Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 62 (2010) 262–265
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Measurement and anisotropy of grain boundary energy in Cu–1 wt.% Pb

D. Empl, V. Laporte[1] and A. Mortensen*

Laboratory for Mechanical Metallurgy, Institute of Materials, Ecole Polytechnique Fédérale de Lausanne (EPFL, Station 12), CH-1015 Lausanne, Switzerland

Received 3 November 2009; revised 8 November 2009; accepted 9 November 2009
Available online 12 November 2009

A method is presented for the simultaneous measurement of relative grain boundary energy and all five macroscopic grain boundary degrees of freedom in leaded copper. When compared to the Wynblatt–Takashima model, results suggest a lowered boundary energy when there are equal broken-bond densities on either side of the boundary.

Keywords: Copper; Copper alloys; Electron backscattered diffraction (EBSD); Grain boundary energy; Dihedral angle

The three-dimensional (3-D) dihedral angle Φ presented by individual lead inclusions straddling a grain boundary in polycrystalline copper–lead alloys can be measured by means of a method presented in Ref. [1]. The method consists of dissolving inclusions selectively along a metallographic cut of the alloy and then reconstructing numerically, in space, the visible part of the 3-D liquid/solid interface using stereographic analysis software coupled with scanning electron microscopy (SEM). The technique is eased by the fact that the liquid Pb/solid Cu interfacial energy γ_{SL} is essentially isotropic (except for a slight faceting tendency at temperatures near the lead melting point) [1]. Inclusions situated along a flat grain boundary therefore have the classical lenticular shape, namely two equal-radius spherical caps that intersect, making the appropriate dihedral angle Φ along the $\text{Grain}_1/\text{Grain}_2$/inclusion triple line situated within the grain boundary plane; see illustration in Fig. 1. While constant Φ-values are obtained across several inclusions straddling a single grain boundary, it is found that Φ varies from one grain boundary to another, suggesting, in turn, that the grain boundary energy varies within the alloy [1,2].

The grain boundary between two adjacent grains (Grain_1 and Grain_2) is characterized by three microscopic and five macroscopic degrees of freedom (DOF). Microscopic DOF describe translations of the grains in relation to each other, parallel or perpendicular to the grain boundary plane. These are experimentally less accessible than the macroscopic DOF and not independent from the latter [3]. Therefore most work on the subject (e.g. [4–6]) has sought to relate the macroscopic DOF to the physical properties of grain boundaries. In the interphase plane scheme [7], four DOF are specified by the grain boundary plane normals N_1 and N_2 with respect to the adjacent crystals, while the fifth is given by the twist angle ψ about the grain boundary plane normal, generally measured with $\psi = 0$ corresponding to a low-energy cusp.

Electron backscattered diffraction (EBSD) can be used to measure the grain orientation on either side of a grain boundary along a metallographic cut. Determining the inclination of the grain boundary plane is somewhat more difficult. Usually, at least two metallographic analyses of the same region are conducted along two parallel metallographic planes of known separation distance [8].

The circle formed in the grain boundary plane by the triple line along the inclusion edge is determined directly in the dihedral angle measurement method of Ref. [1]; the method therefore enables acquisition, in addition to the value of Φ for each inclusion, of the orientation of the corresponding grain boundary plane normal. It is therefore possible to measure, by coupling the method of Ref. [1] with EBSD, both the value of Φ and all five macroscopic DOF of grain boundaries intersected by dissolved lead inclusions. Although, as will be indicated below, two polishes of the surface are needed to couple

* Corresponding author. Tel.: +41 21 693 29 12; fax: +41 21 693 46 64; e-mail: andreas.mortensen@epfl.ch
[1] Present address: Interdisciplinary Center for Electron Microscopy, Ecole Polytechnique Fédérale de Lausanne (EPFL, Station 12), CH-1015 Lausanne, Switzerland.

1359-6462/$ - see front matter © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.scriptamat.2009.11.012

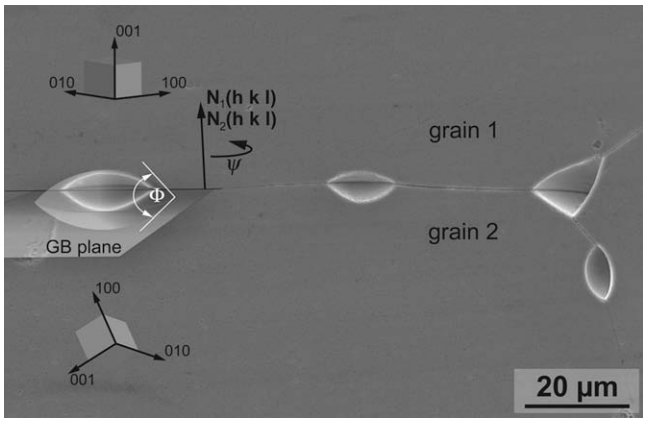

Figure 1. Schematic illustration of the parameters measured by the present 3-D dihedral angle measurement method (yielding Φ and the boundary plane normal) and the EBSD measurements (yielding normals N_1 and N_2 to the grain boundary plane relative to the respective crystal axes) of two grains adjacent to a lenticular, dissolved inclusion. From both measurements the twist angle ψ can be deduced. The sketch is superimposed on an actual metallographic section through Cu–1 wt.% Pb after dissolution of the lead inclusions.

the two characterization methods, the amount of material removed is marginal, so that the present method is effectively conducted along a single metallographic cross-section of the material.

As the solid Cu/liquid Pb interfacial energy γ_{SL} is isotropic (or at lower temperature essentially so) and lenticular lead inclusion morphologies show no sign of the influence of torque terms in the capillary equilibrium that dictates the shape of intergranular liquid lead inclusions, the Smith equation can be used a priori to link the dihedral angle Φ at the Grain$_1$/Grain$_2$/inclusion triple line with relevant interfacial energies:

$$\cos\left(\frac{\Phi}{2}\right) = \frac{\gamma_{gb}}{2\gamma_{SL}} \tag{1}$$

where γ_{gb} is the grain boundary energy [9,10]. The method, when coupled with EBSD, therefore gives direct access to the relationship that associates macroscopic grain boundary orientation parameters, as measured by the five DOF, with a measured relative value of grain boundary energy γ_{gb} (or, if γ_{SL} is known with precision, the absolute values of γ_{gb}). Here we give a "proof-of-concept" demonstration of the method, and compare data thus gathered for Cu–1 wt.% Pb with the Wynblatt–Takashima model for grain boundary energy in pure face-centred cubic (fcc) metals.

Specimens were prepared from cast 99.999% Cu alloyed with 1 wt.% Pb. The microstructure of the material was equilibrated at 600 °C under Ar (900 °C–3 h + 600 °C–40 h), this being a time sufficient for capillary shape equilibration of the liquid lead inclusions [11]. Samples were then quenched in water and mounted in conductive resin for metallographic preparation by grinding and mechanical polishing. On these metallographic samples the 3-D dihedral angle of individual lead inclusions was determined using the technique described in Ref. [1]. In order to obtain a correct numerical reconstruction of the inclusions it is important that some small features remain on the prepared surface so that the software for 3-D reconstruction can correctly adjust the microscopic images taken. A last step of polishing with 1 μm and slight etching with Klemm-III solution was therefore used [1].

For EBSD measurements the observed surface must be as smooth and clean as possible; for this reason an additional polishing step was needed. First the sample was marked with microhardness indentations to identify inclusion(s) for which Φ was measured, then the sample was repolished using a suspension of Al_2O_3-particles (200 Å), primarily to remove the oxide layer that formed during etching.

The EBSD measurements were done in a scanning electron microscope (Philips XLF 30 at the University of Neuchâtel), under a voltage of 25 kV. The chosen regions were analysed using step sizes varying from 0.85 to 1.5 μm. For EBSD measurements grains surrounding seven inclusions previously characterized for Φ were used. The four DOF related to the grain orientations were obtained following the procedure described in Ref. [8]. Computed orientations for the grain boundary plane normals are usually not integers. When transforming these into $N_1[h\ k\ l]$ and $N_2[h\ k\ l]$ having integer values h, k and l, the Miller indices were chosen to be as small as possible to keep the difference between the calculated normals and the integer normals below 3°, this being the uncertainty of the EBSD measurement.

Based primarily on the results of Wolf [12,13] for grain boundaries in fcc metals and on the nearest-neighbour bond model for coherent boundary energy [14], Wynblatt and Takashima proposed a model for the energy of grain boundaries in pure fcc metals [15–18]. The model is analytical and is based on a simple, geometrical view of grain boundaries that is useful in the analysis of data presented here. The Wynblatt–Takashima model takes into account three principal contributions to the grain boundary energy: (i) the nearest-neighbour bond energy; (ii) the free volume of the grain boundary; and (iii) variations in the grain boundary energy linked with the value of the twist angle ψ.

In essence, this model constructs a grain boundary by joining together two flat fcc crystal free surfaces cut parallel to the grain boundary plane. Corresponding crystal surface energies, γ_1 and γ_2, are calculated using a broken bond model that, knowing $N_1[h\ k\ l]$ and $N_2[h\ k\ l]$, counts the number, z_j, of broken bonds in all exposed atomic planes, numbered from 1 to J from the free surface inwards.

The energy of a special grain boundary formed by "gluing" together two "free surfaces" of identical $(h\ k\ l)$ is expressed as

$$\gamma_{gb(h\,k\,l)} = B\frac{1}{\sqrt{h^2+k^2+l^2}}\sum_{i=1}^{J}\sum_{j=1}^{J}(z_j - z') \tag{2}$$

where B is a constant that depends on the crystal lattice parameter and the crystal bond energy. The topology of the "surfaces" is decomposed into combinations of microfacets (terraces, steps and kinks), terraces being of (1 0 0) or (1 1 1) orientation [18,19]. Grain boundary cusps are found when grains can "interlock", meaning when steps associated with one of these two microfacets in one grain are parallel to such steps in the other.