

TGBJ -THREE GRAIN BOUNDARY JUNCTION - SOLUTION FOR COPPER PLATES NICKEL COATED IN THE TUNDISH / CRYSTALISOR CONTINUOUS CASTING

OLARU Paul¹

¹SETEC- SCO Expert, Luzern, Switzerland

Abstract

One solution to overcoming these challenges is to optimize by tailoring microstructures of the copper plates used in the new tundish plate's critical components. An approach that has proven effective in improving the thermal resistance of material to intergranular degradation is grain boundary junction in copper (GBJC) [1]. Results showed that the triple line tension has a considerable effect on grain growth, particle-boundary interactions and void shape, especially for nano-crystalline materials. Copper has been and will continue to be vital to thermal transmission and heat transfer applications. The copper plates of a tundish thin slab caster coated by electrodeposited Ni (Co) coating presented cracks and small Ni detachments on the meniscus area after some charge sequence (7 heats cast). We have observed on the copper plates more cracks and detachments of the Ni (Co) coating below the meniscus area. The cracks have mainly longitudinal direction and lead to the detachment of the coating. The remaining coating on the area below the meniscus has a dark grey colour while where the coating was completely detached the copper substrate presented a yellow colour due to the formation of brass alloy. Moreover on the bottom part of the plate some scars are present due to the wear between the solidifying metal and the protective coating. The presence of the wear scars on this area is normal for the mould plates. Nevertheless, on the same area the protective coating is cracked even if in a less intense mode compared to the meniscus area.

Keywords: Grain, junction, tundish, continual casting, nickel

1. INTRODUCTION

1.1. Three grain boundary junction -TGBJ

TGBJ is a technologically process for optimizing & tailoring the population of "special" boundaries in an effort to improve component material performance. The steps used in the general application of grain boundary engineering are two-fold. The lines of intersection of three grain boundaries are called three grain boundary junctions (TGBJ). The following assumptions are usually made. The system migrates under the action of a driving force which is provided by the energy σ of the curved grain boundaries. The system is considered either as uniform or as symmetrical. In a uniform system all three grain boundaries (**Figure 1**) possess equal energies and motilities. A symmetrical system has two identical curved grain boundaries GB 1 and GB 2 and a deferent straight boundary GB 3. In what follows we consider a symmetrical system, since nowadays it is usually used in the majority of tri-crystal experiments. The relationships between respective grain boundary energies and motilities' are given by:

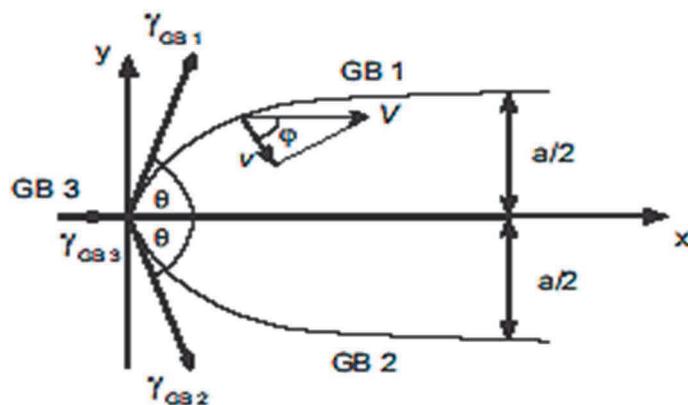


Figure 1 Grain boundary with triple junction TGBJ in course of steady -state motion

$$YGB1 = YGB2 \equiv Yb \neq YGB3,$$

$$mGB1 = mGB2 \equiv mb \neq mGB3 \quad (1)$$

1.2. Grain boundaries

It is possible to describe these distinct grain boundary structures using the so called Coincident Site Lattice (CSL). Numerous studies [2, 4 -6] have shown that low Σ CSL grain boundaries (usually $\Sigma \leq 28$) can possess "special" chemical, mechanical, electronic, kinetic, and energetic properties. Of particular relevance to industrial materials, these "special" grain boundaries have been shown to display a high resistance, and in many cases immunity to: (1) sliding, cavitation and fracture, (2) corrosion and stress corrosion cracking, (3) sensitization, and (4) solute segregation. Models have been developed to predict the effect of the special boundary population on these various properties. **Figure 2** shows an OIM map where the low Σ CSL boundaries are highlighted in colour along with a plot showing the distribution of the special boundaries. Generally, materials processing is undertaken without regard to resultant "grain boundary structure distributions", thus producing component materials with highly variable populations of "special" grain boundaries (≤ 23 %).

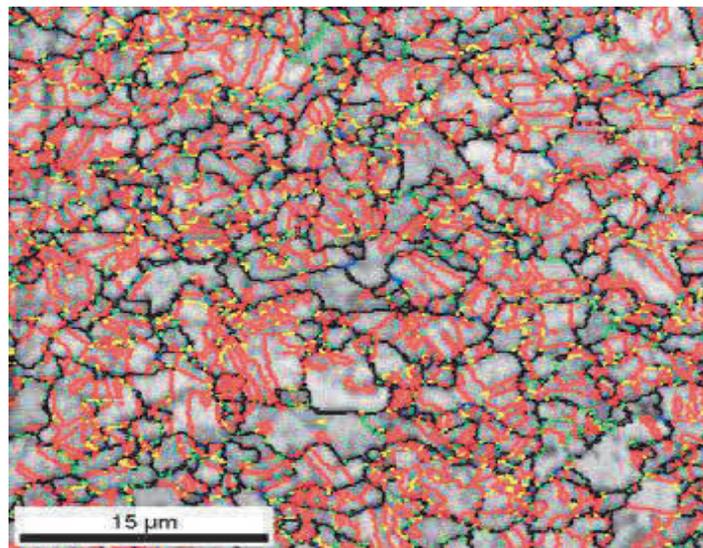


Figure 2 Map-section showing CSL boundaries and the corresponding distribution in a copper ultra-thin film

1.3. Action tailoring force (ATF) for grain boundary migration

The action tailoring force (ATF), is practically equivalent to the pressure force acting per unit area of a grain boundary. It has the dimension of energy per unit volume and appears if the boundary displacement leads to the decrease of the total free energy. Theoretically, the gradient of any intensive thermodynamic variable offers a source of the action tailoring force: the gradient of temperature, pressure, density of defects, density of energy, magnetic field strength. The most frequently used method to study grain boundary motion in bi & tri-crystals is the displacement of curved grain boundary. In the work case the action tailoring force is provided by the reduction of the boundary area. The interaction of the moving grain boundary and the external surface of a specimen (drag effect of "surface" triple junction, groove dragging and effect of outer surface anisotropy on grain boundary motion) are realized. Theories of triple junction migration have been developed by Gottstein et al [3]. But, many issues remain unexplored. Many of them, like the presence of solute atoms or crystallography of triple junctions, on triple junction drag can be studied in experiments on tri-crystal only, (**Figure 3**).

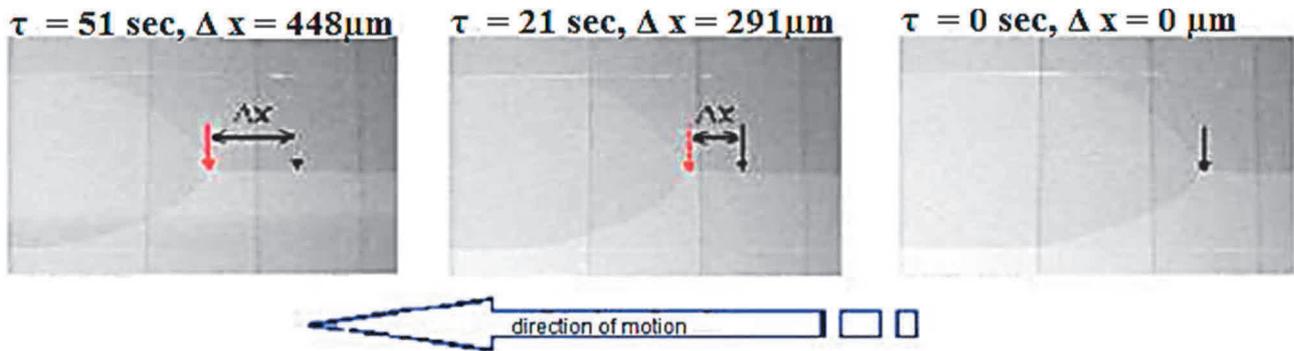


Figure 3 Triple junction drag can be studied in experiments on tri-crystal

2. RESULTS

2.1. Superconductivity

Superconductivity represents the maximum thermos-capacity of the object that depends both on the structure and material. We report a carbon nanotube-copper composite (CNT-Cu), exhibiting similar conductivity ($2.2\text{--}4.9 \times 10^5 \text{ S cm}^{-1}$) as copper ($5.6 \times 10^5 \text{ S cm}^{-1}$), but with a 100-times higher capacity ($6 \times 10^8 \text{ A cm}^{-2}$). Our laboratory vacuum experiments demonstrate that carbon nanotubes suppress the primary failure pathways in copper as observed by the increased copper diffusion activation energy ($\sim 2.2 \text{ eV}$) in carbon nanotube-copper composite, explaining it is higher - super-conductivity [7, 8]. This is the only material with high conductivity, high capacity and high conductivity making it uniquely suited for applications in microscale electronics and inverters. This is because the former requires a strongly bonded system, whereas the latter requires the free electrons from a weakly bonded system. Achieving high electrical conductivity and supra-capacity in the same material has been impossible. Compared with copper, the macroscopic CNT-Cu conductivity ($4.9 \times 10^5 \text{ S cm}^{-1}$) revealed, exceeded and doubled at 23°C , above 80°C and 227°C , respectively from a one-order-of-magnitude lower temperature coefficient of resistivity. To understand the high capacity of CNT-Cu composite, we performed activation energy (E_a) analysis to evaluate the energy required for Cu diffusion in CNT-Cu composite. Our analysis demonstrated that the E_a for Cu diffusion in the composite was $\sim 2.2 \text{ eV}$. In comparison, the primary electro-migration failure pathways in pure Cu have much lower E_a , with surface and grain-boundary Cu diffusion requiring $\sim 0.56 \text{ eV}$ and $\sim 1.20 \text{ eV}$, respectively. Thus, the primary electro-migration failure pathways (surface and grain-boundary diffusion) are suppressed by the presence of CNTs. Further, Cu diffusion is thus smaller (10^4 times) in our composite compared with bulk Cu, explaining its high capacity. The microscopic CNT-Cu composite fabricated in an identical protocol exhibited a room temperature conductivity of $2.2 \pm 0.3 \times 10^5 \text{ S cm}^{-1}$. High CNT volume fraction (45 vol. %) resulted in a 42% density reduction (5.2 g cm^{-3}) compared with Cu (8.9 g cm^{-3}). Therefore, the specific conductivity for our CNT-Cu composite was 27% higher than Cu and exceeded most materials (Au, Ag and Cu) with the exception of Al. The temperature dependence of the conductivity, that is, temperature coefficient of resistivity, of the CNT-Cu composite ($7.7 \times 10^{-4} \text{ K}^{-1}$) was one order of magnitude lower than that of Cu ($6.8 \times 10^{-3} \text{ K}^{-1}$), highlighting one benefit of our CNT-Cu composite. Consequently, the decrease in conductivity with temperature for the CNT-Cu was far less than Cu, and the conductivity was on par at room temperature, exceeded above 80°C , and was double at 227°C . This feature is important for heavy load applications, because the operating temperature is often higher than 80°C .

3. CONCLUSIONS

We realized measurement of the line tension of grain boundary triple lines. We grew crystallographically defined tri-crystals of copper and measured the energy of the grain boundary triple lines with a sophisticated technique based on atomic force microscopy. We measure the energy of triple lines in pure copper on the

basis of a new theory, regarding the influence of triple lines on the properties of nano-crystalline materials. Also, we developed a high-performance copper plates (CNT-Cu) composite that combines the best thermal properties of CNT (high ampacity) and Cu (high conductivity). The copper plates are somewhat larger than the other, but has the highest thermal integrity, while still offering field reparability for the planar-directional freeze-casting tech. (PDFC technology) - Using the planar-directional.

The copper plates are based on the well-established CNT-Cu composite nano-miniature matrix but with an insert designed for high speeds. There is a good new, that our technology continue to evolve and give designers new options in meeting ever-increasing data loads. Moreover, the CNT-Cu composite is the only material satisfying the ampacity and thermo-conductivity levels stipulated by the siderurgy programs for the next applications.

REFERENCES

- [1] GOTTSTEIN, G. *Physikalische Grundlagen der Materialkunde*, 2.nd ed. Berlin, Heidelberg :Springer Verlag, 2001. 145p.
- [2] GOTTSTEIN, G. *Struktur und Eigenschaften von Korngrenzen*, Vorlesungsskript, Wintersemester, 1982/83 RWTH.
- [3] HU, W., MOLODOV, D.A., SHVINDLERMAN, L.S., GOTTSTEIN, G. *Interface Science*, 2000, vol. 8, 335-349.
- [4] BISHOP, G.H., Jr., HARRISON, R.J., KWOK, T., YIP, S. *Simulation of Grain Boundaries at Elevated Temperatures by Computer Molecular Dynamics in Progress in Materials Science*, Chalmers Anniversary Volume, ed. J.W.Christian, P.Haasen and T.B.Massalski, Pergamon Press Ltd., 1981, pp 49-95.
- [5] HARGREAVES, F., HILLS, R.J. Work-Softening and a Theory of Intercrystalline Cohesion, *J. Inst. Met.*, 1929, vol. 41, pp. 257-262.
- [6] KRONGERG, M.L., WILSON, F.H. Secondary Recrystallization in Copper. *Trans AIME*, 1949, vol. 185, pp. 501-514.
- [7] AUST, K.T., RUTTER, J.W. *Trans TMS-AIME*, 1959, vol. 215, pp. 119-126.
- [8] PALUMBO, G., AUST, K.T. *Materials Interfaces: Atomic level structure and properties*. 1st. ed., London: D. Wolf and S. Yip, Chapman and Hall, 1989. 190p.