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Influence of faceting-roughening on triple-junction migration in zinc

Dedicated to Professor Dr. Lasar Shvindlerman on the occasion of his 70th birthday

The faceting and migration of individual triple junctions in Zn tricrystals under a constant driving force was investigated. The triple junction (TJ) was formed by three $[10\bar{1}0]$ tilt grain boundaries (GBs) with misorientation angles θ of 43°, 37° and 6°. The stationary shape of the migrating triple junction was studied, and the migration rate was measured *in-situ* between 670 and 688 K using polarized light. In some experimental runs, a facet was formed on the $\theta = 37°$ $[10\bar{1}0]$ tilt GB. This facet was parallel to the close-packed plane in the constrained coincidence site lattice (CCSL). The length of this facet decreases with increasing temperature and becomes zero at 688 K. The temperature dependence of the facet length is better described by the mean-field Andreev approximation than by the solid-on-solid model. The step energy estimated in the framework of the Bonzel approximation is about 0.1 eV/atom. In other experimental runs, the $\theta = 37°$ $[10\bar{1}0]$ tilt GB did not facet and remained rough in the same temperature interval. This fact allowed us to compare the stationary migration of the same TJ with faceted and rough GBs. A TJ formed by faceted GBs migrates one to two orders of magnitude more slowly in comparison with a rough TJ. An unrealistically high value of the apparent migration activation enthalpy of faceted TJs can appear due to the changing geometry of faceted GBs, similar to the case of migration of faceted twin tips.

Keywords: Grain boundaries; Triple joints; Faceting; Roughening; Migration; Zink

1. Introduction

In the pioneering works of Prof. Dr. L. S. Shvindlerman and his coworkers, the migration of individual grain boundaries (GBs) and triple junctions (TJs) in metals with cubic (Al) and hexagonal crystal structures (Zn) has been thoroughly studied both experimentally and theoretically [1–6]. These works fully describe the situations where GBs and TJs can be considered as isotropic and GB or TJ phase transformations do not occur during GB and TJ migration. The success of these works is based on a refined thermodynamic approach, and they formed a solid basis for further developments. However, it has been recently demonstrated that GB faceting cannot be neglected in experiments on GB and TJ migration. GB faceting mainly occurs close to so-called coincidence misorientations, when the GB structure can be described using the coincidence site lattice (CSL). With decreasing temperature, GB faceting can be observed for CSLs with lower and lower *density of coincidence sites* [7]. If the CSL is fixed, less and less densely packed CSL *planes* appear with decreasing temperature in the faceted GB structure [8]. It has been recently demonstrated that the presence of GB faceting correlates also with the phenomenon of abnormal grain growth. Above a certain temperature, faceted GBs cannot be observed in the microstructure and abnormal grain growth does not occur [9–11]. Particularly, our results clearly indicate that there is a strong effect of GB faceting on the migration rate of a twin tip [12]. To understand this phenomenon, we need to go beyond the classical models of isotropic migration of GBs [1]. This work is devoted to the first investigation of the migration of individual TJs built by faceted and/or non-faceted GBs.

2. Experimental details

Zn $[10\bar{1}0]$ flat tricrystals were grown from Zn of 99.999 wt.% purity, using a modified Bridgman technique [1, 4, 10]. The seeds in this tricrystal form two tilt GBs with misorientation angles θ of 43° and 37°. The 43° and 37° GBs grow parallel, forming at a certain point a triple junction. This TJ contains tilt GBs with misorientation angles of 43°, 37° and 6° (Fig. 1). All GBs in the TJ were perpendicular to the surface of the sample. The $[10\bar{1}0]$ axes in all three grains were also perpendicular to the surface of the sample. Due to its optical anisotropy, zinc allows one to study the shape of the GB with the aid of polarized light. The TJ moves under the action of a constant capillary driving force determined by the width of the TJ middle grain (grain 3 in Fig. 1). The stationary shape of the migrating tip of a twin plate was studied *in-situ* in a hot stage of an optical microscope in the temperature range between 670 and 688 K. In the same temperature interval, the GB migration rate has been measured and, subsequently, the GB mobility has been calculated. The samples were protected from oxidation by a pure nitrogen atmosphere. Before measurement, the samples were electropolished in a $H_3PO_4 + C_2H_5OH$ solution. An additional polarization filter, applied in the reflected beam, permits to distinguish different orientations of the grains by a different intensity of the reflected light. The GB shape was recorded in the course of the experiment by a color video camera connected with the microscope and a video recorder. This method of studying GB migration was originally reported in Refs. [4, 10].

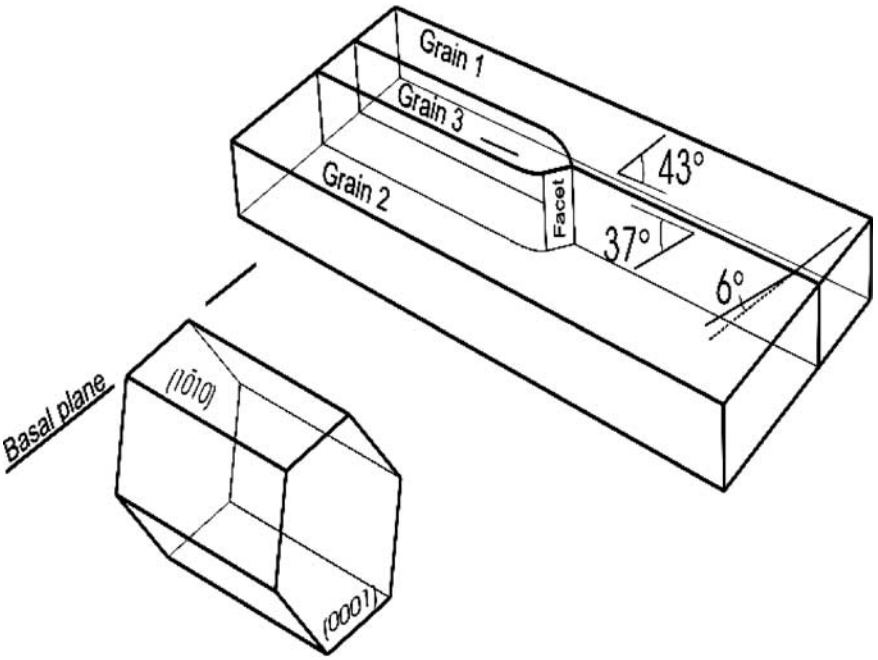

Fig. 1. Scheme of the Zn tricrystal containing three [10$\bar{1}$0] tilt GBs with misorientation angles of 43° (between grain 1 and grain 3), 37° (between grain 2 and grain 3), and 6° (between grain 1 and grain 2). The orientation of the basal plane (0001) is shown in all three grains. The facet formed in the GB with misorientation angle 37° is also shown.

3. Results and discussion

The micrographs in Fig. 2, obtained from *in-situ* hot stage experiments using polarized light, show typical shapes of the TJ, namely (a) with facet in a GB with $\theta = 37°$ and (b) without facet. The facet in the $\theta = 37°$ [10$\bar{1}$0] tilt GB formed in some experimental runs. This TJ shape differs drastically from the rounded shape of the moving GBs in Zn containing non-special GBs [1, 4–6]. However, in other runs, the $\theta = 37°$ tilt GB remained rough (rounded). This fact allowed us to compare the steady-state migration of the same TJ with faceted and rough GBs. The TJ movement during each isothermal anneal remained stationary and the TJ shape remained unchanged both for TJs with faceted and rough GBs. The steady-state character of TJ movement reflected itself in a linear time dependence of TJ displacement (Fig. 3). It can be clearly seen that a TJ with facet migrates much more slowly in comparison with a TJ formed by rough (rounded) GBs.

The *c*/*a* ratio of the lattice constants *a* in the basal plane (0001) and *c* perpendicular to (0001) is irrational in Zn. Therefore, an exact CSL exists in Zn only for GBs with rotation around the [0001] axis. In all other cases, including [10$\bar{1}$0] tilt GBs, only a so-called constrained coincidence site lattice (CCSL) exists [11]. The section of CCSLs per-

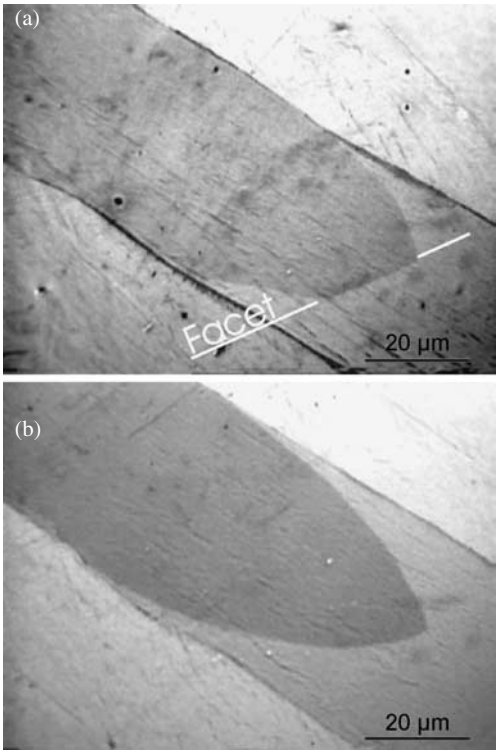

Fig. 2. Micrographs of the TJ obtained in an *in-situ* hot-stage experiment at 679 K using polarized light. Two typical shapes are shown for: (a) with facet in GB with misorientation angle 37° and (b) without facet.

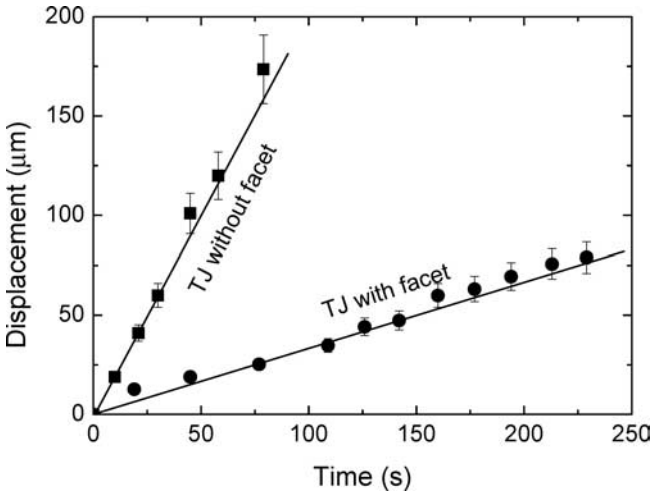

Fig. 3. Time dependence of TJ displacement for a TJ with facet and without facet (679 K).

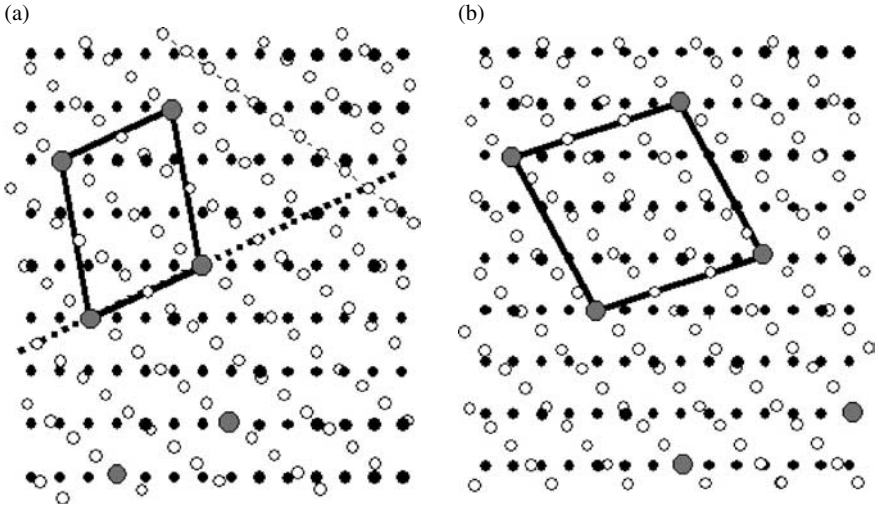

Fig. 4. Sections of CCSLs perpendicular to the $[10\bar{1}0]$ tilt axis for GBs with misorientation angles θ of 37° (a) and 43° (b). Filled and empty circles mark the sites of the two misoriented Zn lattices. Large circles mark the sites of the CCSL. The inverse density of the coincidence sites, Σ, is $\Sigma = 13$ for the $\theta = 37°$ GB and $\Sigma = 21$ for the $\theta = 43°$ GB. Unit cells of respective CCSLs, the position of the basal plane (0001) for grain 3 (cf. Fig. 2a), and the position of the most densely packed plane in the CCSL for the 37° GB are also shown.

pendicular to $[10\bar{1}0]$ tilt axis is shown in Fig. 4 for GBs with misorientation angles of 37° (a) and 43° (b). Filled and empty circles mark the sites of the two misoriented Zn lattices. Along the $[10\bar{1}0]$ direction, four layers [shifted for 0, $a/2$, $c/2$ and $(a + c)/2$] define the lattice periodicity. Only one layer with zero shift is shown in the Fig. 4. Large grey circles mark the CCSL sites. The sites of both lattices do not coincide exactly, the difference reaches about 30 % of the lattice spacing. This situation is similar to near-coincidence GBs in materials with cubic lattice, when the misorientation angle is close, but not equal to the misorientation of the exact coincidence angle, θ_Σ, but is still inside of the area of existence for special GBs [1]. The inverse density of coincidence sites, Σ, is $\Sigma = 13$ for $\theta = 37°$ GB and $\Sigma = 21$ for $\theta = 43°$ GB. The tolerance for CCSL is in our work higher than normally used in previous works [11, 12]. The unit cells of the respective CCSLs, the position of the basal plane (0001) for grain 3, and the position of the most closely packed plane in the CCSL for the GB are also shown. It can be clearly seen that the facet observed in the $\theta = 37°$ GB (cf. Fig. 2a) lies parallel to the most closely packed plane in the $\theta = 37°$ CCSL. The c/a ratio in Zn is temperature dependent [13]. The CCSLs in Fig. 4 are shown for 690 K. The CCSLs at 493 K were also constructed. They are slightly different and correspond to $\Sigma = 14$ for the $\theta = 37°$ GB and $\Sigma = 33$ for the $\theta = 43°$ GB. The change from one CCSL to another with increasing temperature can be the reason for a change of faceting in Zn (like in the case observed in [9]). This cause for GB phase transformations is unique for irrational c/a and does not exist in materials with cubic lattice.

In Fig. 5, the temperature dependence of the facet length in the $\theta = 37°$ GB is shown. In the experimental runs, when this facet appears, its length decreases gradually with increasing temperature. At a roughening temperature, T_R, of about 688 K the length reaches zero and the facet completely disappears. It means that a GB roughening transition proceeds in a $\theta = 37°$ GB at 688 K. By cooling of the sample, the facet appears again below $T_R = 688$ K. It indicates that the faceting-roughening of the $\theta = 37°$ GB is an equilibrium transition.

The idea of a faceting-roughening transition for free crystal surfaces was firstly proposed by Burton et al. [14]. They assumed that the free energy of an elementary step for each crystal surface decreases with increasing temperature, due to thermal fluctuations (configurational entropy). As a result, for each singular crystal face, a roughening temperature T_R exists. At T_R, the free energy of a step at the surface becomes zero. As a result, a flat surface becomes unstable above T_R. T_R is different for crystallographically different surfaces, the highest T_R corresponds to the surfaces with lowest Miller indices. For GBs, the CSL (= superlattice formed by the lattices of two grains) plays a role similar to a crystal lattice for the free surface. In other words, GB facets almost always coincide with CSL planes densely packed with coincidence sites. GB faceting correlates to the so-called special GB properties close to the coincidence misorientations [7]. According to the idea of Burton et al., a surface facet has to gradually disappear for $T \to T_R$. However, due to large experimental difficulties, the surface roughening (i. e., the vanishing of surface facets) has been directly observed for the first time only 30 years later by the growth of solid ^{4}He crystals [15]. Our *in-situ* measurement of the facet length in Zn TJ allows to observe for the first time the gradual disappearance of a GB facet. In the mean-field approximation, proposed by Andreev, the radius of the facet R has to decrease close to T_R according to a square-root law $R \sim \tau^{0.5}$, where $\tau = |T_R - T|/T_R$ [16]. A more sophisticated theory, based on the solid-on-solid (SOS) model, proposed a weaker temperature dependence of T_R in the form of $R \sim \exp(c\tau^{-0.5})$, thus exhibiting an essential singularity [17]. The $R(T)$ dependence for the ^{4}He facets follows the SOS law. In our case, the temperature dependence of the GB facet length (Fig. 5) is better described by the mean-field Andreev approximation than by the SOS model.

Bonzel and Edmunds proposed the novel calculation method for kink and step free energies based on the known temperature dependence of the facet radius [18]. Changes of temperature will change the step free energy and, hence, also the facet radius $R(T)$. The following relationship between facet radius, R, and step free energy, f, holds:

$$\frac{f(T)}{f(0)} = \frac{R(T)}{R(0)} \tag{1}$$

The temperature dependence of the step free energy related to kink formation is given in the framework of an Ising

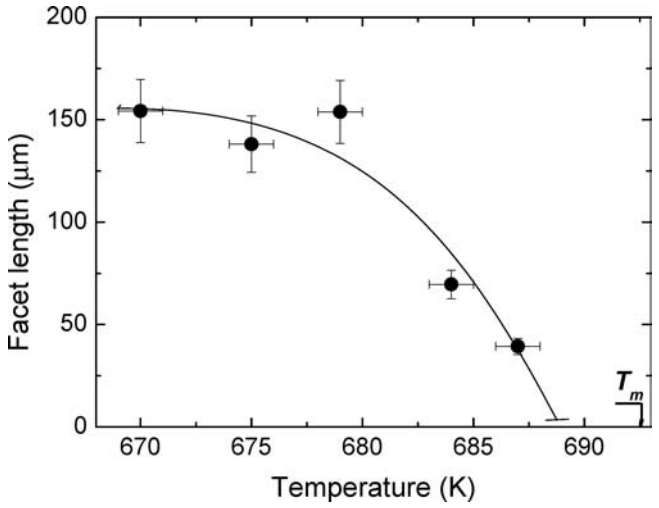

Fig. 5. Temperature dependence of the facet length in the $\theta = 37°$ GB.

model by [19–21] (for $T < 0.8\ \varepsilon_k/k$, where ε_k is the kink formation energy)

$$f(T) = f(0) - 2kT \exp\left(-\frac{\varepsilon_k}{kT}\right) \quad (2)$$

Combining both Eqs. (1) and (2) and rewriting the expression such that a ratio of facet radii appears on the left, we have [18]

$$\frac{T_m}{T}\left(1 - \frac{R(T)}{R(0)}\right) = \frac{2kT_m}{f(0)} \exp\left(-\frac{\varepsilon_k}{kT}\right) \quad (3)$$

where T_m is the melting temperature. If measurements of $R(T)$ for a certain facet can be carried out for a range of temperatures, a plot of $\ln[T_m\ (T(1-R(T)/R(0))]$ versus $1/T$ according to the Eq. (3) should yield a straight line. The ordinate intercept equal to $\ln[2kT_m/f(0)]$ gives the step free energy at zero temperature, $f(0)$, and the slope of the line gives ε_k/k. Let us assume that $R(0)$ is equal to the maximal possible length of the GB facet (243 μm, from the TG to the GB "Grain 3"/"Grain 2", cf. Fig. 1). In this case, the Bonzel plot yields quite reasonable values for the step free energy at zero temperature, $f(0) = 0.1$ eV/atom. To the best of our knowledge, it is the first value for the GB step energy obtained from experimental data on GB faceting. Typical $f(0)$ values for the surfaces are in the interval between 0.01 and 0.08 eV (obtained by theoretical calculations [22]) and about 0.1 eV (obtained experimentally for Pb(111) surfaces [23]). However, the slope of the Bonzel plots yields in our case a very high value for the kink energy $\varepsilon_k = 2$ eV. In case of Pb(111) surfaces, ε_k is about 0.05 eV [24]. The reason for the high ε_k value can be that we calculated the slope very close to the T_R temperature, where the validity of Bonzel method is questionnable. We have tried to find GBs in Zn where the facet length substantially decreases with increasing temperature (as that of Pb facets in [25]), but does not go to zero.

Why did another moving $\theta = 43°$ GB in TJ not facet in our experiments? From Fig. 4 follows that the inverse density of coincidence sites is only $\Sigma = 21$ for the $\theta = 43°$ GB. Σ for the $\theta = 43°$ GB is almost two times higher than $\Sigma = 13$ for $\theta = 37°$ GB. For materials with cubic lattices, it has been demonstrated that coincidence and near-coincidence GBs can lose their special properties with increasing temperature [7]. Most probably, GB roughening is the reason for this process [8–11]. The temperature where a GB loses its special properties decreases nearly linearly with increasing Σ [7]. GBs in Zn are analogous to the near-coincidence GBs in cubic materials and, therefore, T_R for the $\theta = 43°$ GB with $\Sigma = 21$ has to be much lower than T_R for the $\theta = 37°$ GB with $\Sigma = 13$. In other words, the temperature interval of our experiments is well above T_R for the $\theta = 43°$ GB, and this GB remains rough and continuously curved.

In each experimental run, the stepwise cooling of the migrating TJ continues till the TJ cannot move any more and is stopped by the surface groove [1]. By repeating the heating the GB starts to move again. However, in some runs, GB faceting in the $\theta = 37°$ GB did not appear at all, and both GBs migrated without facets. The TJ with rough GBs migrates with a velocitiy up to two orders of magnitude higher than that of the TJ containing the faceted $\theta = 37°$ GB. In other words, the dissipation of enthalpy by migration of the TJ with rough GBs also proceeds almost two orders of magnitude more intensively (Fig. 6). From the viewpoint of non-equlibrium thermodynamics [24], it can be the reason why the faceting of the $\theta = 37°$ GB is kinetically suppressed in some experimental runs. A kind of bifurcation obviously occurs during the beginning of heating, when the GBs break away from the surface groove and the TJ starts to move. As

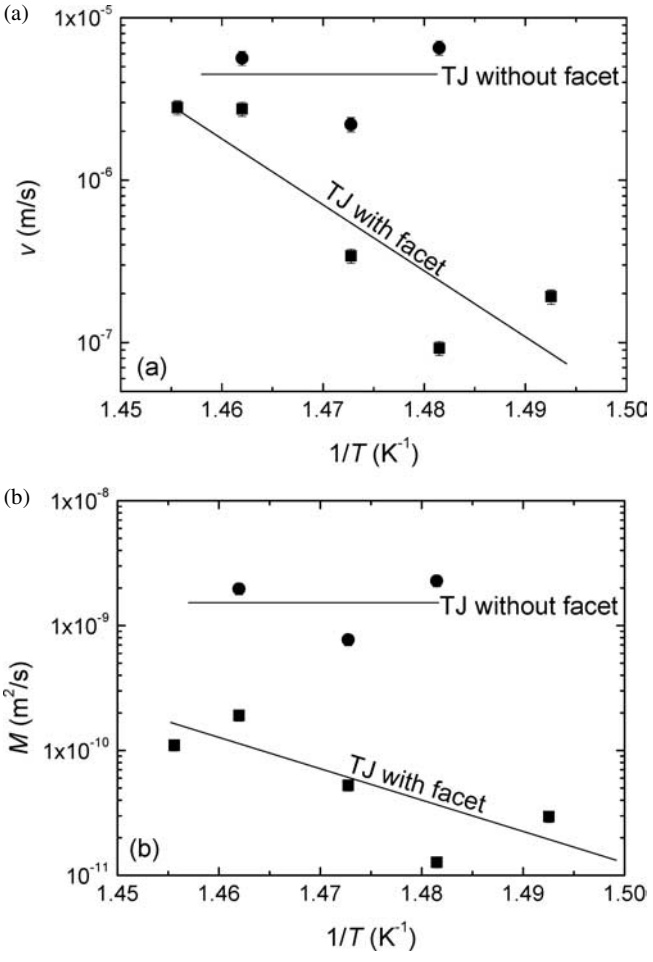

Fig. 6. (a) Temperature dependence of the migration rate v and (b) mobility M of TJs with rough (circles) and faceted GBs (squares) in Arrhenius coordinates.

a result, the TJ can "choose" either a faceted shape corresponding to the (relatively) slow movement branch or a rough shape with a high speed of movement and enthalpy dissipation.

In Fig. 6, the temperature dependence of the TJ velocity, v, (Fig. 6a) and the TJ mobility, M, (Fig. 6b) is shown in Arrhenius coordinates for the movement of TJs with and without the $\theta = 37°$ GB facet. At the same temperature, TJs with facet always migrate much more slowly in comparison with TJs formed by rough (rounded) GBs. The GB migration can be considered as growth of grain 1 and grain 2 at the cost of grain 3. The growth of faceted ^{4}He crystals proceeds also much more slowly than the growth of ^{4}He crystals with rough surface [15]. In the case of isotropic behavior, the velocity of GB motion, v, is given by [24]

$$v = Mr \tag{4}$$

where M and r are the GB mobility and radius of curvature, respectively. The usual approximation for the GB curvature radius, r, for the case of a capillary driving force has been used for TJs with rough GBs [1]. It is assumed to be equal to $r = a/2$, where a is the width of the grain 3 (cf. Fig. 1). The narrow temperature interval and the experimental scatter of v (or M) do not allow a calculation of the activation enthalpy for TJ migration with rough GBs. However, the velocity of a TJ with facet increases very quickly with increasing temperature, and its activation enthalpy is about 10 times higher than that of Zn self-diffusion along random GBs, 54.4 kJ/mol [26] (Fig. 6a). The mobility of a TJ with faceted GB has been calculated using the corrected value of r (the length of the flat facet has been subtracted from a). Even in this case (Fig. 6b), the activation enthalpy is about 6 times higher than that of Zn self-diffusion along random GBs. This value is unrealistically high and obviously, as in the case of migration of a faceted twin tip in Zn [9], does not correspond to the real activation barrier. As in [9], the reason for the high activation enthalpy may be the changing geometry of the faceted GB, and it is well possible that the high activation enthalpies for GB migration often reported in the literature are actually related to the faceting/roughening of these boundaries on the microscale [27, 28].

5. Conclusions

The faceting and migration of individual triple junctions in Zn tricrystal under a constant driving force was investigated. The triple junction (TJ) was formed by three $[10\bar{1}0]$ tilt grain boundaries (GBs) with misorientation angles θ of 43°, 37° and 6°. The stationary shape of the migrating triple junction was studied, and the migration rate was measured *in-situ* between 670 and 688 K using polarized light. In some experimental runs, a facet formed in the $\theta = 37°$ $[10\bar{1}0]$ tilt GB. This facet was parallel to a close-packed plane in the constrained coincidence site lattice (CCSL). The length of this facet decreased with increasing temperature and became zero at 688 K. The temperature dependence of the facet length is better described by the mean-field Andreev approximation than by the solid-on-solid model. The step free energy at 0 K, estimated in the framework of the Bonzel approximation, is about 0.1 ev/atom. In other experimental runs, the $\theta = 37°$ $[10\bar{1}0]$ tilt GB did not facet and remained rough in the same temperature interval. This fact allowed us to compare the stationary migration of the same TJ with faceted and rough GBs. The TJ formed by faceted GBs migrated one to two orders of magnitude more slowly than a rough TJ. An unrealistically high value of the apparent migration activation enthalpy of the faceted TJ can appear due to the changing geometry of the faceted GB, similar to the case of migration of faceted twin tips [9].

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