

PRESSURE EFFECT ON PREMELTING TRANSITION IN A TILT GRAIN BOUNDARY IN AN Fe-Si ALLOY

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ABSTRACT - The effect of pressure on the diffusion of zinc along a $43^\circ\langle 100 \rangle$ tilt grain boundary in an Fe-6at%Si alloy was investigated. Zinc penetrated into the grain boundary from a 100 μm thick liquid layer on the surface of the bicrystal. It was found that penetration of zinc causes a premelting phase transition in the grain boundary. The phase transition was suppressed for pressures higher than 0.5 GPa.

INTRODUCTION - Phase transitions in interfaces attract increasing attention of physicists and materials scientists. They were studied by means of computer simulation (1,2), electron microscopy (3,4), measurement of electric and magnetic properties (5,6) of grain boundaries (GBs) as well as by studying GB migration, surface tension and diffusion (7,8). Particularly, interface phase transitions accompanying wetting are of interest (9-11). They were predicted by Cahn (11) for two component fluid in contact with solid. The phase transitions on interfaces can be classified analysing the free energy of the wetting layer (11):

$$\gamma = 2 \sigma_{LS} + l\Delta g + f(l) \quad (1)$$

Here σ_{LS} is the surface tension of the interface between the crystal and the wetting phase, l is the thickness of the wetting layer, Δg is the excess bulk free energy of the wetting phase and $f(l)$ describes the interaction of the two opposite interfaces between the crystals across the wetting phase (fig.1).

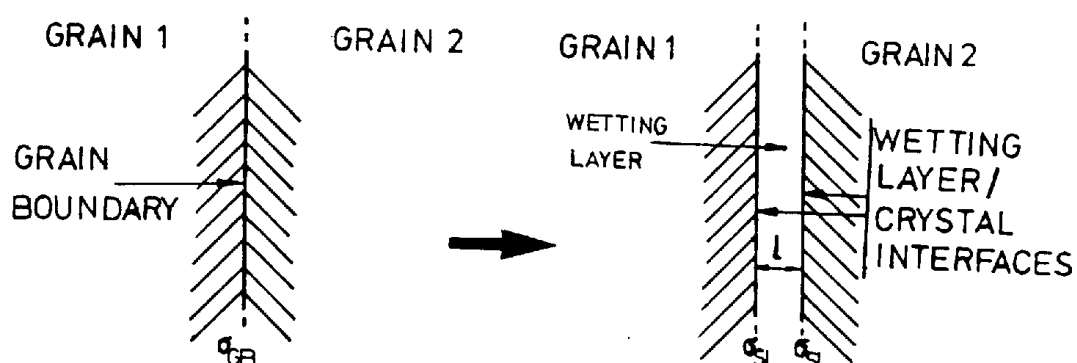


Fig.1. Schematic illustration of the premelting transition at a grain boundary.

It has to be pointed out that σ_{LS} in general may denote the energy of any interface between the wetting phase and the adjoining grains, even if the wetting phase is solid. We have adopted the LS subscript because in the below presented case we shall consider the "premelting" phase transition, where the GB becomes wetted by

a fluid. It may take place if $\gamma < \sigma_{GB}$, where σ_{GB} is the GB free energy. The thickness of the wetting layer depends on the value of l_0 corresponding to minimum of the function $\gamma(l)$.

Generally, f is a decreasing function of l . Far from phase co-existence line wetting is unfavourable because Δg takes high values (fig.2a). If there is such a value of l that $\sigma_{GB} = \gamma(l_0)$, a thin layer of wetting phase penetrates the GB (figs.1 and 2b). As the phase co-existence line is approached, Δg further decreases to zero and l_0 increases to infinity (figs.2c and d). Complete wetting/melting may occur under two conditions:

$$a) \sigma_{GB} > 2\sigma_F + f(\infty) \quad (2a)$$

$$b) f(l) \text{ has a global minimum for } l = \infty \quad (2b)$$

If the function $f(l)$ is not decreasing monotonically, the situation may complicate significantly. When Δg decreases, the following transitions take place: the premelting transition (fig.2f), the transition thin film + thick film (figs.2g and h) and complete wetting (fig.2i). The situation is also possible where premelting takes place but wetting is incomplete (fig.2e). The phase diagrams shown in figs.2j-1, illustrate the sequence of grain boundary phase transformations as the phase co-existence line is approached.

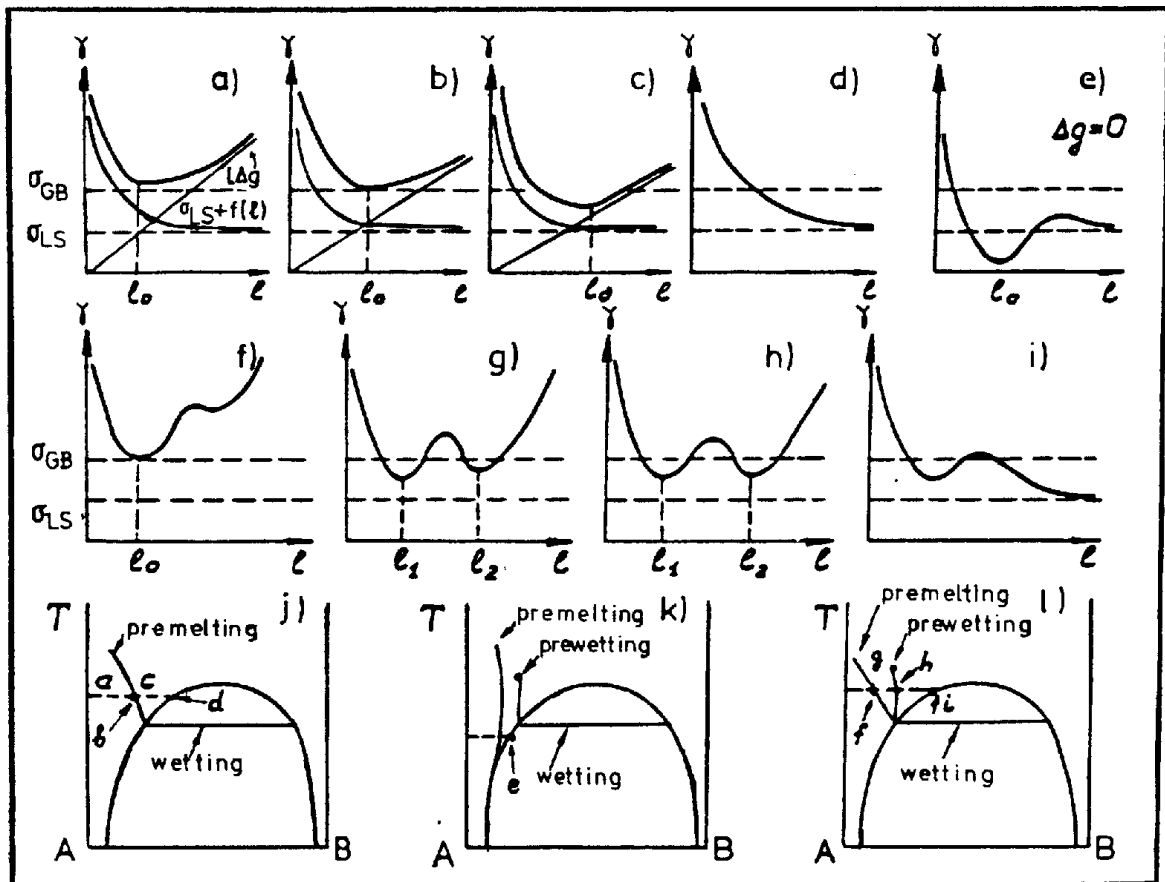


Fig.2. The interface energy γ as a function of the thickness of the wetting layer l .

a-d: For a monotonic dependence of $f(l)$ on l , Δg decreases from the left to the right.

e-i: For a non-monotonic variation of $f(l)$ with l .

j-l: Phase diagrams illustrating the thermodynamic coordinates of the system in each of the above presented cases.

In our previous work (8,12) we have studied the penetration of liquid zinc along symmetrical tilt GBs in an Fe-5at%Si alloy. We observed the formation of a GB groove with a dihedral angle $\theta \approx 0$. Zinc diffused along the tilt axis of the GBs. Close to the grain boundary groove GB diffusion coefficients of Zn were by two orders of magnitude higher than in the region more distant from the groove and of lower Zn concentration. We assumed a GB premelting transition to occur for Zn concentrations exceeding a value c_w . For the premelting transition a change of specific volume of the GB should take place. Hence, the parameter Δg controlling the thickness of the wetting layer should be pressure dependent. The purpose of the present work was to apply high pressures as an additional thermodynamic parameter in order to obtain more insight in the nature of the above phase transformation.

EXPERIMENTAL PROCEDURE - A bicrystal with a $43^\circ \langle 100 \rangle$ symmetrical tilt boundary was prepared from an Fe-6at%Si alloy. The method of preparation of specimens and of analysing Zn diffusion profiles is described in detail in refs. (8,12). For the high pressure experiments, the following modifications were introduced. Bars 10 mm long and 1.5×1.5 mm² in cross-section were cut from the as-grown bicrystal. The grain boundary tilt axis was parallel to the long faces of the bars. The bars were immersed in liquid Zn. Afterwards, all zinc was removed except for a 100 μ m thick layer parallel to the tilt axis of the grain boundary. The bars were placed in a stainless steel container of external diameter 9 mm and separated by sheaths of titanium foil. On the bottom of the container 50 mm³ of liquid Zn was deposited in order to prevent evaporation of Zn from the bars.

The containers were placed in the high pressure furnace. The temperature was measured by means of a Chromel-Allumel thermocouple inserted in a hole in the container. The furnace was inserted in a high pressure cell produced by UNIPRESS. Pressure was measured by means of a manganin gauge with accuracy of 2%. Annealings were carried out in pure argon atmosphere. The annealing temperature was 1178K. The temperature oscillations were less than ± 1 K. The thermocouple calibration was corrected taking into account the pressure effect on its thermopower. The pressures and times of annealing are listed in tab.1. After high pressure annealings, the specimens were mechanically grinded and polished. Zn concentration profiles were measured by means of electron beam microprobe taking into account all necessary corrections and precautions.

RESULTS - Fig.3 shows the GB groove after annealing under two different pressures. Fig.4 shows the pressure dependence of the dihedral angle of the GB groove. For pressures below 0.6 GPa, $\theta \approx 0$. When the pressure was higher than 0.5 GPa, the groove angle started to increase. Fig.5 shows the penetration profiles of Zn along the grain boundary. The same features as in refs. (8,12) are observed. For Zn concentration higher than a concentration c_w , the Zn concentration in the grain boundary varies gently. For Zn concentrations lower than c_w , the rate of Zn penetration along the grain boundary decreases abruptly. The region corresponding to high Zn diffusion coefficient disappears for a pressure of 0.6 GPa.

TABLE 1

Pressure [GPa]	Time [h]
0.004	1
0.050	1
0.145	2
0.450	2
0.580	2
0.740	3
0.830	4
1.170	4
1.400	5

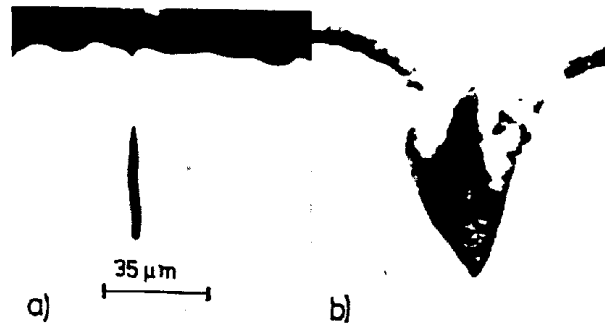


Fig.3. Scanning electron microphotographs of grain boundary grooves at the surfaces of the bicrystal which are wetted by liquid zinc. After annealing under pressure 0.05 GPa (a) and 0.74 GPa (b).

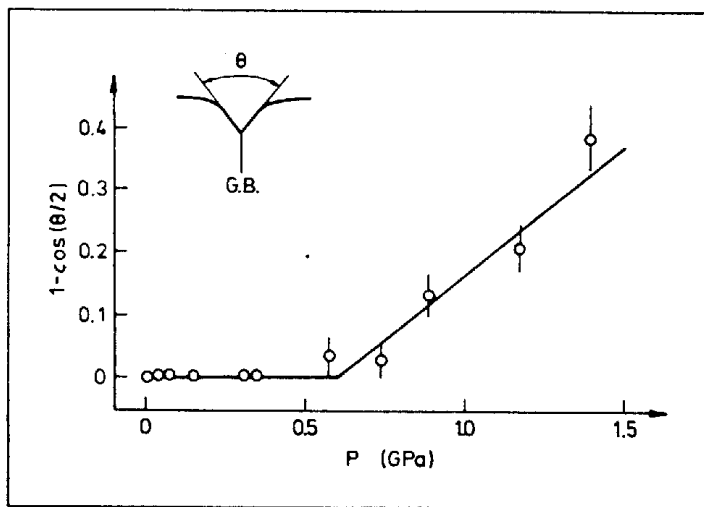


Fig.4. Pressure dependence of the dihedral angle of the grain boundary groove.

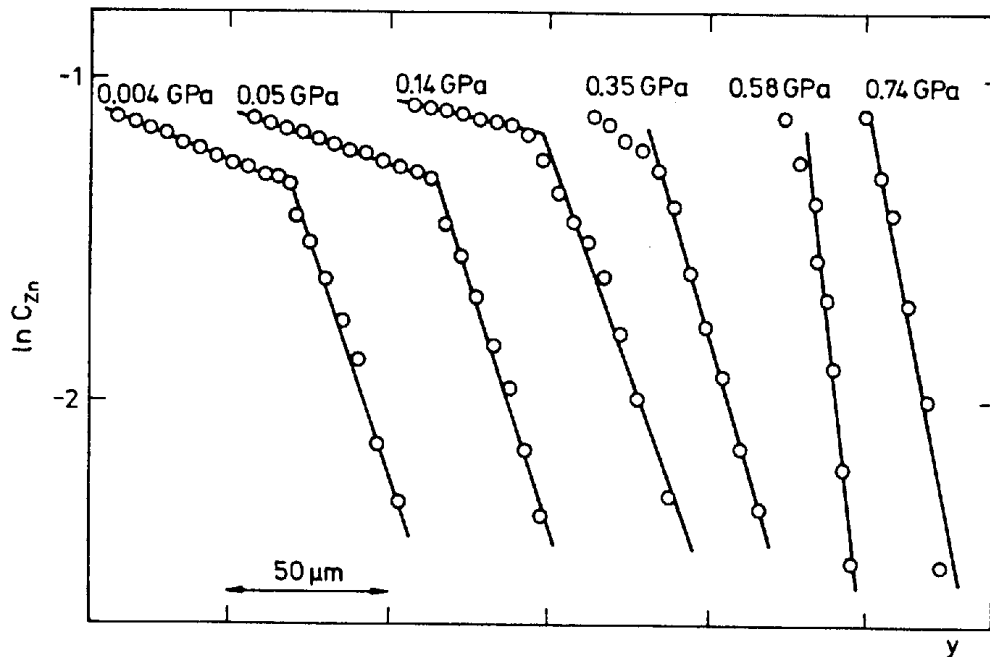


Fig.5. Concentration profiles of Zn at the grain boundary after annealing at 1178K at various pressures.

Fig.6 shows the pressure dependence of the measured concentration of zinc (c_w) at the point of grain boundary phase transformation as well as the solid solubility limit of Zn in the Fe-6at%Si alloy. The latter one was measured by the usual diffusion couple method. For pressures between 0.5 and 0.6 GPa c_w becomes equal to the solubility limit.

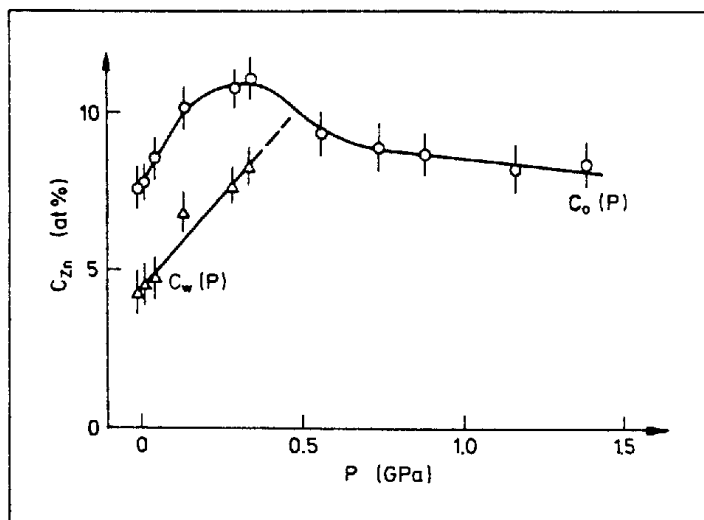


Fig.6. The pressure dependence of the measured concentration of Zn at the point of GB phase transformation (c_w) and of the Zn solid solubility limit (c_0).

DISCUSSION - It can be seen from the above figures, that at about 0.5 GPa a GB phase transition occurs. Below 0.5 GPa the melt with high zinc concentration wets the grain boundary. Above this pressure wetting of the GB by the melt is absent. Simultaneously with wetting disappears also the region of rapid grain boundary diffusion of zinc. It seems that in above region the GB has undergone a premelting transition induced by a high concentration of zinc. Thus we have obtained one more confirmation to our hypothesis (8,12) that wetting of the grain boundary by the liquid phase is a necessary condition for the premelting transition.

An essential result of the present work is that the premelting transition is suppressed for pressures above 0.5 GPa. In order to understand the reason of such a strong pressure effect, let us assess the order of magnitude of the pressure necessary to suppress the phase transformation.

The necessary condition for transition from incomplete to complete wetting is:

$$\sigma_{GB}(p_w) = 2 \sigma_{LS}(p_w) \tag{3}$$

The pressure p_w can be calculated within the framework of the Gibbs method. The excess volume of the interfaces are neglected and only changes of adsorption coefficients are taken into account;

$$\sigma_{GB}(p) = \sigma_{GB}^0 - \Delta\mu_1 \Gamma_1^{GB} - \Delta\mu_2 \Gamma_2^{GB} \tag{4a}$$

$$\sigma_{LS}(p) = \sigma_{LS}^0 - \Delta\mu_1 \Gamma_1^{LS} - \Delta\mu_2 \Gamma_2^{LS} \tag{4b}$$

Here the subscripts $i=1,2$ denote Fe and Zn, respectively. Γ_i are the adsorption coefficients and LS denotes the boundary between the wetting phase and the crystal. $\Delta\mu_1$ and $\Delta\mu_2$ are equal to $V_{1,p}$ and $V_{2,p}$, respectively, where $V_{1,2}$ are the atomic volumes. We assume that Γ^{LS} is negligible comparing to Γ^{GB} . This assumption may be explained in the following way: Considerable absorption of

Zn on the crystal-wetting phase interface would simply correspond to a shift of the interface by an appropriate distance. We assume the grain boundary solution to be a substitutional one. Hence:

$$\Gamma_{\text{Fe}}^{\text{SL}} \approx -\Gamma_{\text{Zn}}^{\text{SL}} \approx nKn_{\text{a}} \quad (5)$$

where n_{a} is the number of atoms in unit of surface of one atomic layer on grain boundary, n is the number of atomic layers in grain boundary, K is the concentration of Zn atoms in the grain boundary. Combining eqs.(3-5) one obtains:

$$p_{\text{w}} = \frac{\sigma_{\text{GB}}^{\text{SL}} - 2\sigma_{\text{LS}}^{\text{SL}}}{nK(V_1 - V_2)n_{\text{a}}} \quad (6)$$

The physical interpretation of eq.(6) is as follows: If premelting is associated with replacing iron in the grain boundary with a Zn rich phase of higher specific volume than Fe, then the grain boundary phase transition should be suppressed under pressure p_{w} . Let us calculate this pressure. Typically for metals (13) $\sigma_{\text{GB}}^{\text{SL}} - 2\sigma_{\text{LS}}^{\text{SL}} \approx 100 \text{ mJ/m}^2$ and $n_{\text{a}} \approx 10 \text{ m}^{-2}$. The differences of atomic volumes may be assessed from differences of specific volumes of body-centred cubic iron and hexagonal close-packed zinc: $V_1 - V_2 \approx 4 \times 10^{-29} \text{ m}^3$. From the Fe - Zn phase diagram one may conclude that the Zn concentration in the melt close to the solid-liquid interface is close to 70%. Hence, we assume K to be the Zn concentration in the wetting phase, i.e., 0.7. For a grain boundary thick by 3 atomic layers we obtain:

$$p_{\text{w}} \approx 0.9 \text{ GPa} \quad (7)$$

This is in reasonable agreement with our experimental result $p_{\text{w}} \approx 0.5 \text{ GPa}$. An even better agreement with our experimental result would be obtained if it is taken into account that the GB width may increase during the premelting transformation. For an expansion of the GB by 30%, $n_{\text{a}} \approx 4$ and $p_{\text{w}} \approx 0.7 \text{ GPa}$. Such an expansion is reasonable in the light of the recent computer simulation of the phase transitions in grain boundaries (1,2). CONCLUSIONS - Under the influence of diffusion of zinc, a premelting phase transition may take place in grain boundaries in an Fe-6at%Si alloy. In the case of the investigated $43^\circ \langle 100 \rangle$ tilt grain boundary this phase transformation can be suppressed if zinc penetration takes place at pressures higher than 0.5 GPa.

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