Mechanism of the Mechanochemical Formation of Metastable Phases from the Reaction between Sulfur and Copper

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The formation of metastable copper sulfide phases by rubbing a sulfur-covered copper surface in ultrahigh vacuum is investigated by preparing copper samples with different crystallite sizes and therefore different values of strain-rate sensitivity and by measuring the rate of surface-to-bulk transport of these sample in ultrahigh vacuum. An electron microcopy analysis of focused-ion-beam (FIB) prepared samples reveals that both the presence of dislocations and grain boundaries facilitate the shear-induced transport of sulfur into the copper bulk.

Keywords: metastable materials, shear-induced processes, materials properties

1. Introduction

A previously identified shear-induced transport of sulfur into the subsurface region of copper [1] is investigated by modifying the properties of the copper by using different annealing temperatures (500, 850 and 1020 K) during the vacuum cleaning procedure. The diffusion kinetics are modeled by a theory proposed by Karthikeyan and Rigney [2] which predicts that the transport rate should be proportional to the strain-rate sensitivity, *m*, of the substrate. The rate of surface-to-bulk transport, measured by Auger spectroscopy from the loss of sulfur from the surface during rubbing, is found to depend on the copper annealing temperature. Nanohardness measurements were used to estimate the value of *m* and demonstrated that the sulfur surface-to-bulk transport rate depended linearly on *m*. The mechanism was investigated by preparing thin samples of copper using a focused-ion-beam (FIB) and by measuring the crystal structure and elemental composition of the copper subsurface by electron microscopy. The measured sulfur depth distributions agreed with the values calculated from the sulfur surface-to-bulk transport rates, where subsurface sulfur was found in crystalline regions of the sample suggesting that the transport kinetics are mediated by dislocations. However, in a sample that had small crystallites, sulfur was also found to be concentrated along grain boundaries, implying that surface-to-bulk transport of sulfur into copper is facilitated by the presence both of dislocations and grain boundaries.

2. Methods and Results

Experiments were carried out on a methyl thiolate overlayer on a copper substrate in ultrahigh vacuum where the rate of surface-to-bulk transport into copper was measured from the loss of sulfur from the surface for samples that had been annealed at different temperature (Fig. 1). This showed that the surface to bulk transport kinetics scaled with the strain-rate sensitivity (Fig. 1, Inset).

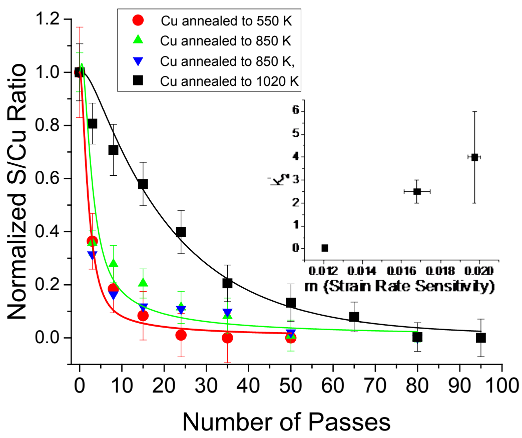

Figure 1: Plot of the relative sulfur-to-copper (S/Cu) Auger ratio measured inside the wear track as a function of the number of times that the copper samples had been rubbed after being cleaned and annealed at 550 (●), 850 (▲,▼) and 1020 (■) K. Shown as an inset is a plot of the surface-to-bulk transport rate as a function of the strain rate sensitivity*, m.*

Measurements of a FIB-prepared samples showed that the transport rate correlated with both the dislocation density and the presence of grain boundaries.

3. References

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