

PRESSURE EFFECT ON GRAIN BOUNDARY DEWETTING AND PREMELTING TRANSITION IN A Fe-6 at.%Si BICRYSTAL

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The pressure effect on diffusion of Zn along a $45^\circ\langle 100 \rangle$ grain boundary (GB) in an Fe-6at.%Si bicrystal was studied in the pressure range up to 1 GPa. A Zn layer was deposited on the surface of the bicrystals. It was found that at low pressures the Zn rich liquid wetted the grain boundary perfectly. Next to the GB groove there was a region where Zn diffusion along the grain boundary was enhanced by two orders of magnitude. It is postulated that in the enhanced diffusion region a GB premelting transition has taken place. Increasing pressure caused a dewetting transition at the grain boundary. At the same time the premelted GB region disappeared. The transition pressure was a function of the temperature. There was a minimum transition pressure of 175 MPa at about 790°C. The above results were interpreted based on the heterophase fluctuation theory.

INTRODUCTION

Wetting of grain boundaries (GBs) by liquids is a phenomenon that attracts considerable attention [cf.1,2]. One can distinguish two wetting states:

- a) Complete wetting, when the dihedral angle at the intersection of the GB and liquid is zero.
- b) Incomplete wetting, when the dihedral angle has a non zero value.

Upon a change of intensive thermodynamic variables a transition between the above two states can take place.

We will further call the $a \Rightarrow b$ transition a "dewetting transition" while the $b \Rightarrow a$ transition will be called "wetting transition". In a recent study of wetting of a $45^\circ[100]$ tilt boundary transition in a Fe-6at.%Si bicrystal by liquid zinc, it was [3,4] discovered that the pressure causes a de-wetting transition. Furthermore, the dihedral angle value increased with increasing pressure. At the annealing temperature of 1178K, the transition pressure was about 0.5GPa.

The wetting angle measurements were carried out parallel to studies of diffusion of zinc along the grain boundary. It was found that complete GB wetting occurred then and only then,

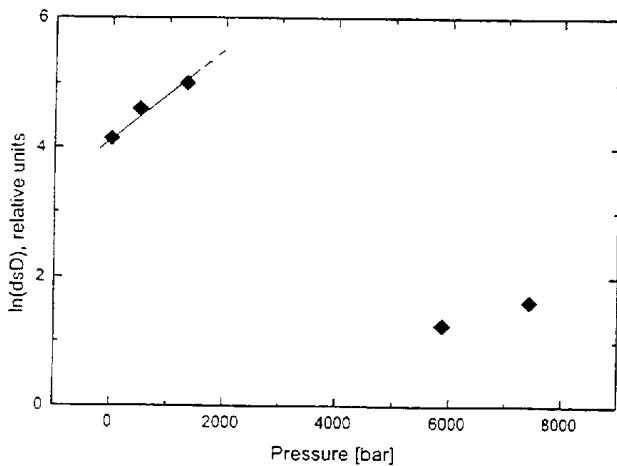


Fig.1 Pressure effect on the triple product for Zn diffusion in the $45^\circ[100]$ tilt grain boundary in the Fe-6at.%Si bicrystal. D- Zn GB diffusion coefficient, d- GB thickness, s - Zn segregation factor.

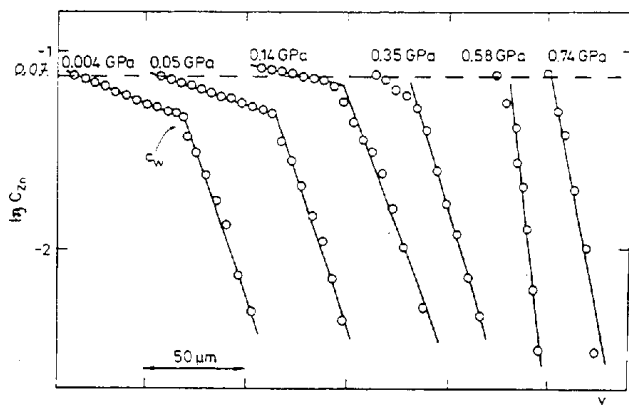


Fig.2. Pressure effect on the concentration profiles of Zn along the grain boundary. y - depth along the GB. Dashed line: the 7% Zn concentration level according to Rabkin et al [5].

when the GB in the regions adjacent to the liquid zinc layer had undergone a phase transformation, which was identified as GB premelting. The characteristic feature of this transformation was a discontinuity of the GB diffusion coefficient. Figure 1 shows the pressure effect on the Zn GB diffusion coefficient, at constant Zn concentration

$C_{Zn} = 0.07$. A similar transition takes place when the Zn concentration decreases. Figure 2 shows the pressure effect on the Zn concentration profiles. Under the conditions that pressure is less than 0.5 GPa, at the high-Zn-concentration side, the GB displays a more than two orders of magnitude higher diffusion coefficient than on the low-zinc-concentration side. The unusually high diffusion coefficient led Rabkin et al. [3-5] to the conclusion that the GB is in a "premelted" state. In other words, under the above conditions a thin liquid-like structure is thermodynamically stable in the GB. Thermodynamic calculations lead to the layer thickness of about 10 nm [5].

The purpose of this paper is to present the results of our study of the pressure effect on the wetting-dewetting transition temperature and to propose an interpretation of the premelting and dewetting transition in terms of the effect of bulk phase transitions on the GB structure.

EXPERIMENTAL

The bicrystals were prepared from vacuum melted Fe-6at.%Si alloy by the floating zone method. The orientation of the bicrystal axis and misorientation of the crystals were measured by X-ray Laue diffraction with the accuracy of $\pm 1^\circ$.

The as grown bicrystal was cut by electro-spark cutter into specimens of 12 mm length (parallel to the [100] direction) and $1.5 \times 1.5 \text{ mm}^2$ crosssection. The GB was situated in the middle of the samples, parallel to the [100] axis. A zinc layer was deposited on each sample by immersion into liquid zinc. After the immersion, zinc was removed from all sides of the samples except for the ones perpendicular to the [100] axis. Excess zinc was removed so that only a 100-150 μm layer remained. For the high pressure annealing, the specimens were placed in a stainless steel container of I.D. 7.9 mm. In the bottom part of the capsule about 50 mm^3 of zinc were placed to ensure equilibrium zinc vapour concentration in the capsule during

high pressure annealing. The capsule was not tight, so that argon under high pressure could penetrate it. The high pressure experiments were carried out in a high pressure cell. The temperature in the capsule was measured with an accuracy of $1 \pm K$. Pressure was measured with accuracy better than 1% using a manganin coil.

After the high pressure annealing, the samples were polished and examined by light microscopy and the dihedral angle at the GB groove was measured.

RESULTS

The results of annealing are presented in Fig. 3; open circles correspond to complete wetting, whereas the solid circles indicate incomplete-wetting. This figure shows how the pressure at which wetting transition occurs depends on temperature. It can be seen that around $T=790^\circ C$, the minimum transition pressure was observed.

Fig. 4 shows the optical micrographs of the GB groove at the contact place of the liquid zinc and grain boundary after annealing at high pressure. The photographs in the first row indicate the first occurrence of incomplete wetting after transition wetting-dewetting.

The second row photographs correspond to the last occurrence of complete wetting prior to the transition. The transition temperature has a minimum close to 1063K ($790^\circ C$).

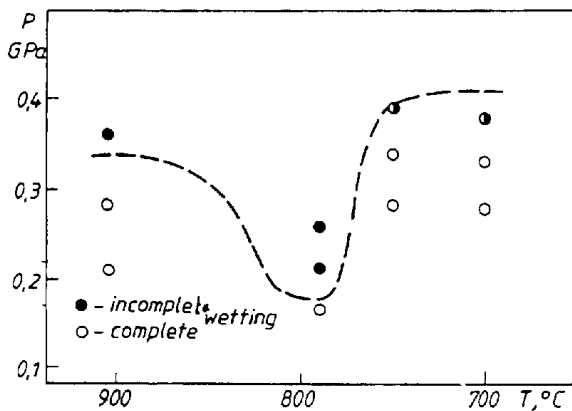


Fig.3. Temperature effect on the wetting-dewetting transition pressure.

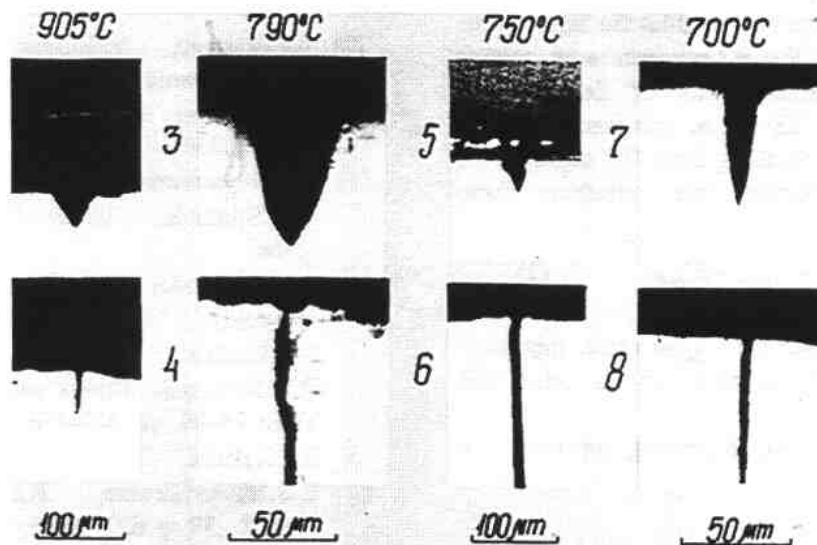


Fig.4. Optical micrographs of the GB groove at the contact place of the liquid Zn and grain boundary.

DISCUSSION

The pressure effect on the wetting transition can be explained under the assumptions that the energy of the pre-melted GB increases with pressure more rapidly than of the GB with regular structure.

The following equations describe the equilibrium of surface tensions for the complete-wetting state:

$$\gamma_{GB} = 2\gamma_{SL} + g \quad (1)$$

where γ_{GB} is the surface tension of a regular grain boundary, γ_{LS} is the liquid-solid interface surface tension and g is the energy of the pre-melted layer per unit surface [5]. It follows that complete wetting takes place if $2\gamma_{SL} + g < \gamma_{GB}$. Hence, the wetting and premelting behaviour depends on the energy of the thin layer of the grain boundary that is in the pre-melted state.

In order to explain the occurrence of the minimum at temperature 790°C Fig. 3, which corresponds to peritectic temperature of Fe 6% Si-Zn, we assume that the energy of the GB depends on the zinc concentration in the grain boundary. The higher the zinc concentration, the more the GB structure reassembles the liquid state. This is so, since all the experiments were carried out above the melting point of Zn. The Zn concentration in the GB can be split into two parts: the equilibrium one resulting from GB segregation, and the nonequilibrium one, resulting from diffusion.

$$C_{Zn} = C_{Segr} + C_{Diff} \quad (2)$$

Hence, the higher the C_{Segr} value, the lower the C_{Diff} concentration necessary to cause GB premelting.

We propose the following equation for C_{Segr} :

$$C_{Segr} = C_o \exp\left(\frac{Q + a(T - T_p)}{T}\right) \quad (3)$$

Where T_p is the peritectic temperature and $a(T - T_p)$ is the energy difference between Zn - liquid phase and the Γ phase, which forms below the peritectic temperature. $a=0$ for

$T > T_p$. In other words, below the peritectic temperature, Zn in the grain boundary forms with iron atoms solid clusters of the Γ phase, and is not any more available for the liquidlike grain boundary phase. As a consequence, at T_p the highest concentration of Zn in liquid clusters in the boundary is present. Therefore, the density of the interface is lowest and the pressure effect on its energy is highest.

This interpretation of the existence of the minimum of transium pressure at T_p is consistent with the heterophase fluctuation theory, where it is assumed that thermal fluctuations at lattice defects take the structure of the closest neighbourhood phase in the phase diagram [6].

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