

## Effect of Temperature and Pressure on Grain Boundary Segregation and Wetting

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**Abstract** — The paper concerns the recently observed phenomenon that in Fe–6at.%Si bicrystals wetted by a Zn-rich melt under high pressure the dewetting transition is observed not only when the temperature is lowered but also when it is raised. There is also a temperature at which the lowest pressure is necessary to suppress grain boundary (GB) wetting. This unusual behaviour of a system at the peritectic temperature is explained based on the concept that the GB is built up from clusters of atoms, whose properties depend on the chemical composition and local coordination. Perfect GB wetting is connected with the coalescence of clusters with a liquid-like structure. This transformation takes place if the concentration of Zn in the GB achieves a threshold value  $c_T$ . It is assumed that the Zn concentration in the GB can be divided into three parts:

- $c_1$ : Zn atoms bonded with iron in clusters of a structure like the intermetallic compound  $\Gamma$ .
- $c_2$ : The maximum possible equilibrium Zn concentration of atoms non-bonded into intermetallic phases.
- $c_3$ : The nonequilibrium concentration of Zn atoms that accumulated in the GB from kinetic reasons, measurable experimentally in the bulk close to the GB.

The assumed condition for the wetting transition is  $c_2 + c_3 = c_T$ . The concentration  $c_2$  decreases at high temperatures because of desegregation of Zn. Therefore, to induce the transition,  $c_3$  must increase with temperature. The above phenomenon that GB premelting occurs at higher Zn concentration with increasing temperature, was called „GB solidification with increasing temperature”.

### 1. Introduction

The main parameter describing GB wetting is the dihedral angle  $\theta$  formed by the two liquid/solid interfaces, merging into the grain boundary. A variation of the thermodynamic parameters can cause the wetting transition:  $\theta \neq 0 \Rightarrow \theta = 0$  or dewetting transition:  $\theta = 0 \Rightarrow \theta \neq 0$  [1–7]. Recently the wetting of Fe–6at.%Si bicrystals by liquid zinc was extensively investigated [1–6]. The thermodynamic variables determining the state of the boundary were temperature ( $T$ ), pressure ( $p$ ) and the concentration of zinc close to the boundary ( $c_{o,GB}$ ). It was observed that the GB diffusivity had unusually high values even in the sections of the GB ahead of the wetted zone [1]. This was attributed to the premelting transition in the GB. A particular feature of the system investigated was that upon rising the temperature above the peritectic temperature the inverse to premelting transition took place (Fig. 1). When the wetting experiments were carried out under high pressure, it was observed that at high temperatures GB dewetting transition takes place. It was further found that there is a minimum transition pressure at the peritectic temperature (Fig. 2).

The purpose of the present paper is to propose a model for the GB structure that explains the role of the peritectic temperature for GB wetting.

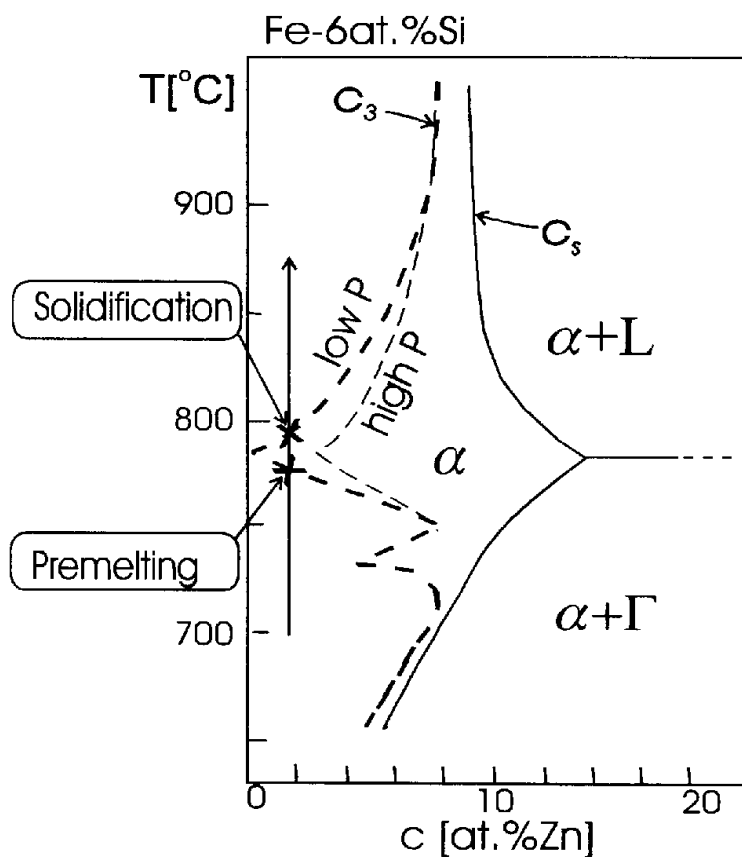


Fig. 1. Segment of the bulk (solid lines) and GB phase diagram (broken lines) for a  $45^\circ\langle 100 \rangle$  GB in Fe-6at.%Si wetted by Zn (according to Rabkin et al. [1]). The effect of Si on the phase diagram was neglected.  $c_3$  is defined as the concentration of Zn in the bulk close to the GB above which the GB wetting and premelting transition take place. The lowest  $c_3$  value is for the peritectic temperature. The small cusp is connected with the Curie point.

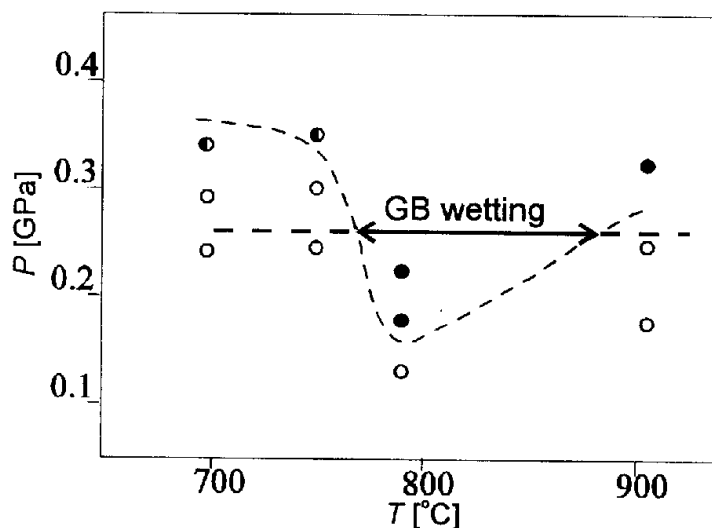


Fig. 2. Temperature effect on the dewetting transition pressure in Fe-6at.%Si wetted by Zn (according to Rabkin et al. [5]). The transition pressure has a minimum close to the peritectic temperature. Black points – wetted GB. White points – dewetted GB. Black-white points – partially wetted GB.

## 2. Model

Let us consider an Fe-6at.%Si bicrystal wetted by a layer of Zn perpendicular to the GB. The grain boundary is initially free from Zn. We make the following assumptions.

1. The Zn atoms that diffuse along the GB can occupy three types of GB sites:
  - (a) Corresponding to a local coordination similar to the intermetallic phase  $\Gamma$  (called „bonded Zn atoms”). The concentration of bonded atoms will be noted as  $c_1$ .  $c_1 \rightarrow 0$  as  $T$  approaches the peritectic temperature.
  - (b) Zn atoms in „solid solution” positions in the GB. Their concentration  $c_2$  corresponds to the equilibrium segregation of Zn at a given temperature and pressure.
  - (c) Zn atoms of concentration  $c_3$  that accumulated in the GB owing to Zn diffusion towards the GB. The concentration that is measured by electron probe microanalysis close to the boundary before the wetting and premelting transition is proportional to  $c_3$ .

Premelted clusters form around GB sites rich in non-bonded Zn atoms. At a threshold value  $c_T$  of the concentration of such clusters, the premelting transition takes place. So the transition takes place when the concentration of non-bonded Zn atoms (no matter whether in solid solution sites or non-equilibrium sites) reaches the value:

$$c_T = c_2 + c_3 \quad (1)$$

From Eq.(1) follows: the lower  $c_2$ , the higher is  $c_3$ . Below the peritectic temperature  $c_2$  decreases as the temperature decreases because „bonded” sites are energetically favourable. Above the peritectic temperature  $c_2$  decreases because desegregation of Zn from grain boundaries becomes energetically favourable. Therefore, the minimum  $c_3$  value corresponds exactly to the peritectic temperature. The relations between the above three concentrations are illustrated schematically in Fig. 3. Figure 4 shows the model of the diffusion fluxes leading to the GB wetting transition.

## 3. Discussion

The paper bases on the concept that the segregation of low melting point elements to GBs enhances GB wetting. The new observation was that under pressure an increase of the temperature causes the dewetting transition. Further, exactly at the peritectic temperature the pressure to suppress wetting was smallest. The explanation proposed bases on the following ideas:

1. GB wetting is preceded by a phase transformation and formation of a thin liquid-like film.
2. The agent causing the transformation is diffusion of the low melting point element along the grain boundary. Therefore, we can say that a GB is susceptible to wetting if a small diffusion flux causes the transformation.

The GB is composed of clusters of different chemical composition and thermodynamic properties.

In the present case, we consider the following types of clusters:

- (a) Clusters of iron atoms. These clusters do not display any melting-like behaviour up to the melting point of iron.
- (b) Clusters of Zn atoms and Fe atoms bonded in a similar way as in the  $\Gamma$  phase. They can be regarded as solid up to the peritectic temperature.
- (c) Clusters of Zn atoms. These clusters contribute to the GB premelting transition.

It is assumed that the GB undergoes the wetting transition when the concentration of melted-like clusters reaches a threshold level. As a consequence, the higher is the concentration of clusters with a structure similar to the melt, the more the GB is susceptible to the transition. A measure of the susceptibility is the measured excess concentration of Zn that diffused to the GB from the melt. This concentration increases as the equilibrium concentration lowers.

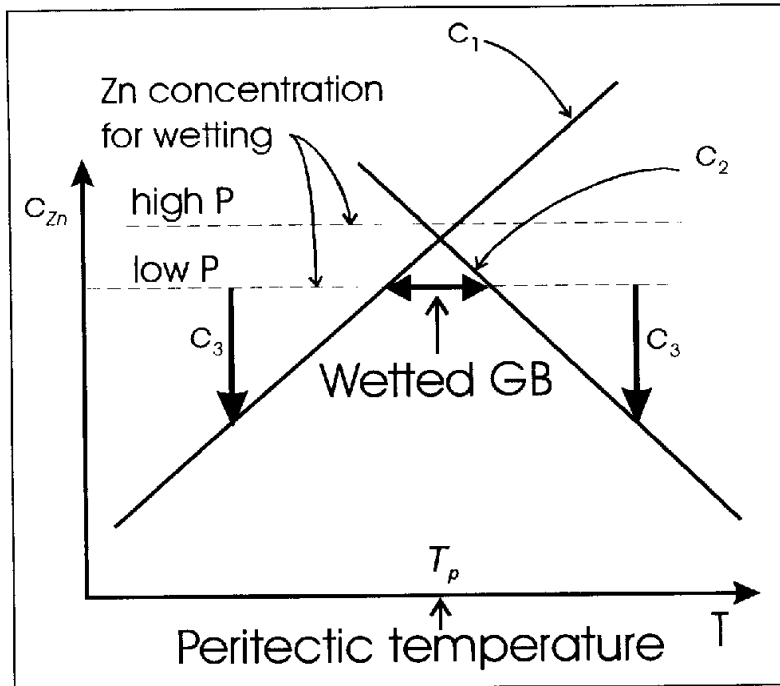


Fig. 3. Schematic representation of the variations of  $c_1, c_2$  and  $c_3$  as a function of temperature and pressure. See text for explanations.

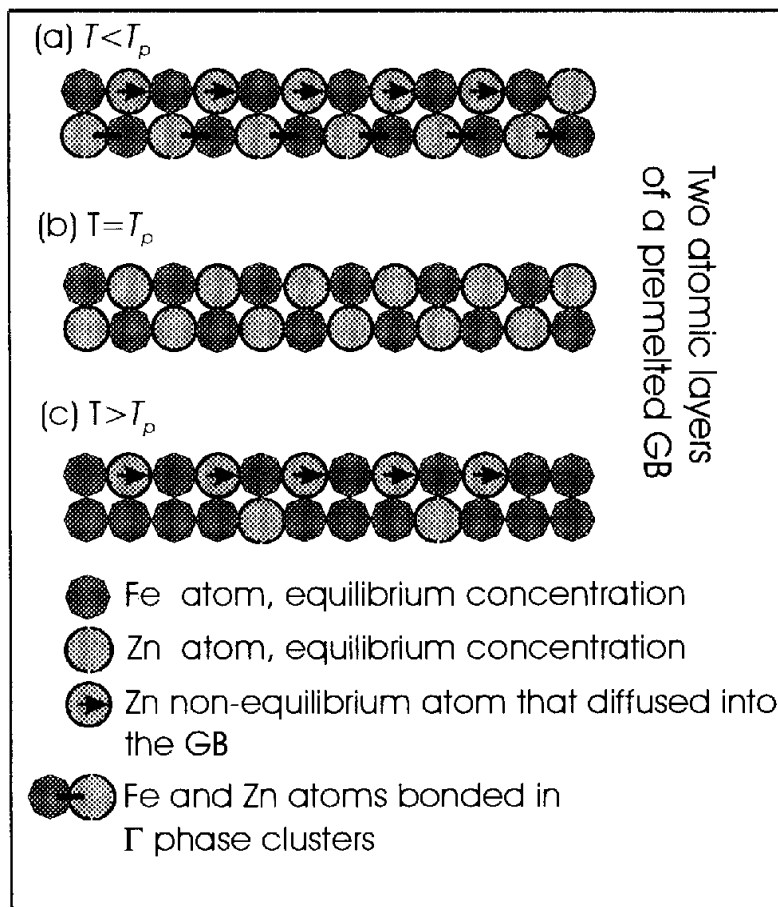


Fig. 4. Model of the GB phase transition before GB wetting. Three temperatures are considered: below  $T_p$ , at  $T_p$ , and above  $T_p$ . For the sake of illustration, it is assumed that to cause the transition every fourth GB atom must be a non-bonded Zn atom. At low temperatures the Zn atoms are bonded, and a relatively large amount of Zn atoms must reach the GB by diffusion. On the other hand, at high temperatures Zn desegregates, and again to cause GB wetting a large number of atoms must reach the GB by diffusion.

The following equation for  $c_{o,GB}$  was proposed [8]:

$$c_{o,GB} = c_o \exp\left(\frac{Q + \alpha(T - T_p)}{RT}\right) \quad (2)$$

$$T > T_p \Rightarrow \alpha = 0$$

Here  $Q$  is the segregation energy for Zn atoms to the GB,  $R$  is the gas constant and  $\alpha(T - T_p)$  is the energy difference between two types of GB clusters: "premelting" clusters close to Zn atoms and "solid" GB clusters with  $\Gamma$ -type coordination.  $\alpha=0$  for  $T > T_p$ .

A consequence of Eq.(2) is that at high temperatures the concentration of „premelting“ clusters is low and the GB is less susceptible to wetting and premelting than close to the peritectic temperature. This leads to the concept of „solidification of the grain boundary with increasing temperature“. In fact, the experiments with very pure aluminium at temperatures close to the melting point did not show any premelting and wetting phenomena [9]. It was shown in previous papers that the formation of a liquid-like phase at the GBs is suppressed at high pressure. If the formation of liquid-like clusters is connected with an increase of the volume per atom, the segregation of Zn to grain boundaries would be associated with a positive segregation volume. The segregation volume  $V_s$  is defined as [10,11]:

$$V_s = V_1 - V_2 \quad (3)$$

where  $V_1$  is the volume of the crystal before a Zn atom jumped into the GB and  $V_2$  is the volume after the Zn atom jumped into the GB. As a consequence, the Gibbs energy of segregation changes according to the equation:

$$G_s = Q_s - TS_s + pV_s \quad (4)$$

The  $pV_s$  term causes that at high pressure the GB with a high Zn concentration is energetically unfavourable (Fig. 2). So the equilibrium concentration of Zn clusters is decreased and the susceptibility of the GB to the wetting transition is decreased.

Recently, the importance of the segregation volume for GB diffusion under pressure was demonstrated by Lojkowski et al. [10, 11]. It was found that the activation volume for In diffusion along GBs in copper bicrystals was negative (cf. Fig. 5). At the same time the activation volume for bulk diffusion of In was  $0.96 \Omega$ , where  $\Omega$  is the atomic volume of copper and the atomic volume of In is a factor 2.3 larger than the atomic volume of copper. Lojkowski et al. [10, 11] pointed out that the measured activation volume for GB heterodiffusion is the sum of the true activation volume for diffusion and the segregation volume:

$$V_p = V_s + V^* \quad (5)$$

where  $V_p$ ,  $V_s$  and  $V^*$  are the measured activation volume for the GB diffusivity, the segregation volume and the true GB diffusion activation volume, respectively.

To assess the true activation volume an upper limit for the segregation volume must be defined. It was assumed that  $V_s$  is less than difference of the atomic volume of an indium and copper. In other words, when an indium atom replaces a copper atom in the GB, the boundary volume is constant while the total volume of the bulk decreases.

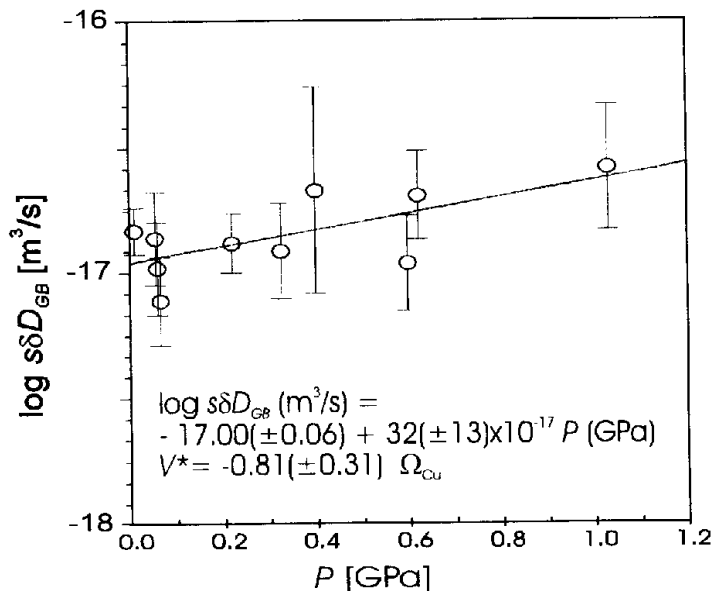


Fig. 5. Pressure effect on  $^{115}\text{In}$  diffusion along a  $45^\circ\langle 100 \rangle$  tilt GB of Cu [10, 11].

#### 4. Conclusions

A model of the structure of GBs containing segregated low melting point elements is proposed. It is assumed that around the atoms of the low melting point element liquid-like clusters form in the GB. An exception is if the above element forms intermetallic compounds with the matrix atoms. A consequence of the above model is that the susceptibility of the GB to the wetting transition depends on the concentration of such clusters. However, it decreases at high temperatures owing to de-segregation, and at low temperatures it may decrease owing to formation of clusters of intermetallic compounds. The above model leads to the possibility of GBs becoming less susceptible to the wetting transition at high temperatures than at intermediate temperatures. This phenomenon was observed in the case of an Fe-6at.%Si bicrystal wetted by Zn and was called „solidification of the GB with increasing temperature”.

The above model explains also the pressure effect on GB wetting. The key concept is there the segregation volume, i.e., the change of the volume of the crystal when the solute atom jumps into the grain boundary.

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