

Ultra-Fast Diffusion in Severely Deformed Materials

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1. Introduction

Severe plastic deformation (SPD) is nowadays used to produce sizeable amounts of bulk nanocrystalline materials, which renders them suitable for different innovative applications, owing to favourable combinations of high mechanical strength and enhanced ductility they offer. Enhanced grain boundary diffusion is largely responsible for the resulting property combinations.

SPD processing of metals is demonstrated to create bulk nanostructured materials with a hierarchy of internal interfaces [1]. In this contribution, the defects that represent the constituents of the fast diffusion network are analysed.

2. Hierarchy of short-circuit pathways

Grain boundary (GB) diffusion measurements in ultra-fine grained (UFG) Cu and Cu-rich alloys yielded generally two-step penetration profiles revealing the hierarchy in the short-circuit pathways. The skeleton of ultra-fast transport channels, which has a characteristic length on a micrometer scale, co-exists with a network of 'fast' diffusion paths formed by high-angle GBs that are abundant in SPD processed material (a typical scale for grain boundary separation distance being 300 to 500 nm for pure metals). Applying the general treatment of interface diffusion in a hierachic microstructure [2], the effective diffusivities of Ni tracer corresponding to the 'fast' and 'ultra-fast' paths were determined. In Fig. 1, these data are compared with the Ni GB diffusivity in annealed coarse-grained pure Cu [3]. The 'fast' paths in UFG materials are associated with relaxed high-angle GBs of the kind present in annealed coarse grained reference materials.

The ultra-fast diffusion paths reveal Ni diffusivities being several orders of magnitude higher than those associated with fast diffusion paths. A 'master' Arrhenius-type fit for Ni diffusion in UFG pure Cu and Cu-rich alloys may be drawn, the dashed line in Fig. 1. The enhanced penetration rates and a lower activation enthalpy of diffusion (by about 20 kJ/mol) may hypothetically be related to a 'non-equilibrium' state of these interfaces.

However, the atypical dependence of the shape of the penetration profiles on diffusion time found at low temperatures for UFG Cu-1wt.%Pb alloy [4] suggests strongly that there should be additional contributions to the ultra-fast penetration, especially at low temperatures. Such a contribution partially persists after high-temperature annealing of SPD-processed pure Cu [5] or Cu-rich alloys [4].

The severely deformed copper was annealed for thermal grooving under high vacuum conditions. The specimen surface was then analysed by scanning electron microscopy in

combination with the focused ion beam technique, see Fig 2. The results confirm the existence of a hierarchy of internal interfaces in the deformed material. The original grain microstructure of the SPD-processed material, at a scale of about 300 nm, can be recognized as 'ghost lines' corresponding to the 'old', pre-existing grain boundaries. Additionally, deep grooves corresponding to interfaces with unusually high energies (presumably, the 'non-equilibrium' grain boundaries) are seen.

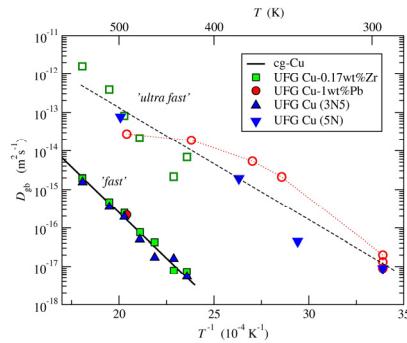


Fig. 1. The temperature dependence of the 'fast' (filled symbols) and 'ultra-fast' (open symbols) diffusivities D_{gb} in severely deformed pure Cu [5], Cu(Zr) [1] and Cu(Pb) [4] alloys. The solid line represents the GB diffusivity of ^{63}Ni in annealed coarse-grained (cg) high-purity Cu [3].

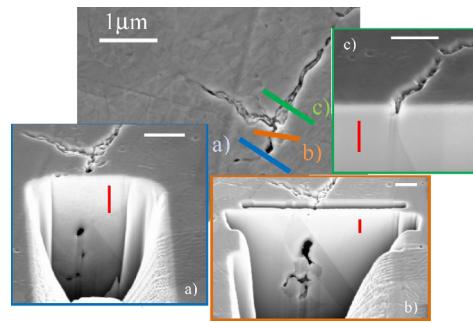


Fig. 2. Scanning electron microscopy images of SPD-processed Cu after annealing. The sample surface was cut in depth by FIB at the marked places near a triple line. The colour of the marks indicating the positions of the sections corresponds to the colour of the respective frame. The scale bars correspond to 1 μm.

An important and new feature is that in addition to those defects we observe considerably deeper grooves which tend to be located near triple lines between the high-energy grain boundaries. Application of the focused ion beam technique revealed the structures around a triple junction, Fig. 2. The corresponding frames demonstrate the existence of microcracks and internal porosity in SPD-processed copper. These microcracks/voids were typically found to be formed at the non-equilibrium grain boundaries near triple lines.

3. Conclusion

Non-equilibrium grain boundaries, non-equilibrium triple junctions, and microvoids were identified as constituents of the ultra-fast diffusion channels, which represent an important, and until recently unknown, feature of severely deformed materials.

References

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