

**DE-FG02-01ER45940**

**Diffusion in Grain Boundary Triple Junctions, and its Effects on the Behavior of Nanostructured Materials**

**FINAL REPORT**

**A.H. King and M.A. Dayananda**

School of Materials Engineering  
Purdue University  
West Lafayette IN 47907-2044

The principal goal of this project was to develop a means of studying diffusion in controlled tricrystal specimens that allow access to consistent grain boundary triple junctions (GBTJs). This project has produced the following results:

**1. Technical Outcomes**

***1.1 Development of a methodology for designing stable GBTJs.***

It has not been possible, before this work, to choose sets of grain boundaries that will form stable triple junctions, and are easily grown into physical tricrystal specimens. In order to achieve this for the most general case, a full knowledge of the grain boundary energy, including its anisotropy, is required for every set of possible grain boundary parameters. This calls for a five-dimensional data set, with full coverage of each of the grain boundary parameters, for each material that we seek to use, and such data sets simply do not exist. We have therefore identified a subset of possible tricrystal parameters in which all three misorientations, and all three grain boundary planes are fully determined, and are expected to form stable triple junctions. The method for doing this has been established and published [4.1] in the Journal of Materials Science. The paper identifies preferred designs for stable triple junctions with common crystallographic directions parallel to [100], [110] and [111], which form the test-beds for all future experiments on controlled triple junctions.

***1.2 Development of a means of growing controlled tricrystal specimens.***

We have successfully grown a series of copper tricrystal specimens with common [100] directions, using an adapted Bridgman growth method. This has been the most challenging component of the work to date, and a large number of experimental difficulties have been overcome systematically, providing for the accurate alignment of seed crystals and subsequent growth without the nucleation of new grains and/or twins in the grown specimens. Several methods of tricrystal preparation have been tried and abandoned in pursuit of this goal. Tricrystals with [110] common axes have also been prepared.

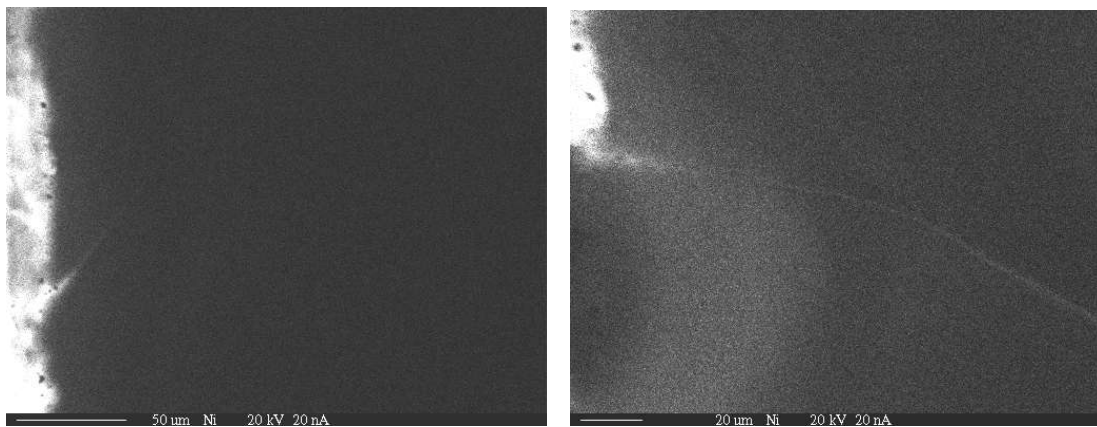
***1.3 Experimental evaluation of the required parameters for stable tricrystal structures.***

We have used the growth method described above, and the tricrystal designs developed earlier in the work, to grow tricrystals of similar nominal design (i.e. having the same nominal

grain boundary parameters) but varying slightly in the precision with which the parameters were set. It is observed that some of the tricrystals embody stable triple junctions, with constant geometry over several centimeters of length, while others have large variations in geometry, particularly the dihedral angles, over the length of the Bridgman tricrystal specimen. The stability is found to be a function of the precision with which the grain boundary misorientations are set in the seed set-up process, prior to the final stage of the Bridgman growth. A set of rules about the required precision can be deduced and this will be the subject of an invited presentation at the TMS Spring Meeting of 2006, and the work will subsequently be published. The rules are similar to, but distinct from the usual geometrical rules such as the “Brandon Criterion” that are used to determine whether a grain boundary should be considered to be “special.”

#### ***1.4 Experimental demonstration of enhanced diffusion in triple junctions***

Preliminary diffusion experiments have been carried out, using nickel sources attached to copper tricrystals. Figure 1 shows a clear demonstration of enhanced diffusion in the triple junction, as demonstrated by sectioning along one of the grain boundaries, with a sectioning plane nearly parallel to the triple junction. Far from the GBTJ, the diffusive penetration of nickel is restricted to the grain boundary, and is about  $80\mu\text{m}$ .

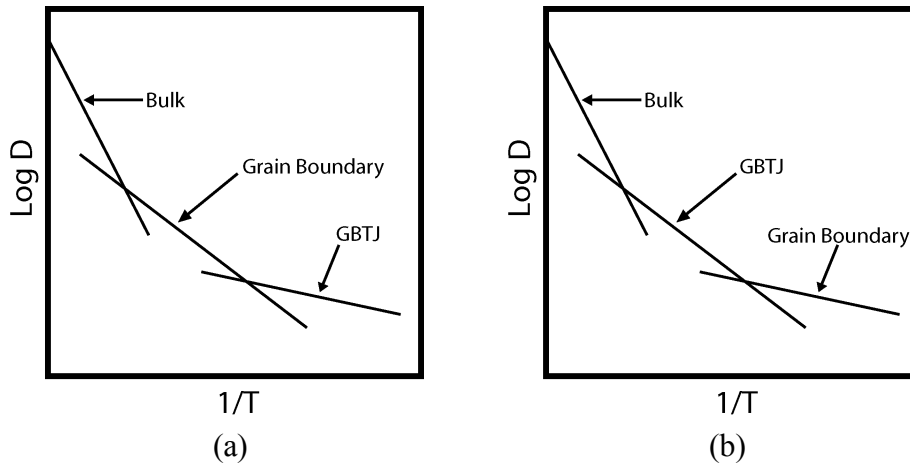


**Figure 1.** Nickel penetration into a copper tricrystal specimen after 48 hours at  $700^\circ\text{C}$  ( $0.72T_m$ ). The nickel source is at the left in both images, and nickel has bright contrast in these electron microprobe elemental maps. (a) Penetration of about  $80\mu\text{m}$ , along a grain boundary. (b) Penetration exceeding  $300\mu\text{m}$ , at a sectioning plane within  $80\mu\text{m}$  of the GBTJ. (Micrographs by R. Narayanan.)

As the sectioning plane approaches the triple junction, the penetration from the surface is found to increase to at least  $300\mu\text{m}$ . Even though it is not possible to section precisely to the GBTJ itself, it is certain that the section shown in Figure 1b is within  $80\mu\text{m}$  of it, and the solute penetration that is observed in the grain boundary results from leakage out of the triple junction. This result has been included in an invited presentation at the fifth conference on Solid-Solid Phase Transformations [4.3], and was also the subject of a presentation at the MRS Fall Meeting of 2005 [3.4].

A surprising feature of this observation is that it occurred in a specimen for which the diffusion anneal was carried out at  $700^\circ\text{C}$ , or  $0.72T_m$ . This is a high temperature for a grain

boundary diffusion observation, and our expectation had been that triple-junction diffusion would be significant only at very low temperatures. This calls for re-evaluation of our original hypothesis 2(a) concerning the activation energy for triple junction diffusion, and suggests that the activation energy may be intermediate between those of bulk and grain boundary diffusion, rather than being lower than both, as indicated in Figure 2 (b).



**Figure 2.** Schematic Arrhenius plots to show the relationships between bulk, grain boundary and triple junction diffusion. (a) Original hypothesis; (b) relationship inferred from preliminary results.

### ***1.5 Experimental demonstration of diffusion induced triple junction migration***

In one diffusion couple, we have observed a significant lateral translation of the triple junction, accompanying nickel diffusion into the copper specimen. This is an apparent case of diffusion-induced triple junction migration, paralleling the now well-established phenomenon of diffusion-induced grain boundary migration. This finding is based only on a single observation, so far, and calls for further investigation of what might be a very interesting phenomenon.

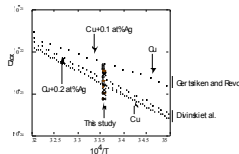
### ***1.6 Preliminary investigation of the thermal stability of triple junctions***

In response to the above observation, we have undertaken some studies of the stability of GBTJs in response to annealing in the absence of a solute source. As-prepared tricrystals exhibit straight GBTJs, with constant dihedral angles, when they are properly made. We have found that subsequent annealing of the tricrystal at relatively low temperatures can induce displacement of the triple junction, while annealing at higher temperatures has smaller effects or no effect at all on the GBTJ morphology. It seems that there is a tendency of the GBTJ to re-arrange at low temperature, while it is stable at high temperature. This behavior might be explained by a change in the relative energies of the grain boundaries, as the temperature is changed. This would indicate a difference of grain boundary entropy among the constituent grain boundaries, and we believe that we are the first to be able to observe such a variation in a systematic experiment. This work was reported at the 2005 MRS Fall Meeting [3.3].

### ***1.7 Measurement of room-temperature grain boundary diffusivity, and verification of Arrhenius extrapolations as a means of obtaining low-temperature data***

In order to estimate the room-temperature grain boundary diffusivity of silver in copper, we have performed a study of the penetration of silver, from a surface cladding, into a copper substrate

in a 200-year old specimen of Sheffield plate. This is a unique form of silver-clad copper whose age can be established with reasonable accuracy, allowing the evaluation of long-term, low-temperature diffusion. The grain boundary diffusivities were determined from measured concentration profiles using algorithms developed by Profs. Dayananda and Ram-Mohan, and were found to correspond very accurately to values extrapolated from higher-temperature, short-term experiments, as shown in Fig. 3. This finding provides great confidence that the detailed mechanisms of grain boundary diffusion are unchanged between the higher temperatures and room temperature.



**Figure 3:** Comparison of room temperature grain boundary diffusivity determined in this study, with data extrapolated from recent studies performed at higher temperatures, over shorter times. [12-14]

### ***1.8 Summary***

During this project, we have overcome several significant challenges, especially in the production of reliable tricrystal specimens. With these beginnings of tricrystals produced in a more routine manner, we have undertaken several studies of the behavior of the GBTJs, both with and without a solute source, and have made several tantalizing observations that call for more intense systematic study.

## **2. Students Supported on the Project**

### ***2.1 Raymond Kremer***

MS, July 2004 “Low temperature grain boundary diffusion and triple junction design.”

## 2.2 *Raghavan Narayanan*

PhD anticipated, May 2007.

## 2.3 *Shashank Shekhar*

PhD anticipated, May 2007.

### **3. Conference Presentations**

- 3.1 Max-Planck Institut Workshop on Structure and Composition of Interfaces, Kloster Irsee, Germany, August 2002: "Measuring Triple Junction Properties."
- 3.2 Fourth SIAM Conference on Mathematical Aspects of Material Sciences, 2004: "Can Triple Junction Energy Contribute to the Driving Force for Grain Growth?" (invited presentation).
- 3.3 MRS Fall Meeting, 2005: "Growth and Stability of Grain Boundary Triple Junctions in Copper" (Shashank Shekhar and Alex King.)
- 3.4 MRS Fall Meeting, 2005: "Observation of Enhanced Diffusion at Triple Junctions in Copper" (Raghavan Narayanan, Mysore A Dayananda and Alex King.)
- 3.5 TMS Annual Meeting, 2006 (Brandon Symposium): "What does it mean to be Special?" A.H. King and S. Shekhar (Invited Presentation).
- 3.6 TMS Annual Meeting, 2006 (Dayananda Symposium): "Rapid Diffusion in Grain Boundary Triple Junctions" A.H. King M.A. Dayananda, R. Narayanan and S. Shekhar.

### **4. Refereed Publications**

- 4.1 R. Kremer, R. Narayanan, S. Shekhar and A.H. King, *Journal of Materials Science* **40** (2005) 2795-2802: "On the design of controlled tricrystal specimens for the systematic study of static grain boundary triple junctions."
- 4.2 R.J. Kremer, M.A. Dayananda and A.H. King in *Materials Issues in Art and Archaeology VII*, Eds. P. Vandiver, J. Mass, A. Murray & J. Merkel; MRS Symp. Ser. **852** (2005) OO1.5.1-OO1.5.6 "Low-Temperature Grain Boundary Diffusion Data Measured from Historical Artifacts."
- 4.3 A.H. King in *Solid Solid Phase Transformations in Inorganic Materials 2005, volume 2*, Eds. J.M. Howe, D.E. Laughlin, J.K. Lee, U. Dahmen and W.A. Soffa; TMS Warrendale PA; pp411-420, "The Roles of Interfacial Junctions in Nucleation and Growth Processes" (invited paper).
- 4.4 R.J. Kremer, M.A. Dayananda and A.H. King, *Zeitschrift fur Metallkunde* **96** (2005) 1187-1192: "Low temperature diffusion data measured from historical artifacts."

- 4.5 S. Shekhar and A.H. King, *J. Mat. Sci.* (in press): “What does it mean to be special? The significance and application of the Brandon criterion.”
- 4.6 A.H. King, *Mater. Sci. Tech*, (in press): “Triple junction energy and the prospects for measuring it.” (Invited Paper.)