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Compensation Effect for the Kinetic Properties of Triple Junctions

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Abstract. The compensation effect or Meyer-Neldel rule has been observed in a wide range of phenomena. It seems to be a fundamental property of the many families of activated processes following an Arrhenius dependence on temperature. The kinetic properties of grain boundaries and triple junctions depend strongly on their crystallographic parameters and obey the Arrhenius law. The data on the Meyer-Neldel rule for grain boundaries and triple junctions in Al and Zn and the values of the compensation temperature for the migration of grain boundaries and triple junctions are presented in this paper.

Keywords: compensation effect, Meyer-Neldel rule, grain boundaries, triple junctions

1. Introduction

The compensation effect or Meyer-Neldel rule (MNR) [1] is observed in a wide range of phenomena in physics, chemistry and biology. Most frequently it was observed in the case of the thermally activated electrical conductivity. The MNR seems to be a fundamental property of many families of activated processes following an Arrhenius dependence on temperature:

$$\rho = \rho_0 \exp(-H/kT) \tag{1}$$

Here, ρ is the absolute rate of a thermally activated process, ρ_0 is the pre-exponential factor, H is the activation enthalpy, T is the absolute temperature and k is Boltzmann's constant. Commonly, by the evaluation of the experimental data the activation enthalpy is determined from the slope H/k of an Arrhenius plot ln ρ vs. $1/T$. It is frequently found that, when the activation enthalpy H is varied within a family of processes (for example, related chemical reactions), then the pre-exponential factor ρ_0 in Eq. (1) obeys the empirical relationship

$$\rho_0 = \rho_{00} \exp(H/H_0) \tag{2}$$

Here, ρ_{00} is a constant and H_0 is the Meyer-Neldel energy for the processes in question. Thus, the increase in the pre-exponential factor ρ_0 when H increases [Eq. (2)], compensates for the decrease in the activation factor [Eq. (1)], so that the processes actually take place at a rate larger than would be expected from the knowledge of H alone. Equations (1) and (2) imply the existence of a temperature T_C, called the compensation temperature, where all reaction rates ρ of the considered group of thermally activated processes are the same, i. e., the lines for the corresponding Arrhenius plots intersect at the temperature T_C.

The origin of the MNR is still under discussion. The more traditional theory [2] relates the MNR to the temperature-induced shift of the energy levels, and in particular that of the Fermi level, E_F. The shift of E_F with temperature ("the statistical shift") is a consequence of the asymmetry in the density of states around it. An approximation of this shift with a linear temperature dependence leads to a discrepancy between the apparent activation energy and E_F, and a related discrepancy between the apparent and the microscopic [2] prefactors. Though this model is useful in explaining many of the MNR problems, it cannot explain the MNR behavior in annealing processes.

It has been shown [2–6] that the MNR arises naturally for kinetic processes for which H is large in comparison with the energies of the excitations, which contribute to the activation, as well as to kT. The exponential term in Eq. (2), which is not at the origin of the effect, results rather from the entropy of combining multiple excitations (or fluctuations [7, 8]) in the thermal reservoir available for the kinetic processes. The

Meyer-Neldel energy H_0, therefore, is expected to be of the order of the energy of the excitations in the reservoir, times a logarithmic correction term [3, 5, 6], which is frequently found to be of the order of unity. An important class of phenomena exhibiting the Meyer-Neldel behaviour are the kinetic properties of grain boundaries and triple junctions. Already in the early experiments with the aid of individual grain boundaries in bicrystals it has been shown that the spread of the mobility, m, of moving grain boundaries can reach several orders of magnitude [9–15]. The mobility of grain boundaries and triple junctions depend hardly on their crystallographic parameters. Particularly, at certain misorientations, the lattices of both grains form a superlattice, namely the so-called coincidence site lattice (CSL). The CSL in turn is characterized by the reverse density of coincidence sites, Σ. Close to coincidence misorientations with low Σ value the grain boundaries possess a special structure and special properties [16]. Therefore, the grain boundaries and triple junctions form families of objects where the Meyer-Neldel behaviour of thermally activated processes can be observed. A thermodynamic model for the compensation effect has been published in [17]. The experimental facts for the compensation effect or Meyer-Neldel behaviour of grain boundaries and triple junctions are presented here.

2. Experimental

Individual tricrystals [9–11, 18–20] were grown using a modificated Bridgiman technique. For the investigation of the mobility of triple junctions, the special geometry of the tricrystal is used containing an elongated grain boundary loop with parallel grain boundaries (Fig. 1). The velocity of a moving triple junction can be measured *in situ* using X-ray diffraction [21] or polarized light if the material under investigation possesses optical anisotropy (like, for example, zinc) [11]. The mobility of triple junctions can be investigated using tricrystals and the method of a constant (capillary) driving force (Fig. 1).

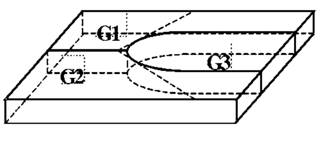

Figure 1. Scheme of a tricrystal grown for the investigation of triple junction motion in the condition of a constant (capillary) driving force. G1, G2 and G3 are grains with different orientations.

3. Results and Discussion

Generally, the grains in metals are strong by bonded. Therefore, it can be suggested that not only the bulk phase transitions but also the grain boundary phase transformations can govern the structure of an activated state and the resulting Meyer-Neldel-behaviour. Experiments with individual triple junctions have been started only recently [18–20, 22, 23]. However, already the first data on triple junctions reveal the MNR. In all cases studied, the triple junctions possess higher H values than comparable individual grain boundaries (cf. Figs. 2 to 6). In these figures the data on the migration of triple junctions are shown and there is a direct comparison with the data on the migration of grain boundaries [9–11, 14, 18–20, 22–25]. These experiments were performed with individual triple junctions

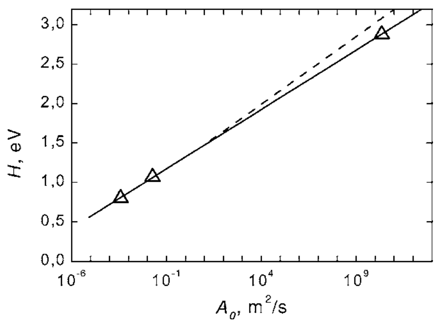

Figure 2. The dependence of the migration activation enthalpy H on the pre-exponential (reduced) mobility factor A_0 of $\langle 110\rangle$ triple junctions in Al (triangles, $T_C = 490°C$) [20] and of $\langle 110\rangle$ tilt grain boundaries in Al (dashed line [9, 21], $T_C = 590°C$).

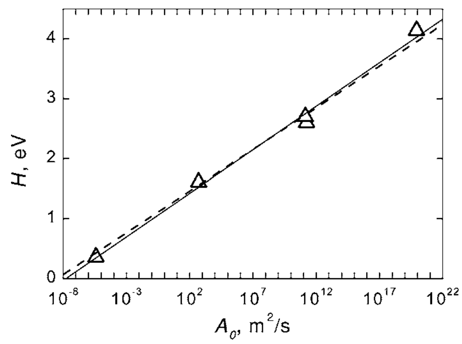

Figure 3. The dependence of the migration activation enthalpy H on the (reduced) pre-exponential mobility factor A_0 of $\langle 111\rangle$ triple junctions (triangles, [19, 20]) and of $\langle 111\rangle$ tilt grain boundaries in Al (dashed line [9, 14, 21]). For triple junctions $T_C = 460°C$ and for grain boundaries $T_C = 430°C$.

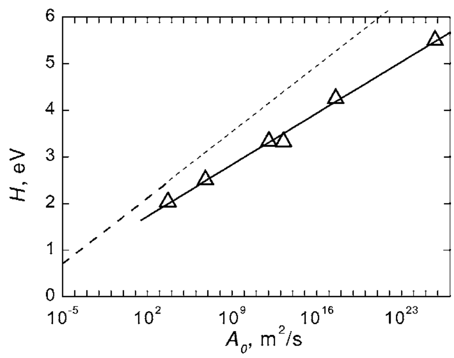

Figure 4. The dependence of migration activation enthalpy H on the (reduced) pre-exponential mobility factor A_0 of ⟨100⟩ triple junctions in Al (triangles [22, 24]) and of ⟨100⟩ tilt grain boundaries in Al (dashed line [10, 14]). For triple junctions $T_C = 520°C$ and for grain boundaries $T_C = 740°C$.

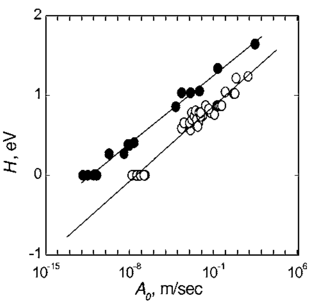

Figure 5. The dependence of migration activation enthalpy H on the (reduced) pre-exponential mobility factor A_0 of $\langle 11\bar{2}0\rangle$ twin grain boundaries in Zn (full circles [24]) and of $\langle 11\bar{2}0\rangle$ tilt grain boundaries in Zn (open circles [11]). $T_C = 350°C$.

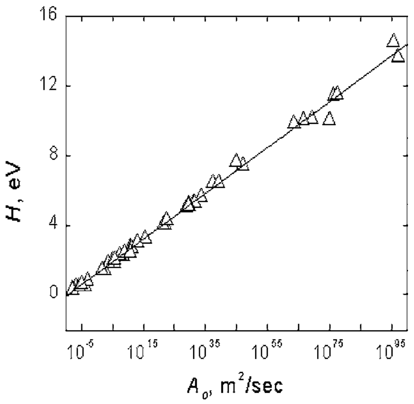

Figure 6. The dependence of migration activation enthalpy H on the (reduced) pre-exponential mobility factor A_0 of $\langle 11\bar{2}0\rangle$ and $\langle 10\bar{1}0\rangle$ tilt and general triple junctions in Zn. $T_C = 420°C$.

in conditions of a constant (capillary) driving force (cf. Fig. 1). The mobility A reduced to the same driving force was measured. The MNR was observed in the cases presented in Figs. 2 to 6. In case of ⟨110⟩ tilt triple junctions in Al $T_C = 490°C$ ($T_C/T_m = 0.82$; T_m—absolute melting temperature, Fig. 2) lies inside the studied temperature interval 470–590°C [9, 10, 14, 21]. In case of ⟨100⟩ tilt triple junctions in Al, $T_C = 520°C$ ($T_C/T_m = 0.85$, Fig. 4) lies inside the studied temperature interval 460–610°C. In case of ⟨111⟩ tilt triple junctions in Al, $T_C = 460°C$ ($T_C/T_m = 0.79$, Fig. 3) lies inside the studied temperature interval 400–510°C. This fact leads, particularly, to the complicated behaviour of the mobility of tilt triple junctions with different misorientations of the elongated tilt grain boundaries. Namely, the maximum of the mobility appears for triple junctions with a high-angle elongated tilt grain boundary at temperatures $T < T_C$. This maximum of A disappears at $T > T_C$. The same behaviour was observed for ⟨111⟩ tilt grain boundaries close to the Σ7 coincidence misorientation 38.2° ⟨111⟩ [25]. Namely, the maximum of the mobility appears at 38.2° at low temperatures $T < T_C$. This maximum of A disappears at $T > T_C$. Therefore, the MNR of ⟨111⟩ tilt grain boundaries and triple junctions in Al can be attributed to grain boundary phase transitions rather than to the bulk ones. This hypothesis is supported also by the behaviour of $\langle 11\bar{2}0\rangle$ tilt grain boundaries in Zn (Fig. 5) [11, 24]. Two groups of data are presented in Fig. 5. The open circles correspond to bicrystals with a single tilt grain boundary. The full circles correspond to the "natural" individual twin plates obtained by a slight deformation of the Zn single crystals. The values of the activation enthalpy of Zn twins are definitely higher that those of the $\langle 11\bar{2}0\rangle$ tilt grain boundaries (Fig. 5). However, both groups of grain boundaries possess the same $T_C = 350°C$ ($T_C/T_m = 0.9$). This temperature lies, like in case of tilt triple junctions in Al, below the melting point and inside of the temperature interval studied (200–419°C). In both cases of triple junctions in Al (Fig. 4) and in Zn (Figs. 5 and 6) the compensation temperature differs from that of the respective grain boundaries [25]. Such a behaviour can be explained by possible grain boundary phase transitions among the various constrained CSL grain boundary structures predicted in [26]. The intriguing high H values in Zn (see, for example, Fig. 6) force the investigator to think about possible mechanisms of the migration of triple junctions. Both in case of ⟨100⟩ and ⟨110⟩ triple junctions in Al (Fig. 4) and in Zn (Figs. 5 and 6) the compensation temperature differs from that of the respective grain boundaries. This fact and the high H values for triple junctions support the suggestion that the migration of triple junctions is controlled by processes in the triple junction itself and not by the mobility of grain boundaries forming the triple junction.

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