

## PRESSURE EFFECT ON GRAIN BOUNDARY KINETICS AND PHASE TRANSITIONS

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*Topics: grain boundary energy, grain boundary migration, grain boundary diffusion, activation volume, wetting*

### ABSTRACT

We performed investigation of the pressure effect on grain boundary migration (GBM), diffusion and wetting. In the case of GBM in Al, activation volume values in the range from  $0.6\Omega$  up to  $2.85\Omega$  were found. Investigations of the pressure effect on GB wetting and diffusion were carried out in a Fe-5%Si bicrystal. The diffusing element was zinc. Zinc was deposited as a liquid layer on the bicrystal surface. Near to the liquid zinc layer there was a region of unusually high diffusion coefficients. This region, as well as grain boundary wetting, disappears above a transition pressure. The transformation pressure ranges from 0.2 up to 0.5 GPa. This seems to be a first rapport about pressure effect on phase transformations in grain boundaries.

### INTRODUCTION

The grain boundary (GB) structure is different from that of bulk and different from amorphous materials [1]. Therefore, the atomic transport mechanism in GBs might be different from that the bulk case. The it should depend on the grain boundary free volume. For large free volume, it can be speculated that relatively large atoms might move by an interstitial mechanism or that the vacancy structure might be considerably relaxed. The relative free volume of the GB is [3]:

$$f = \frac{\text{grain boundary atomic volume}}{\text{bulk atomic volume } (\Omega)} \quad (1)$$

The GB atomic volume is not known yet. The pressure effect on the grain boundary energy is:

$$\gamma = \gamma_0 + fp\Omega \quad (2)$$

where  $p$  is pressure. Hence  $f$  can be evaluated measuring the pressure effect on the GB energy.

One of the methods to identify atomic transport mechanism is to measure the pressure effect on the transport rate. The pressure effect on the kinetics of thermally activated processes (denoted here  $A$ ) depends on the activation volume  $V$ .  $A$  and  $V$  are related as follows [2]:

$$A = A_0 \exp\left(\frac{-Q - pV}{RT}\right) \quad (3)$$

$$V \approx -RT \frac{\partial \ln(A)}{\partial p} \quad (4)$$

The pressure effect on the pre-exponential factor is linear and was neglected.  $V$  depends on the diffusion mechanism, type of defect controlling the diffusion rate and degree of lattice relaxation around the defect. High pressure research provides a way to measure  $V$  [1,5-11].

### PRESSURE EFFECT ON GRAIN BOUNDARY MIGRATION IN ALUMINIUM

We performed measurements of the pressure effect on grain growth and GB migration in bicrystals with predetermined crystallographic orientation relationship.

#### i) Grain growth under high pressure.

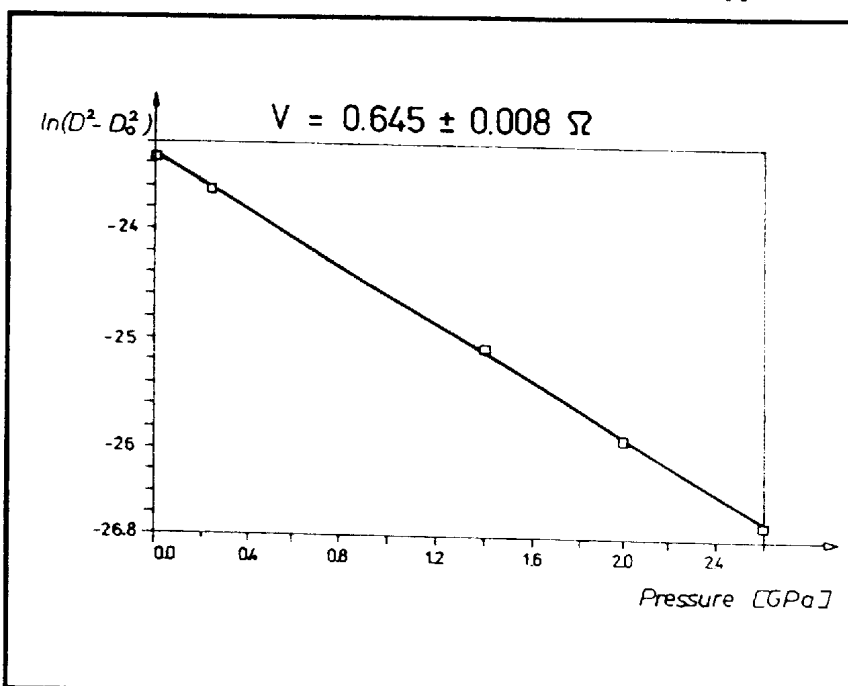
The pressure effect on grain size in 99.99% purity aluminium was measured for pressures up to 2.5 GPa. The initial grain size was  $4.2\mu\text{m}$ . The annealing temperature was  $400^\circ\text{C}$ . Table 1 lists the impurity content in the polycrystal. We found that the activation volume for grain growth was  $0.64 \pm 0.01\Omega$ . The relationship between the square of the grain size and pressure was exactly linear (fig. 1).

Table.1 Impurity content in the Al samples

Si	Fe	Zn	Cu	Ba	S	P	Ca	Cr	Mn	Pb	K	V
24	24	21	19	16	12	5	2	1	1	1	1	1

#### ii) Grain boundary migration in bicrystals under high pressure.

Aluminium bicrystals were prepared by crystallisation from a bi-crystalline seed, using a 5N material. The Fe content in the bicrystals was 20-30 ppm. The sum of the other impurities didn't

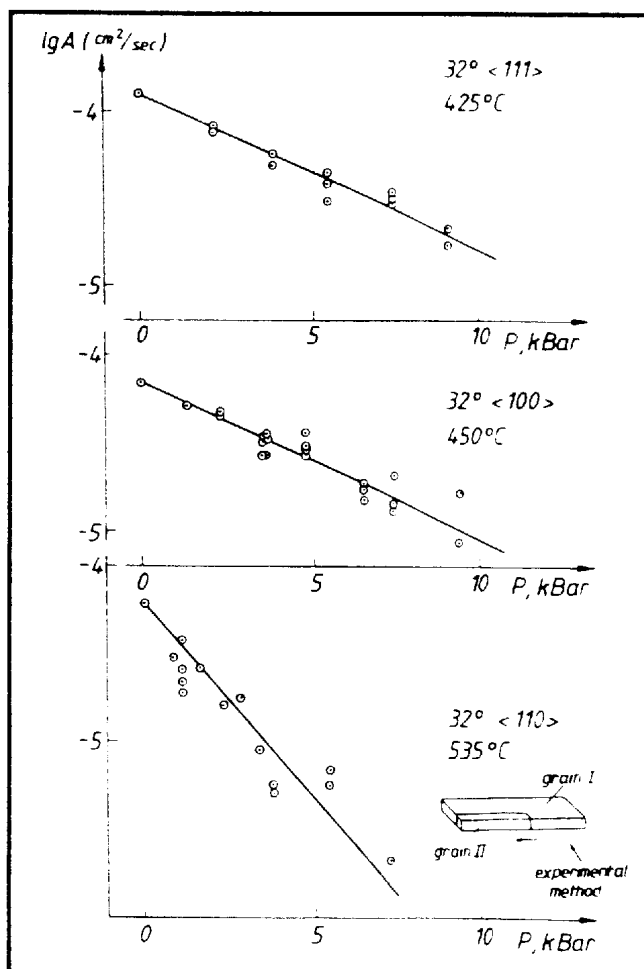


exceed 40 ppm in total. For all boundaries the  $\{100\}$ ,  $\{110\}$  and  $\{111\}$  tilt axis was perpendicular to the migration direction. For each tilt axis, one low  $\Sigma$  coincidence boundary and one general boundary were prepared. Figure 2 shows the experimental scheme for grain boundary migration at constant driving force and some experimental results. The bicrystals were annealed in a high pressure argon atmosphere, at pressures up to 1 GPa. Table 2 lists the activation volumes and activation energies measured.

Fig.1. Pressure effect on final grain size in Al. Initial grain size:  $4.2\mu\text{m}$ . Annealing temperature:  $400^\circ\text{C}$ .

Annealing time: 1 hour.  $V=0.65 \pm 0.01\Omega$

## SUMMARY OF THE INVESTIGATIONS OF THE PRESSURE EFFECT ON GRAIN BOUNDARY MIGRATION



**Fig.2.** Pressure effect on grain boundary migration in aluminium bicrystals.

### High activation volumes for low index tilt boundaries might indicate that in such boundaries the migration is connected with jumps of groups of atoms or with a divacancy mechanism. Assuming that the grain growth rate is controlled by GB's mobility and the activation volume $0.6\Omega$ is the average activation volume for GB migration, there should be boundaries with activation volumes less than $0.6\Omega$ .

The above results lead to the following general conclusions:

- The activation volume for GB migration and diffusion is for the GBs investigated positive. It depends on the crystallographic orientation relationship of the boundaries. Tilt boundaries with [110] tilt axis are characterised by higher activation volume for migration than other boundaries.
- The correlation between activation energy and volume is not straightforward. It seems the the GB structure factor influences this correlation.
- For constant misorientation axis, coincidence GBs have higher activation energies for GB migration than non-coincidence ones.

**Table 2**

Activation Energy and Volume for Grain Boundary Migration and Diffusion in Aluminium

Bicrystals: grain boundary migration	Misorientation			Activation		T[K]
	Axis	Angle	$\Sigma$	Energy [kJ/mol]	Volume [V/ $\Omega$ ]	
	<100>	$36.9 \pm 0.4$	5	112.9	$1.20 \pm 0.12$	723
	<100>	$31.8 \pm 0.4$		196.5	$1.15 \pm 0.09$	808
	<111>	$37.1 \pm 0.4$	$\cong 7$	163.0	$1.14 \pm 0.08$	698
	<111>	$32.0 \pm 1.0$		196.5	$0.95 \pm 0.10$	698
	<110>	$38.5 \pm 0.5$	9	179.7	$1.38 \pm 0.08$	698
	<110>	$32.0 \pm 1.0$		275.9	$2.85 \pm 0.28$	698
grain growth					$0.64 \pm 0.01$	673
Polycrystal: Zn <sup>65</sup> tracer GB diffusion	sub-boundaries [3,8]			119.0	$0.86 \pm 0.06$	574.5
	general-boundaries			90.7	$0.80 \pm 0.10$	574.5
	two groups [3,8]			59.8	$1.08 \pm 0.14$	574.5
Zn <sup>65</sup> bulk diffusion [3]				119.6	$1.1 \pm 0.1$	

### PRESSURE INDUCED PHASE TRANSFORMATIONS IN GRAIN BOUNDARIES

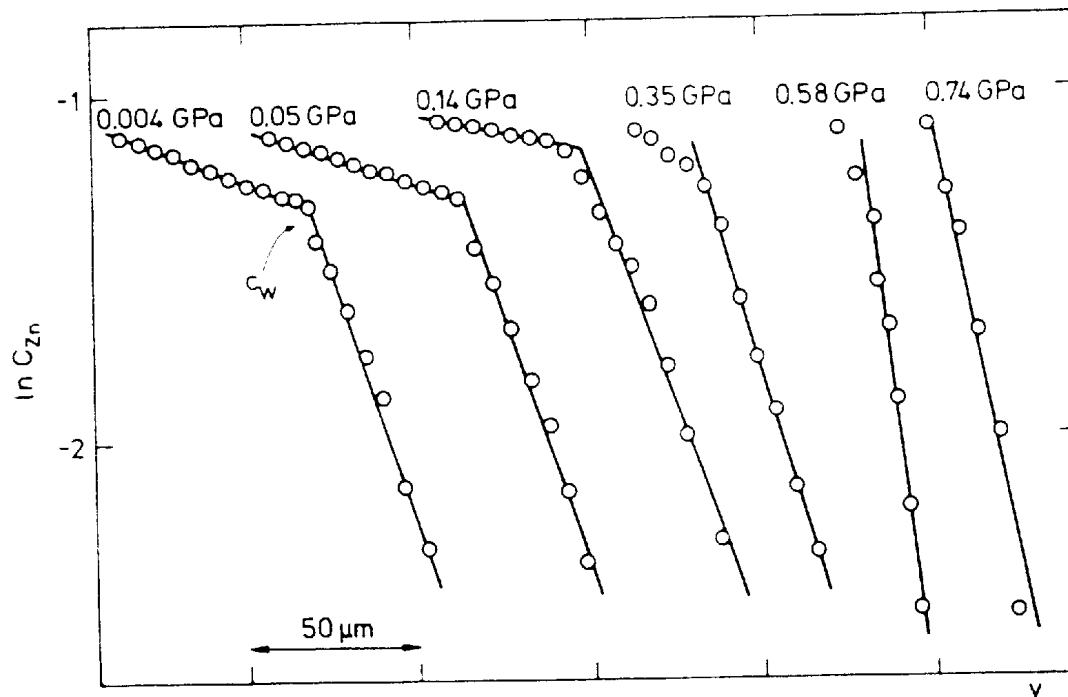
In this part of the paper we review results of our study of pressure effect on Zn penetration along a  $45^\circ[100]$  GB in a Fe-5%Si bicrystal.

Rabkin et al [12] demonstrated that Zn penetration along the above tilt boundary causes a transformation in the grain boundary structure. In the Rabkin et al [12] experiments, zinc was deposited as a liquid layer on the bicrystal surface. During annealing, Zn diffused along the grain boundary. Next to the liquid zinc layer there was a GB region of unusually high diffusion coefficients, followed by a region of normal GB diffusion. Rabkin et al [12] interpreted these results as evidence of zinc induced premelting transition in the grain boundary. In further studies, we carried out high pressure experiments to provide more information about the nature of the above GB transition [5,6]. Fig.3 shows the Zn penetration profiles as a function of pressure for the annealing temperature  $900^\circ\text{C}$ . A transition pressure  $p \approx 0.6$  GPa was found above which this accelerated diffusion region disappears. Furthermore, above this pressure wetting of the boundary by liquid zinc is suppressed. Fig.4 shows the temperature effect on the wetting transition pressure. Fig.5 shows the pressure effect on grain boundary wetting. The wetting transition pressure depends on temperature. At about  $780^\circ\text{C}$  the wetting transition pressure has a minimum of about 0.2GPa.

#### DISCUSSION OF THE WETTING EXPERIMENTS.

As discussed in ref.[12,5], the pre-melted GB (with energy  $\gamma_{GB}$ ) can be interpreted in terms of two solid liquid (S/L) interfaces separated by a liquid-like layer of a few atomic layers thickness  $d$ . This layer is not in equilibrium as a bulk phase but is in equilibrium as a thin layer between two S/L interfaces. When the GB is replaced by two S/L interfaces, the energy is lowered even if between the two S/L interfaces there is a thin wetting layer with energy  $\eta > 0$ .

$$\gamma_{GB} = 2\gamma_{SL} + \eta(d) \quad (5)$$



**Fig.3.** Pressure effect on Zn concentration profiles for Zn diffusion along a  $45^\circ[100]$  tilt boundary in a Fe-5%Si bicrystal. Annealing temperature:  $900^\circ\text{C}$ . Between 0.58 GPa and 0.74 GPa the fast diffusion - high Zn concentration region of the boundary disappears [5].

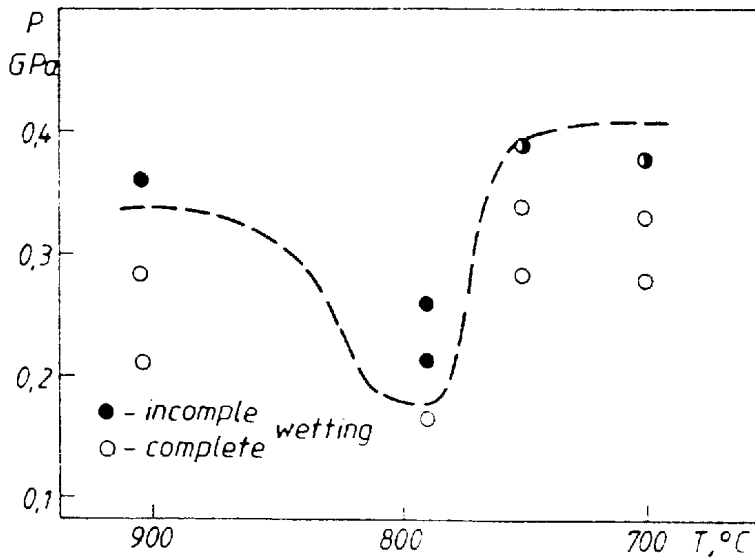
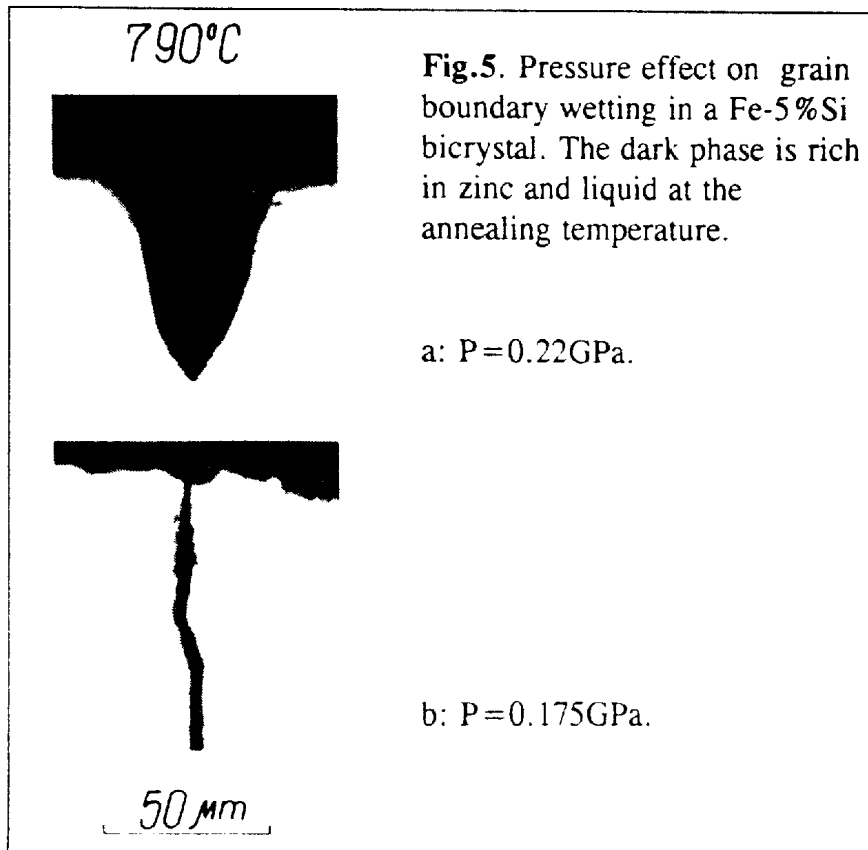


Fig.4. Temperature dependence of the wetting transition pressure.



The free volume of such a pre-melted boundary is higher than for a normal GB, so that the pre-melted state disappears when pressure is higher than a transition pressure [5]. The transition pressure has a minimum at 780°C, close to the peritectic temperature in the Fe-Zn system. This might indicate a maximum of the GB free volume for this temperature. At the same time for this temperature the zinc concentration required to cause the transformation has a minimum [12]. We might propose a following interpretation of the above results. The phenomena taking place in the boundary depend on the Zn concentration in the GB and Zn atoms' coordination. When temperature decreases, Zn segregation increases. Since Zn is a low melting point element, high Zn concentrations may favour GB premelting. Therefore, at low temperatures a low Zn bulk concentration may be sufficient to cause GB premelting. This is true however only above the peritectic temperature. Below this temperature, Zn atoms in the GB may form bonds with Fe atoms similar to those in the solid  $\Gamma$  phase. The lower the temperature, the stronger the Fe-Zn bonding in the  $\Gamma$  phase clusters. As a consequence,

higher Zn concentrations are required to cause GB premelting.

Let us consider the pressure effect on the GB premelting. For constant Zn concentration in the bulk, above the peritectic temperature the Zn concentration increases with decreasing temperature. High Zn concentration regions may have a disordered structure with high free volume. Therefore, the transition pressure decreases at low temperatures. On the other hand,

hand, below the peritectic temperature, the Fe-Zn bonds form. We may expect the GB density to increase and the transition pressure to increase with decreasing temperature.

In such a way we explained qualitatively two phenomena at the same time: that close to the peritectic temperature there is a minimum of Zn concentration for GB premelting and a minimum transformation pressure for GB premelting and wetting .

Here a tacit assumption was made: we assumed that wetting and premelting are correlated. Therefore, we didn't perform diffusion profiles measurements for all the temperatures. This subject, as well as a quantitative description of the above model will be a subject of papers in preparation for publication.

## CONCLUSIONS

- 1) the activation volume for grain boundary migration depends on the crystallographic parameters of the boundary.
- 2) [110] tilt boundaries are characterised by high activation volumes compared to [111] and [100] tilt boundaries and grain growth.
- 3) collective migration mechanism for some boundaries is not excluded.
- 4) pressure effect on the premelting transition and wetting transition in a grain boundary in a Fe-5%Si bicrystal was discovered.
- 5) there is a correlation between the premelting transition pressure and Zn concentration causing GB premelting.

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## **DISCUSSION**

**Bokstein, B. S.**

Q What is the connection between grain boundary free volume and grain boundary activation volume? I think that there is no connection. Free volume is a thermodynamic factor and depends on grain boundary density, and activation volume is a kinetic factor and depends on many factors: structure and so on.

**Lojkowski, W.**

A Use of magic words 'kinetic factor' or 'thermodynamic factor' is hardly an argument. The free volume is surely one of the characteristics of the grain boundary structure. You stated yourself that the activation volume depends on the structure. Hence the activation volume depends on the free volume as well.