse along the grain boundaries and exploiting the x-ray absorption contrast between Al and Ga. Because aluminum and gallium are immiscible in the solid state, we expected Ga to “mark” the location of the boundaries, much as it was observed to do in previous tomographic studies of the Al/Ga system [1].

The motivation behind this measurement is a recently proposed non-mean-field model for grain growth, which is able to predict the evolution of the crystallite-size distribution from the topology of the growth-induced microstructure [2]. Specifically, the model requires as input the contact-area-weighted probability $p(R|R')$ that a grain (i.e. crystallite) of size R' is bordered by a nearest-neighbor grain of size R. In experiment ME-142, which was carried out in Nov. 2000 and Feb. 2001 at beamline ID22, we succeeded in obtaining $p(R|R')$ from tomographic images of the grain-boundary network of polycrystalline Al alloyed with up to 3 at.% Sn in the liquid state and then quenched rapidly to room temperature. Upon solidification, the Sn atoms segregated to the grain boundaries, thus permitting detection by absorption-contrast tomography. Unfortunately, we found that the presence of Sn in the grain boundaries profoundly modified the coarsening of the microstructure, resulting in a much narrower grain-size distribution than that expected in a microstructure generated by normal grain growth [3].

By using Ga instead of Sn to identify the locations of the grain boundaries, we hoped to avoid the influence of grain-boundary segregation on the growth behavior. This is possible because of the anomalously fast rate of Ga diffusion along grain boundaries in Al, even at temperatures well below those required for grain growth [1]. Thus, Ga can be used to mark the grain boundaries of a polycrystalline Al sample *after* solidification and grain growth have taken place in the pure, undoped state, without the Ga atoms modifying the sample microstructure. By deliberately diffusing Ga into pre-annealed samples of Al, we hoped to gain experimental access to the correlation function $p(R|R')$ of a pure sample manifesting normal grain growth.

Samples of polycrystalline Al rod (99.99%) were cut into large pieces, inserted into a vacuum furnace ($P \lesssim 5 \times 10^{-6}$ mbar) and annealed for times of 1, 2, 4, 8 and 14 h. Optical microscopy of polished and etched sections revealed the presence of roughly equiaxed grains, increasing in average size from about 0.3 mm in the unannealed state to $\sim$1.5 mm after 8 h. The Al samples were then machined into cylinders having a diameter of 9 mm and a height exceeding 1.5 cm. Gallium was diffused into the samples by the following procedure: first, each Al cylinder was submerged in an aqueous solution of 10% NaOH in order to remove the surface oxide. Then Ga was applied to the still-wet sample surface; owing to the elevated sample temperature (resulting from reduction of the surface oxide) and the low melting point of Ga (29.8°C), the Ga could be smeared evenly over the entire cylinder surface. Finally, each sample was annealed in air at 200°C for 9 h in order to promote diffusion of Ga along the network of grain boundaries in the polycrystalline microstructure.

Tomographic measurements were performed at beamline ID19 with the Frelon II detector optics so chosen to yield a pixel size of $\sim$5 μm with a field of view of 2048 × 2048 pixels. A total of 1400 projections were recorded at a photon energy of 35 keV, with exposure times ranging from 2 to 5 s per projection. At this energy, the linear attenuation coefficient of Ga (54.7 cm^{-1}) is nearly 24 times larger than that of Al (2.29 cm^{-1}), promising excellent contrast between grain boundaries and grain interiors. Tomographic reconstruction was carried out using HST, ESRF's own filtered back-projection data-processing program [4].

Figure 1 illustrates a section of a typical reconstruction of Al/Ga. The bright regions indicate an increased local x-ray attenuation arising from the presence of Ga. The thick layer of Ga on the cylindrical sample surface is clearly evident, as are several grain boundaries, indicating that Ga diffusion has progressed to the center of the sample. Considering that the average grain size of $\sim$1.5 mm is six times smaller than the sample diameter, we realize that only a small fraction of the overall grain-boundary network is visible in Fig. 1. Apparently, it is possible to detect Ga tomographically only along certain grain boundaries.

Initially, we attributed the "missing" grain boundaries to uneven penetration of the sample surface during the diffusion anneal and/or to slower-than-expected diffusion kinetics preventing the entire grain-boundary network from being wet by Ga. However, longer treatment with NaOH failed to increase the amount of Ga visible in the sample interior, and longer diffusion anneals performed at higher temperatures resulted in no improvement, either. We now believe that Ga *did* diffuse along most of the grain-boundary network of the polycrystalline Al samples—a fact confirmed by investigation of a fracture surface of one sample by scanning electron microscopy—but the Ga wetting layer was apparently too thin at most boundaries to permit tomographic detection. A simple calculation indicates that a detectability threshold of a 10% increase in the local attenuation coefficient necessitates a minimum Ga thickness of $\sim$0.02 μm. Such a layer thickness, which corresponds to about 80 monolayers of Ga, implies that significant thickening of the wetting layer must occur before the underlying grain boundary can be detected by absorption-contrast tomography. Since such a thickening transition appears to take place only along a small fraction of the grain boundaries in each sample, we were unable to extract the information—grain sizes and contact areas—needed to compute the desired correlation function $p(R|R')$ from these experimental data.

[1] W. Ludwig and D. Bellet, *Mater. Sci. Eng.* **A281** (2000) 198.
[2] D. T. Wu, *Mater. Res. Soc. Symp. Proc.* **343** (1994) 61.
[3] K. M. Döbrich, C. Rau and C. E. Krill III, *Metall. Mater. Trans.* (in press).
[4] `www.esrf.fr/computing/scientific/HST/HST_REF/hst.html`

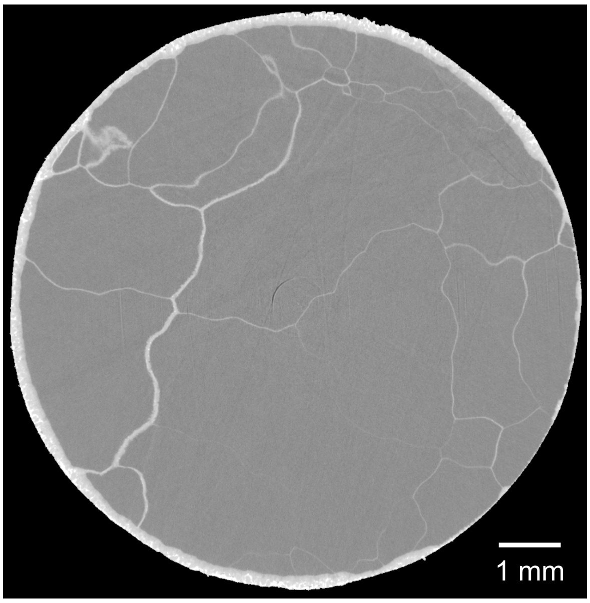

Fig. 1: Tomographic reconstruction of polycrystalline Al, following an anneal at 400°C for 14 h and Ga interdiffusion at 200°C for 9 h. Light areas correspond to increased Ga concentration. A thick layer of Ga is visible on the outer surface, and thinner layers are present along several grain boundaries, indicating that Ga has diffused to the center of the sample. The large regions demarcated by visible grain boundaries are composed of multiple grains, the boundaries of which are either free of Ga or wet below the detection threshold for absorption-contrast tomography performed at a linear resolution of 5 μm.