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Misorientation Effects on Grain Boundary Grooving of Ni by Liquid Ag

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Abstract. The mechanisms of grain boundary grooving of polycrystalline Ni in contact with molten Ag at 1313 K in pure He are studied. Distribution of groove depths over a wide range of values are observed and explained by misorientation of grain boundaries. A method is proposed allowing to evaluate the anisotropy of grain boundary energy by measuring the angular and linear dimensions of grooves.

Introduction

Interfaces between low or moderate melting point liquid metals such as Pb, Sn, Ag, CuAg eutectic and high melting point metals and alloys (steels, Ni alloys, W etc.) play important role in various processes of practical interest such as soldering, hot dip metallic coating or heat transfer by liquid metals. During these processes one of the phenomena which can cause degradation of the solid is grain boundary (GB) wetting and grooving.

Since the classical work of Smith [1], it is well known that the relationship between GB and interfacial energy can be obtained from measurements of dihedral angles formed at the intersection of GB with solid/liquid interface:

$$\sigma_{gb}=2\sigma_{sl}\cos\frac{\phi}{2}. \qquad (1)$$

At high temperatures the anisotropy of f.c.c. metal – metallic melt interfacial energy is only a few percent [2]. On the contrary, GB energies vary in a very wide range depending on grains misorientation and plane position. For example, Murr [3] reported for Ni 866 mJ/m^2 at 1333 K for general GBs and 43 mJ/m^2 for twin GBs. Such differences would lead to a large distribution of dihedral angles. The goal of this study is to quantify the effect of GBs misorientation on the shape and growth kinetics of grooves formed at the interface between molten Ag and solid Ni. The Ag / Ni system was chosen because of the low miscibility of its constituents in both solid and liquid states. (The equilibrium molar fraction of Ni in the melt X_{Ni}^{Ag} is equal to $5.6\cdot10^{-3}$ at 1313 K [4]). The study is carried out using classical metallographic techniques to measure groove characteristics and electron back-scatter diffraction (EBSD) to determine the orientation of individual GBs.

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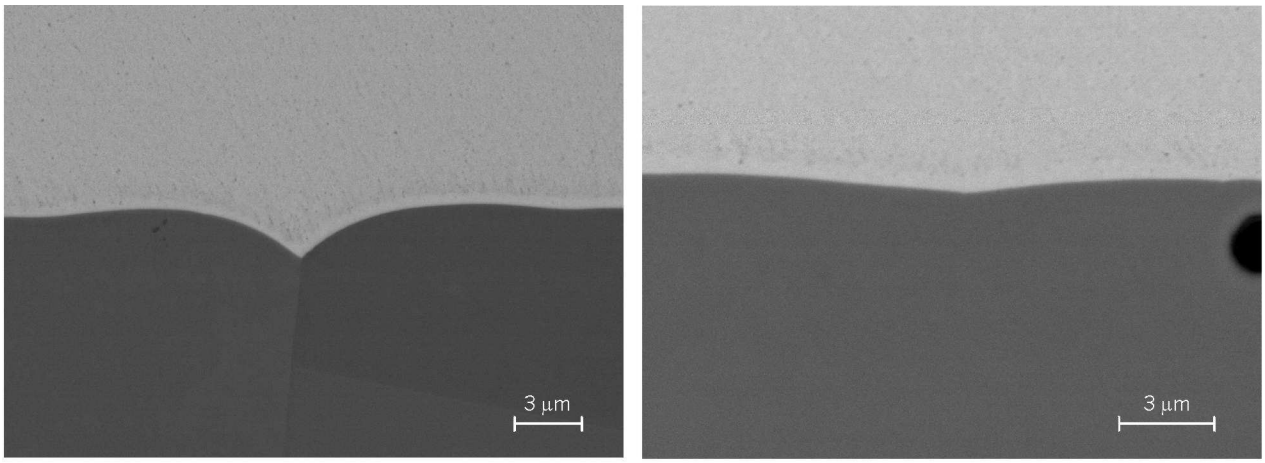
Experimental

High purity materials were used in this study. Silver was pre-melted under high vacuum to reduce possible oxygen contamination. Ni (99.997 % purity, containing 1 ppm of S) was cold wrought, mechanically ground and polished up to 1 μm diamond paste finish. Then the substrate was recrystallised at 1473 K for 8 hours in high vacuum and polished again. The average roughness of the surface measured by a high resolution optical interferometer was about 5 nm. In order to relax strain introduced by polishing, Ni platelet was heated again up to 1473 K for 30 minutes in high vacuum. Grain size about 100 – 200 μm was obtained.



a b

Fig. 1 Scanning electron micrographs of GB grooves on liquid Ag (light gray) / solid Ni (dark gray) interface after 2 hours at 1313 K. The section is perpendicular to Ag/Ni interface. (a) general GB, (b) special Σ3 GB

The experimental procedure consists of placing an Ag drop on Ni substrate directly at the experimental temperature (1313 K) using an introduction device described in [5]. In order to avoid Ni oxidation the experiment was carried out in a static atmosphere of helium purified by passing it through a bed of Zr–Al getter before introduction into the furnace. The good wettability achieved (contact angle close to 10° in agreement with earlier reported results [6]) testifies the absence of oxide film on substrate surface. The Ni platelet covered by silver drop was hold for 2 hs at 1313 K.

After cooling, the sample was cut perpendicularly to the interface, ground and polished up to 0.3 μm alumina suspension. Final finishing with ultra fine SiO_2 suspension was performed in order to eliminate strain that could perturb EBSD analysis used to determine the orientation of Ni grains intersected by solid/liquid (SL) interface. Scanning electron microscopy (SEM) was used to determine the dihedral angle and the linear dimensions of GB grooves.

Results and Discussion

Typical GB grooves, observed on the Ag / Ni interface are presented in Fig. 1. Molten Ag does not wet GBs, the dihedral angle formed at GBs grooves lying between 90° to 175° (Fig. 2b). However this distribution of angles results not only from misorientation effects of GBs but also from the obvious fact that the plane of metallographic section is randomly orientated with respect to the GBs planes. The last factor does not affect the measurement of groove depths. The distribution of groove depths results mainly from misorientation effects of GBs. The groove depths belong to two groups, a “small depth” group (typically a few tenths of microns) and a “high depth” group (a few microns). But even among the “high depth” group, grooves differing in d by a factor 2 to 2.5 have been observed (Fig. 2a). The walls of the grooves are convex and smooth. There is no facets on the groove walls which confirms the weak anisotropy of solid/liquid interfacial energy. According to

Mullins theory [7] during grooving the dihedral angle at the groove root takes its equilibrium value given by Eq. 1. The groove continues to grow driven by differences in curvature at the SL interface leading to a transfer of solid atoms from regions of high curvature near the groove root to regions of small curvature far from the root. If the grooving kinetic is limited by volume diffusion of solid atoms through the liquid, the grooves deepen and widen with time according to a $t^{1/3}$ law (the time exponent is ½ when groove growth is controlled by the dissolution – reprecipitation process at the interface and ¼ when the limiting step is interfacial diffusion):

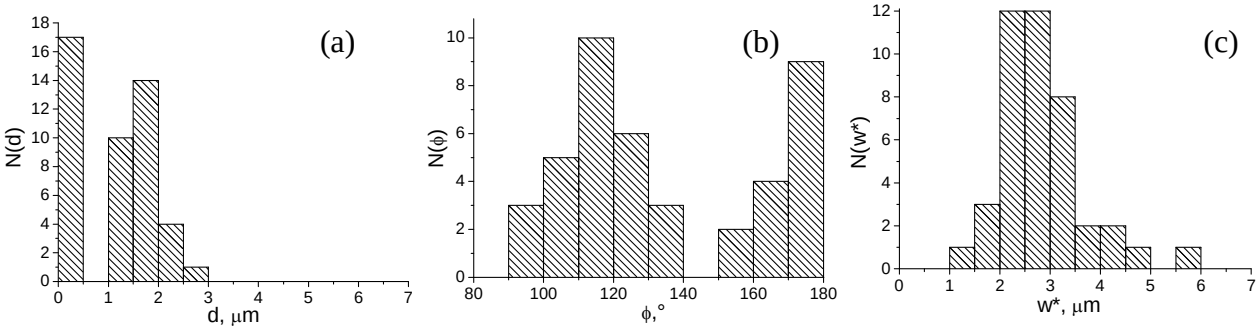


Fig. 2 GB grooving of Ni by Ag at 1313 K for 2 h. Distribution histogrammes for grooves depth d (a), dihedral angle ϕ (b) and reduced width w^* (c)

$$w/5 = d \cdot \mathrm{tg}\frac{\phi}{2} = 1.01 (At)^{1/3}, \tag{2}$$

A in this equation is a rate constant, w is the width and d the depth of the groove. The rate constant is function of the equilibrium concentration of solid in liquid C_0, interfacial energy σ_{sl}, molar volume of solid V_m and diffusion coefficient of solid atoms in liquid phase D:

$$A = \frac{C_0 \sigma_{sl} V_m^2 D}{RT}. \tag{3}$$

From Eq. 2 and Eq. 3 it is follows that the width of a groove as well as the product $d \cdot \mathrm{tg}\frac{\phi}{2}$ are not a function of GB energy and should be constant for a given sample. This is illustrated schematically in Fig. 3. As it is difficult to measure w accurately, we define a reduced width w^*:

$$w^* \equiv d \cdot \mathrm{tg}\frac{\phi}{2}. \tag{4}$$

Thus in the framework of Mullins model, the width w and the reduced width w^* are independent of GB energy in contrast to depth d and dihedral angle ϕ. In the following, as d and ϕ are measured with a much higher accuracy than w, the experimental grooving rate constant in Eq. 2 will be calculated using w^* instead of w.

The values of w^* calculated for all GB grooves, are plotted on Fig. 2c. Contrary to distributions of d and ϕ, the distribution of w^* is unimodal. Large scatter in w^* values results mainly from the difference between observed ϕ values and true ones due to the fact that the plane of metallographic section is randomly orientated with respect to the GBs planes (see above). Now it can be easily shown, by simple geometry, that the true value of w^* is that corresponding to the maximum of the distribution, i.e. it is the most frequently observed $w^* \approx 2.5$ μm. Using this value the experimental grooving rate constant can be calculated by Eq. 2: $A_{exp} = 2.1 \cdot 10^{-21}$ m^3/s.

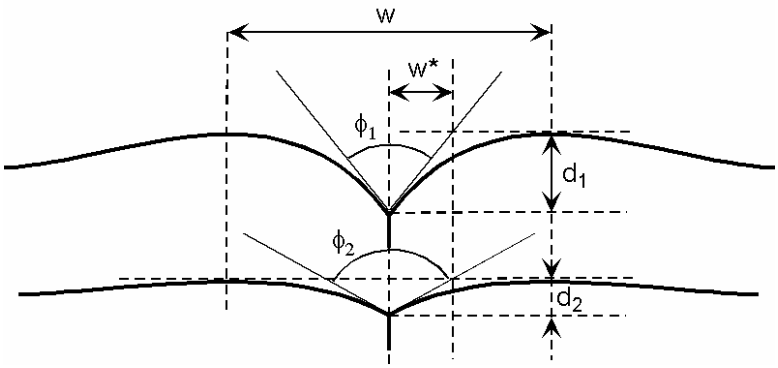


Fig. 3 Schematic presentation of GB grooves formed on high energy (1) and low energy (2) GB

To confirm our assumption of a groove growth limited by volume diffusion of solid atoms through the liquid, the value of A_{exp} will be compared to the value calculated using Eq. 3. This equation contains quantities which are known {D(1313 K) = $3.2\cdot10^{-9}$ m^2/s [8], V_m = $1.09\cdot10^{-29}$ m^3/atom and C_0 = 543.6 mole/m^3} and one unknown, the interfacial energy σ_{sl}.

This value can be estimated according to the following expression based on the simple model described in [9]:

$$\sigma_{sl} = \sigma_{sl}^{0} + \lambda \frac{m_1}{\Omega_m}\left(1 - X_{Ni}^{Ag}\right)^2 . \tag{5}$$

In this equation σ_{sl}^{0} is the interfacial energy of pure solid Ni in contact with pure liquid Ni (equal to 0.307 J/m^2 [2]), m_1 is the fraction of liquid – type bonds for the solid atom on the interface (for a (111) plane of Ni m_1 = 0.25), Ω_m is the molar area of Ni (Ω_m = $3.26\cdot10^4$ m^2/mole) and X_{Ni}^{Ag} is the equilibrium molar fraction of Ni in melt (at 1313 K X_{Ni}^{Ag} = $5.6\cdot10^{-3}$). λ is the regular solution parameter which can be easily estimated from the values of solubility of Ni in liquid Ag measured between 1260 and 1640 K [4] (λ = 55 ± 5 kJ/mole). According to these data, the interfacial energy of solid Ni in contact with liquid Ag is 0.72 ± 0.18 J/m^2.

Introducing this value into Eq. 3 one obtains A_{cal} = $5.0\cdot10^{-21}$ m^3/s. Taking into account the uncertainties on the experimental value of D (usually to a factor 5) and on the estimated value of σ_{sl}, this value of A_{cal} is in good agreement with the experimental rate constant deduced by Eq. 2 (A_{exp} = $2.1\cdot10^{-21}$ m^3/s). This agreement validates the assumption made on the mechanism of groove growth.

In our experimental procedure the depth of individual grooves is measured with a much better accuracy than ϕ. Therefore d values were chosen to calculate the energy of corresponding GB. Combining Eq. 1 with Eq. 4 one can obtain:

$$\sigma_{gb} = 2\sigma_{sl}\frac{d}{\sqrt{w^{*2} + d^2}} . \tag{6}$$

From the average orientation of neighbouring grains (obtained by EBSD technique) GB misorientation was calculated for each junction in form of rotation quaternion q [10,11]. In the framework of coincidence sites lattice model (CSL) [12], all GBs were divided into two groups, general and special. For nine general high–angle GBs the average value σ_{gb}^{G} = 0.91 J/m^2 was obtained. This value is in a good agreement with the value 0.866 J/m^2 reported by Murr [3]. Only one low–angle GB (11.6°) was found with σ_{gb} = 0.77 J/m^2. Almost all general GBs were grooved. For special GBs Σ-values of the closest perfect CSLs were found. Energies of all special GBs were lower than σ_{gb}^{G}. From 40 Σ3 GBs only half had grooves deep enough (depth higher than 0.1 μm) to be measured by SEM. The angular deviation from exact coincidence ν was calculated for each special GB according to Eq. 7, rigorously proved in [13]:

$$\nu = 4\arcsin\left(\frac{1}{2}\left|q - q_0\right|\right), \quad (7)$$

where q and q_0 are the rotation quaternions of experimental and ideal CSL misorientations respectively. In Fig. 4 the energies of Σ3, Σ5, Σ9 and Σ11 GBs are plotted versus ν. There is a tendency for the energy to grow with ν, that is especially evident for Σ3 GBs. Although the average energy of Σ3 GBs close to perfect coincidence is about 0.22 J/m^2 (Fig. 4), the GB energy values lie between ~0.05 and 0.72 J/m^2. We suppose that this dispersion is due to differences in GB plane orientation. GBs with lowest energies are probably the coherent twins and the highest energies correspond to energetically unfavourable GB plane positions.

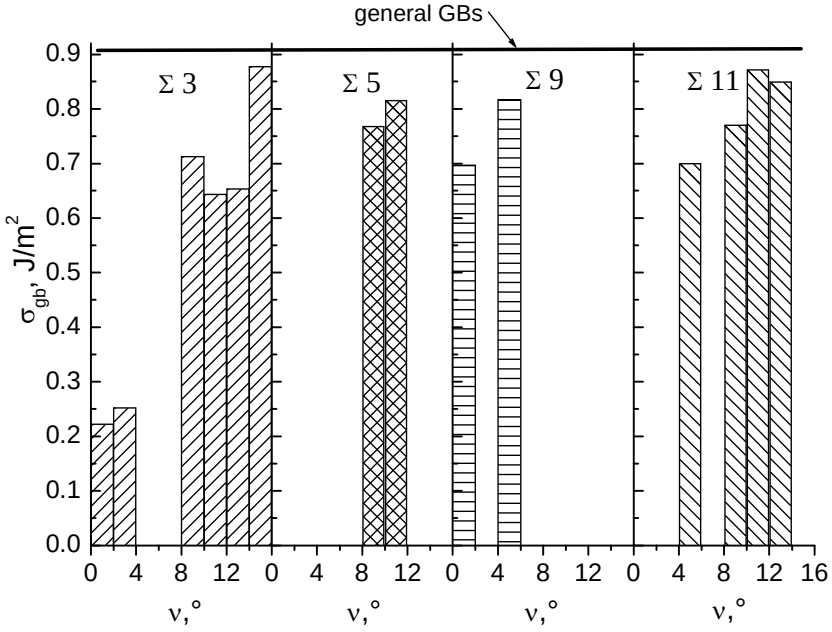


Fig. 4 Energies of special GBs Σ3, Σ5, Σ9, Σ11 plotted versus angular deviation from the corresponding perfect coincidence. The average energy level of general GBs is marked with horizontal line.

Conclusions

It was found, that molten Ag does not wet GBs of Ni, the dihedral angle formed at GBs grooves being close to or higher than 90°. GB grooving in liquid Ag/solid Ni system proceeds according to Mullins mechanism and kinetics of groove growth is controlled by diffusion through the bulk liquid. The groove depths measured in a sample vary by one order of magnitude. A method is proposed allowing to relate groove depths and dihedral angles with the anisotropy of GBs energy. For each Σ value of special GBs there is a correlation between their energy and the angular deviation from the corresponding perfect coincidence.

Acknowledgements

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Discussion

W. Gust: From my point of view, the experiment is not well designed. Instead of polycrystals oriented bicrystal should be used. The disadvantages of polycrystals are as follows:
(a) The inclination of the grain boundaries is unknown
(b) The solid / liquid interfacial energy is dependent on the orientation of the surface.

P. Protsenko: Of coarse, the investigation of liquid metal interaction with individual well defined GB needs the use of bicrystals. Nevertheless, the study of a large range of GBs geometry required the use of a great number of different bicrystals. The use of polycrystals – which usually are the real materials – present moreover the advantage that we can study interactions between liquid metal and different GBs in one experiment.
(a) In principle, orientation of Gb plane in polycrystal can be measured from several consequent metallographic sections, as it was performed by [P. Wynblatt and M. Takashima, Trans. JWRI Vol.30 (2001), p.11]
(b) In literature, it was shown that at elevated temperature the anisotropy of f.c.c. metal/metallic melt interfacial energy is only a few percents [2].

B. Bokstein: I am somewhat confused by the small difference between tension of general and special boundaries. Usually it is more drastic.

P. Protsenko: The difference between tension of general and special GB may be either drastic (for example in the coherent twin / high angle GB their ratio may be higher than 20 as it shown in this study) or even moderate. Indeed, the position of GB plane can significantly change the energy of special GB. It was shown, that the energies of $\Sigma 3$ GBs in Cu vary by one order of magnitude depending on GB plane orientation [B.Straumal, S.Polyakov et al., this issue]