J Mater Sci (2008) 43:3860–3866
DOI 10.1007/s10853-007-2223-4

Motion of the faceted 57° $[11\bar{2}0]$ tilt grain boundary in zinc

Vera G. Sursaeva · Alena S. Gornakova · Viktor P. Yashnikov · Boris B. Straumal

Received: 3 July 2007 / Accepted: 10 October 2007 / Published online: 23 March 2008

Abstract The impact of faceting on the high-angle grain boundary motion was studied. The non-steady-state motion of the 57° $[11\bar{2}0]$ tilt grain boundary (GB) half-loop in a Zn bicrystal has been studied in situ. Above 678 K the slowly migrating GB half-loop was continuously curved. Below this temperature moving GB was fully or partially faceted. The transformation of curved GB into a GB facet with increasing temperature was observed for the first time. Overlapping faceting/roughening of three crystallographically different GB facets lead to the complicated non-steady-state motion. As a result, the GB mobility values and migration enthalpy were not unique, but lay in a certain interval.

Introduction

The faceting of the grain boundaries (GBs) is the spectacular phenomenon which reflects their crystallinity [1–3]. Most frequently, the GB faceting is observed in the so-called special GBs having misorientation angle equal or close to one of the coincidence misorientations. At a coincidence misorientation the lattices of both grains form a coincidence site lattice (CSL). In some cases the non-CSL general large-angle GBs also exhibit low energies [4]. Even the most perfect twin GBs in Cu contains the non-CSL facets with the so-called 9R structure [3, 5]. However, usually the GB facets are parallel to crystallographic CSL planes that are closely packed with coincidence sites [1, 3]. The GBs with CSLs characterized by the high volume density of coincidence sites Σ^{-1} can facet and possess also the special properties different from those of general GBs [6]. The near-coincidence GBs have special properties and can facet only if Σ is below a certain maximum value Σ_{max}. With decreasing temperature, Σ_{max} increases and GBs with high Σ become special (and faceted) [6]. Similarly, for fixed Σ, the amount of crystallographically different GB facets increases with decreasing temperature and facets with lower density of coincidence sites appear [3]. The physical reason for such behavior is the so-called GB roughening transition [1–3]. It is similar to the surface roughening [7]. With increasing temperature, the number of elementary steps in a surface facet increases, increasing the entropy. As a result, above the certain roughening temperature T_R the free energy of a step formation becomes zero, and a flat facet becomes unstable and curved [7]. This simple scheme cannot explain all features of GB faceting. For example, the faceted high-order twins with $\Sigma = 3, 3^2, 3^3, 3^4 \ldots$ much higher than $\Sigma_{max} \approx 65$ [6] were observed [8]. Facets without two-dimensional periodicity were observed in ZnO with hexagonal lattice [9], the transition from two-dimensional to one-dimensional periodicity could also happen [10]. However, the idea of faceting–roughening of near-CSL GBs gives a good framework for further discussion and describes most important cases of GB faceting.

Strictly speaking, only the stationary or very slowly moving facets (like in experiments [1, 3, 11, 12]) can be treated as equilibrium ones. However, it is well known that faceting/roughening strongly influences the GB migration [13]. The mobility of simplest case of isotropic general GBs has been exactly analyzed long time ago [13]. The influence of faceting/roughening on GB properties recently

V. G. Sursaeva (✉) · A. S. Gornakova · V. P. Yashnikov · B. B. Straumal
Institute of Solid State Physics, Russian Academy of Sciences, Chernogolovka, Moscow district 142432, Russia
e-mail: sursaeva@issp.ac.ru

became a hot topic [2, 13–19]. Particularly, it controls the transition from the normal to the abnormal grain growth in metals and ceramics [2, 13–15]. Therefore, it is critically important to analyze experimentally the mutual influence of faceting and migration of a GB, coming from the case of stationary GBs [1, 3, 11, 12], through the case of slow steady-state motion of GBs with one or two facets [16–19] to the case of quick non-steady-state migration of GBs with numerous facets. The latter case has been never analyzed before and its experimental study is the goal of this work.

Experimental

The Zn $[11\bar{2}0]$ flat bicrystal was grown from Zn of 99.999 wt.% purity using a modified Bridgman technique [13, 18]. It contained two equal tilt GBs with misorientation angle θ of 57°. Both GBs grew parallel, forming at certain point a half-loop (Figs. 1 and 2). Flat and curved GB portions were always perpendicular to the surface of the sample. The $[11\bar{2}0]$ axes in both grains were also perpendicular to the surface of the sample. The shape of the migrating GB half-loop was studied in the temperature range between 633 and 683 K in situ in a hot stage of a light microscope using polarized light. Temperature was stabilized with an error of ±0.5 K. Temperature steps among isothermal anneals were 5 or 10 K. The duration of isothermal anneals was 600 s. By the transition from one constant temperature to another, the "new" temperature of a hot stage and sample stabilized in few seconds. The samples were protected from oxidation by the high-purity nitrogen atmosphere. Before measurements the samples were electropolished in the $H_3PO_4 + C_2H_5OH$ solution. It

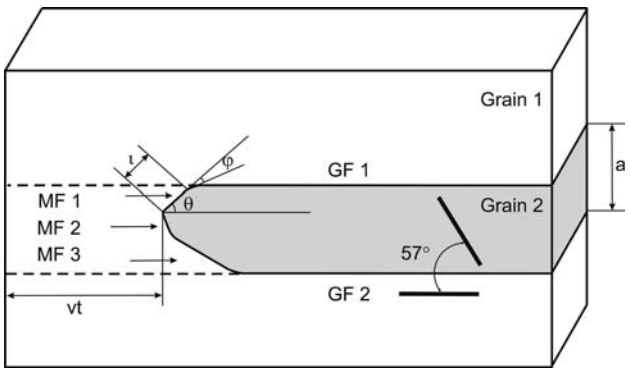

Fig. 1 Scheme of the Zn bicrystal containing the $[11\bar{2}0]$ tilt GB with misorientation angle of 57°. The orientation of basal plane (0001) in both grains (thick lines) and misorientation angle are shown. The positions of facets GF1, GF2, MF1, MF2 and MF3 are shown. Broken line marks the original GB position in the as-grown bicrystal. GB migration (with integral mobility m) is driven by a constant capillary force inversely proportional to the mean curvature radius $a/2$. GB moves with rate v

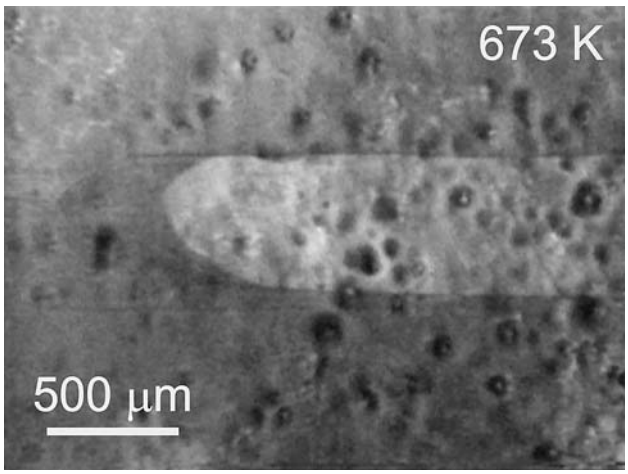

Fig. 2 Video frame of the 57° $[11\bar{2}0]$ tilt GB as half-loop with MF1, MF2 and MF3 facets at 673 K. Positions of MF1, MF2 and MF3 are shown in Fig. 1, their crystallography is explained in Fig. 3

was crucially important to form and keep the polarization contrast between differently oriented grains. An additional polarization filter applied in the reflected beam permitted to distinguish different orientations of the grains by the different intensity of the reflected light. The GB shape was recorded in the course of experiment by a color video camera connected with the microscope and a video recorder.

The *c/a* ratio of lattice spacing *a* in basal plane (0001) and *c* perpendicular to (0001) is irrational in Zn. Therefore, the exact coincidence sites lattice (CSL) exists in Zn only for GBs with rotation around [0001] axis. In all other cases including $[11\bar{2}0]$ tilt GBs the so-called constrained coincidence sites lattice (CCSL) exists [20]. The inverse density of coincidence sites is $\Sigma = 9$ for the studied $\theta = 57°$ GB. The section of this CCSL perpendicular to the $[11\bar{2}0]$ axis is shown in Fig. 3. The as grown long GB portion GF1 and GF2 were parallel to long side of CCSL unit cell (Fig. 3). It is well to bear in mind that the *c/a* ratio in Zn is temperature dependent [21]. The CCSL in Fig. 3 is constructed for 670 K.

Results

The shape of moving GB drastically changed with temperature. At 683 K (highest studied temperature) moving GB part was completely rounded (rough), and only as-grown GB facets GF1 and GF2 remained flat. At lower temperatures of 678 and 673 K moving GB became completely faceted. It contained three crystallographically different facets marked as MF1, MF2, and MF3 (Figs. 1, 3, 4). The crystallographic parameters of all observed facets are listed in the Table 1. At 668 K the facet MF3

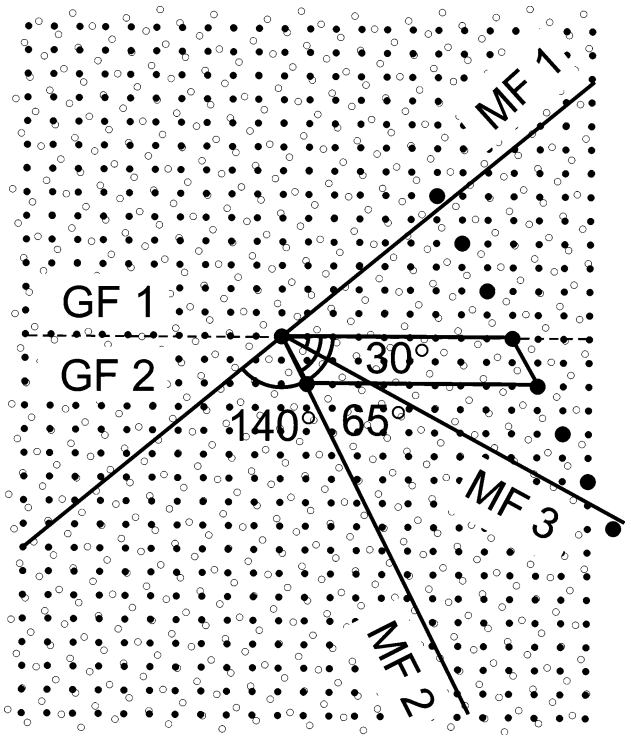

Fig. 3 Section of CCSLs perpendicular to $[11\bar{2}0]$ tilt axis for GB with misorientation angle θ of 57°. Filled and empty circles mark the sites of two misoriented Zn lattices. Large circles mark the sites of the CCSL. The inverse density of coincidence sites is $\Sigma = 9$. Unit cell of respective CCSLs, position of basal plane (0001) for grain 2 and position of CCSL plane parallel to the facet in the moving GB part are also shown. The actual positions of facets GF1, GF2, MF1, MF2 and MF3 in the migration GB half-loop are shown in Fig. 1. These facets are visible in the video-frame (Fig. 2)

(orientation 65°, Table 1) disappeared. The rounded rough GB portion appeared instead (Fig. 4). Only MF1 and MF2 facets remained in moving GB part at 668 K. When temperature decreased further, at 663 K the facet MF2 (orientation 30°, Table 1) disappeared as well. The

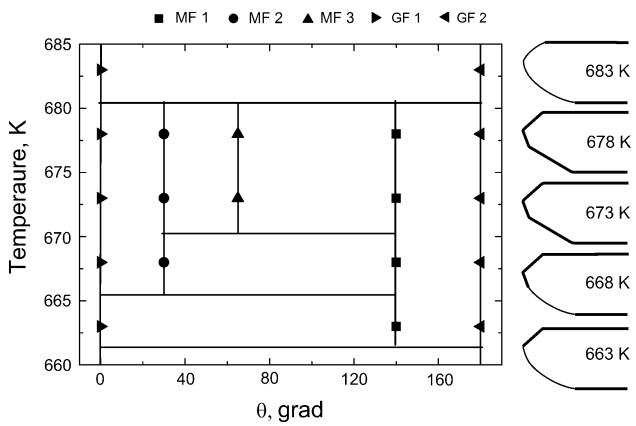

Fig. 4 Temperature dependence of facets coexistence. The respective configurations of a moving GB portion is schematically shown

Table 1 Facets presented in moving and stationary GBs (Figs. 1–3)

Facet name	Angle between GF1 and a facet (°)	Transcript
MF 1	140	Migration facet
MF 2	30	Migration facet
MF 3	65	Migration facet
GF 1	0	Growth facet
GF 2	180	Growth facet

rounded rough GB portion appeared instead (Fig. 4). Only one MF1 facet remained in moving GB part at 668 K. Usually similar to the free surfaces, a faceted GB became rounded (rough) with increasing temperature [1, 17–19]. It has been never observed before, that a GB facet disappears (becomes rounded) by decreasing temperature, as facets MF2 and MF3 did in our experiments.

In Figs. 5 and 6, the time dependence of the GB position (Fig. 5a and 6a) is shown together with the time dependence of facet length (Figs. 5b and 6b) for 668 and 678 K, respectively. The steady-state migration, i.e., linear dependence of GB position on the annealing time was

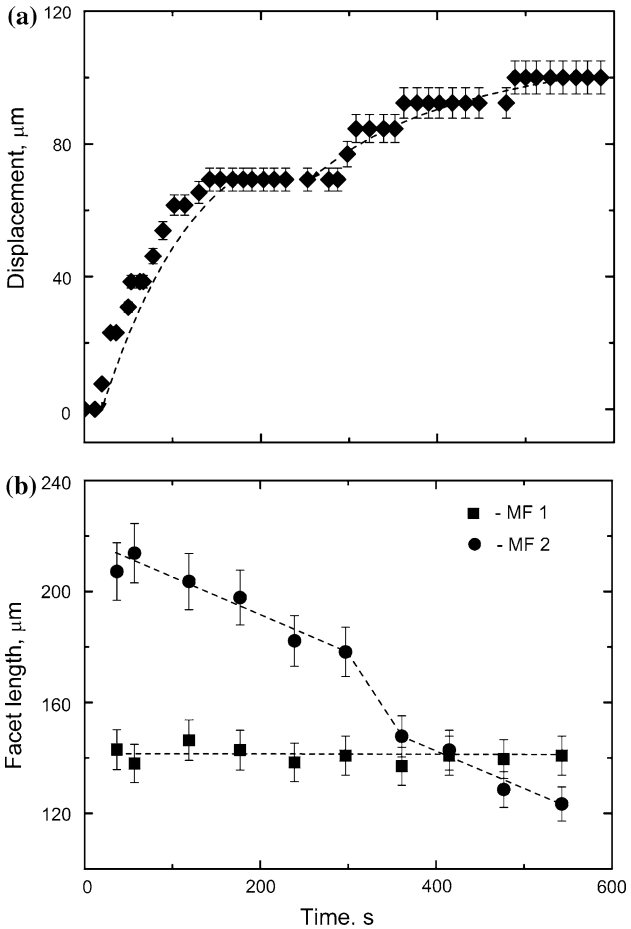

Fig. 5 Dependence of (**a**) GB position and (**b**) GB facet length on the annealing time for 668 K

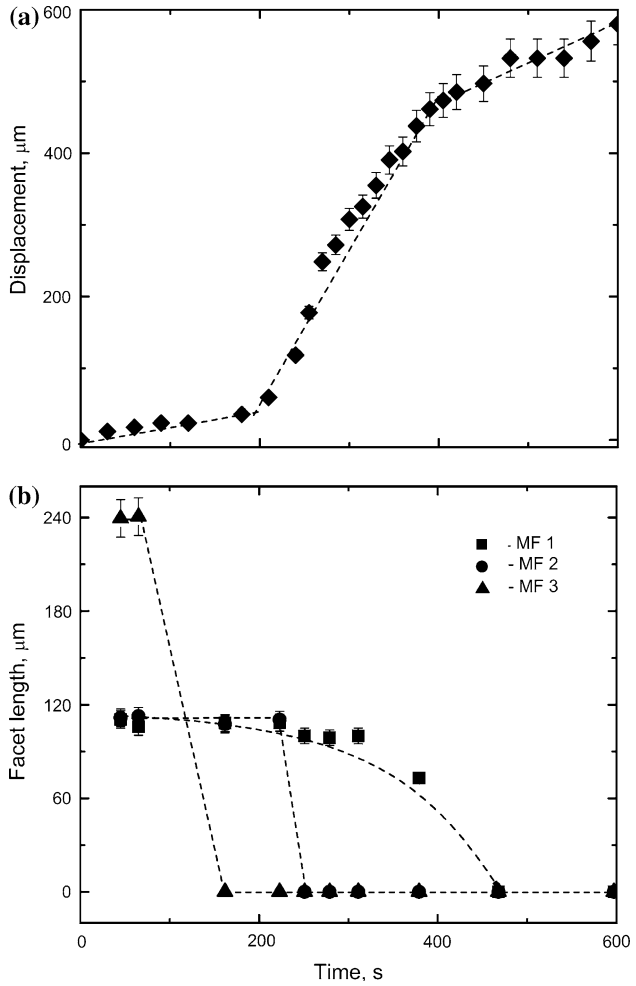

Fig. 6 Dependence of (**a**) GB position and (**b**) GB facet length on the annealing time for 678 K

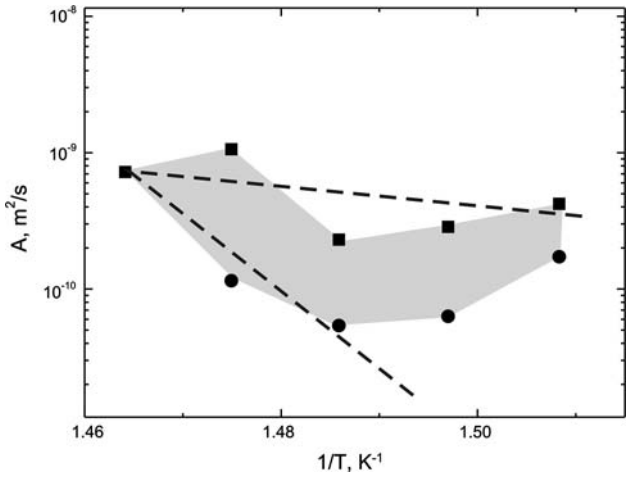

Fig. 7 The temperature dependence of GB mobility $A = va$ in Arrhenius coordinates. Since the velocity v was not constant (except of 683 K), the maximal and minimal values are given for each annealing temperature. Broken lines correspond to the maximal and minimal activation enthalpies

observed only at the highest temperature of 683 K. The moving GB part was completely rounded (rough) at this temperature. Its shape remained unchanged during the isothermal annealing, and one distinct value of GB mobility $A = 8 \times 10^{-10}$ m^2/s (equal to the GB velocity, v, times constant width of the grain 2, a, see scheme in the Fig. 1) could be calculated. Another simple case was represented by the annealing at 663 K. Only one facet MF1 was observed at the moving GB part. Its length slowly decreased with time during isothermal annealing. The overall GB mobility also slowly decreased with time. As a result, two A values appeared in the Arrhenius dependence (Fig. 7) for 663 K, namely maximal $A = 5 \times 10^{-10}$ m^2/s for the beginning and minimal $A = 2 \times 10^{-10}$ m^2/s for the end of the annealing.

During the heating from 663 to 668 K, the edge with slope discontinuity appeared in the formerly rounded GB portion. As a result the formerly rounded GB portion divided into flat facet MF2 and remaining rounded portion. During following isothermal annealing at 668 K the length of the facet MF1 remained unchanged, but the facet MF2 continuously shortened with annealing time (Fig. 5b). It became almost twice shorter after 600 s. The GB velocity also decreased with annealing time. Similar to the case of 663 K, two A values appeared in the Arrhenius dependence (Fig. 7) for 668 K, namely maximal $A = 4 \times 10^{-10}$ m^2/s for the beginning and minimal $A = 6 \times 10^{-11}$ m^2/s for the end of the annealing.

During the heating from 668 to 673 K, the last rounded GB portion edge became flat and new facet MF3 appeared. Moving GB portion became completely faceted and contained facets MF1, MF2, and MF3. However, the length of all three facets was not constant during the isothermal annealing, and the GB mobility was between $A = 3 \times 10^{-10}$ m^2/s and $A = 5 \times 10^{-11}$ m^2/s (Fig. 7).

During the heating from 673 to 678 K, the moving GB portion remained completely faceted and all three facets MF1, MF2 and MF3 were presented at the beginning of isothermal annealing at 678 K (Fig. 6b). However, during the isothermal annealing at 678 K all three facets disappeared one after another (first MF3 after 160 s, then MF2 after 250 s, and MF1 after 460 s). At the end of isothermal annealing the GB moving part became completely rounded (rough) and remained rounded at 683 K. Three velocity values could be defined at 678 K (low, high, middle, see Fig. 6a). Maximal and minimal mobilities appeared in the Arrhenius dependence (Fig. 7) for 678 K, namely maximal $A = 10^{-19}$ m^2/s and minimal $A = 10^{-10}$ m^2/s. As a result, for each studied temperature the GB shape was not steady-state and a number of mobilities can be defined (marked by grey area in Fig. 7). The resulted apparent activation enthalpy E is also not unique, but was in the interval

between $E = 135$ kJ/mol and $E = 1070$ kJ/mol (marked by two dotted lines in Fig. 7).

Discussion

The most important and principal question by discussing the motion of faceted GBs is the relation between thermodynamic equilibrium (governing the GB shape of stationary GBs) and kinetic factors. By GB motion driven by a capillary force, as in our experiments, the criterion of the deviation from equilibrium can be the energy of GB portion disappearing in the time unit. For the stationary GB the Wulff construction [22, 23] (i.e., the GB energy dependence on GB orientation or inclination) can be used for the prediction of GB shape corresponding to the energy minimum. However, even in this case the application of Wulff construction is restricted because, strictly speaking, it determines the shape of a crystal of constant volume, and for GBs the conservation of volume has little sense. However, Wulff developed his method for the surface shape of slowly growing (or slowly dissolving) crystals [22, 23]. Therefore, it can be used with precautions for the treatment of stationary or slowly moving GBs [1, 3, 16, 24]. By small deviations from equilibrium, the GB shape is governed both by facet energies and facet mobilities [16–18]. Most complicated is the case when GB remains faceted, but its shape is governed exclusively by the GB mobility [19].

The simplest isotropic case of migration of non-faceted general GB was studied and theoretically treated long time ago [13]. In this steady-state case the shape of moving GB remained unchanged with changing temperature, and a unique mobility value could be attributed to GB migration at each temperature. Later, the slow migration of fully faceted twin GBs in Zn was studied [17]. It was also a steady-state case, namely the shape of moving GB remained unchanged at each constant temperature, and only one GB mobility value was measured at each temperature. However, the GB shape changed with increasing temperature. At low temperatures and at high temperatures the moving GB portion contained only one facet (different at low and high temperatures). In this case a reasonable migration enthalpy was observed. However, the moving GB part had both facets at intermediate temperatures. There length changed with increasing temperature. As a result, the apparent migration enthalpy was very high in this intermediate temperature interval and did not reflect the mechanism of GB motion. Nevertheless, even in this interval, the GB movement remained steady-state, and only one mobility value was measured for each temperature.

More complicated case was observed in [18]. In different experimental runs the same GB moved as completely rounded (rough) or as completely faceted. It means that for the same temperature two mobility values were observed: high for the movement of rounded (rough) GB or low for the faceted GB. However, at all studied temperatures the steady-state motion and constant GB shape were observed in each isothermal annealing.

The non-steady-state motion of faceted GB was for the first time observed and analyzed in [19]. The 30° $[10\bar{1}0]$ tilt GB in Zn contained a GB facet together with rounded (rough) portion. The GB facet continuously shortened with increasing temperature and disappeared at roughening temperature $T_R = 673$ K. The GB motion was steady state at all studied temperature with two exclusions, namely temperature close to T_R. It took about 80 s before the facet disappears at $T_R = 673$ K after heating from 663 K. It took about 60 s before the facet appears at 668 K after cooling from $T_R = 673$ K. In other words, the facet reached its steady-state length not immediately after change of sample temperature, but with certain retardation. This process was compared with a decomposition of a supersaturated bulk solid solution or dissolution of overheated bulk phase in 3-dimensional case. When a α-solid solution is cooled down from a one-phase α-area of the phase diagram into two-phase $\alpha + \beta$ area, the particles of β-phase have to appear in the α-matrix. However, they need a certain time to nucleate and to grow before the volume portion of a β-phase reaches the value defined by the level rule for phase diagrams. And vice versa, if a two-phase $\alpha + \beta$ alloy is heated up into a one-phase α-area of the phase diagram, β-phase has to disappear. However, β-particles completely dissolve in the α-matrix only after certain time.

The links between grain boundary faceting and grain boundary behavior, in particular, grain growth and grain boundary migration was studied in a number of experimental works [1, 2, 13–19]. However, only in the last few years the quantitative methods to attack this problem were put forward [13–19]. Migration of incoherent twin grain boundaries with facets was studied in [17]. It has been shown that rather complicated kinetics of grain boundary motion, in particular the strongly non-Arrhenius temperature dependence, can be explained considering the motion of two competitive facets. The influence of grain boundary faceting on the grain growth and the motion of 2D grain boundary half-loop were considered in [25]. Under a number of simplifying assumptions it has been shown that the faceting might modify the von Neumann–Mullins relationship for 2D grain growth. It has been also found that the length of the facet in the GB half-loop depends on its mobility, namely the length of the facet increases if the mobility increases. The shape and the mobility of the moving GB are determined by a combination of both thermodynamic and kinetic parameters while the driving force of facet migration is described in the framework of

the approach of the weighted mean curvature (WMC) [16, 25]. It allowed defining the acting curvature of the facet. The WMC approach permitted to describe the steady-state motion of grain boundary half-loop with one facet in Zn [19]. The name of the approach reflects adequately its physical content: the weighted mean curvature is defined as the reduction of total interfacial free energy in the course of infinitesimal facet displacement divided by the volume swept by the displaced facet. Then the velocity of the facet can be expressed as:

$$V = \frac{m_f \gamma_b \sin\varphi \sin\theta}{l}, \quad (1)$$

where m_f, γ_b are the facet mobility and the GB surface tension correspondingly, l is the facet length, φ and θ are geometric constant angles in steady-state motion (Fig. 1). To determine the velocity of the curved grain boundary authors [13, 19] used the Mullins approach [26].

$$V = \frac{m_b \gamma_b (\theta - \varphi)}{\frac{a}{2} - l \sin\varphi}, \quad (2)$$

where m_b is the GB mobility, a is the width of middle grain. From (1) and (2) follows:

$$l = \frac{\frac{a}{2}}{\sin\theta + \frac{m_b(\theta-\varphi)}{m_f \sin\varphi \sin\theta}} \quad (3)$$

It can be seen that the relation (3) describes the reasonable limiting cases. Indeed, if the mobility of the grain boundary m_b is rather large or the mobility of the facet m_f is small, the length of the facet tends to zero. For the facet with large mobility the length tends to the maximal value: $l = \frac{a}{2 \sin\theta}$. The same refers to the thermodynamic parameters in the relation (3). If, for instance, the difference between the surface tension of the facet and curved grain boundary is small—the angle φ is small—the second term in the denominator increases and the length of the facet accordingly decreases.

The relation (3) is a tool which gives us a possibility, to define the mobility of the facet and its temperature dependence using the experimentally measured values of the facet length. We would like to intimate once again that the reduction of the facet length is conditioned exclusively by the increase of the mobility of the curved boundary. It should be stressed as well that the value l determined by the relation (3) is the facet length which fits the steady-state motion of the half-loop. The case of non-steady-state motion was not analytically analyzed up to now.

The case studied in this work is principally similar to the behavior of 30° $[10\bar{1}0]$ tilt GB in Zn with GB facet disappearing with increasing temperature [19]. However, in this work the phenomena were more complicated. Three GB facets MF1, MF2, MF3 appear and disappear in a very narrow temperature interval. The individual roughening temperatures for each of them cannot be resolved. The intervals of overheating and undercooling for the observed facets overlap. A very complicated non-steady-state motion was observed, and the interval of GB mobilities was defined for each temperature. As a result, the migration enthalpy is not unique as well, but lies in a certain interval. We have to underline, that it is actually the apparent migration enthalpy. Therefore, it can be very high and cannot be attributed to the unique mechanism of GB motion. It is because the activation process is also not unique in the studied temperature interval, and the movement of GB loop is controlled by a complicated combination of—parallel and sequential—activation events in various facets and/or rough GB portions.

Conclusions

1. The motion of the 57° $[11\bar{2}0]$ tilt grain boundary (GB) half-loop in a Zn bicrystal was mainly non-steady-state. The value of apparent activation enthalpy lies between $E = 135$ kJ/mol and $E = 1070$ kJ/mol.
2. The reason for that was the overlapping of temperature intervals of three faceting-roughening transitions.
3. Above 678 K the slowly migrating GB half-loop was continuously curved. Below this temperature, moving GB was fully or partially faceted. Fully faceted GB loop consisted of three crystallographically different GB facets.
4. The transformation of curved GB into a GB facet with increasing temperature was observed for the first time.

Acknowledgements Authors thank Profs L. S. Shvindlerman, and G. Gottstein for stimulating discussion. The research was supported by the Deutsche Forschungsgemeinschaft (DFG Grant 436 RUS 113/842/0-1(R)) and the Russian Foundation of Basis Research (Grant DFG-RFBR 06-02-04015).

References

1. Hsieh TE, Balluffi RW (1989) Acta Metall 37:2133
2. Lee SB, Yoon DY, Henry MB (2000) Acta Mater 48:3071
3. Straumal BB, Polyakov SA, Mittemeijer EJ (2006) Acta Mater 54:167
4. Lejcek P, Paidar V, Hofmann S (1999) Mater Sci Forum 294:103
5. Wolf U, Ernst F, Muschik T, Finnis MW, Fischmeister HF (1992) Phil Mag A 66:991
6. Straumal BB, Shvindlerman LS (1985) Acta Metall 33:1735
7. Herring C (1951) Phys Rev 82:87
8. Kopezky CV, Andreeva AV, Sukhomlin GD (1991) Acta Metall Mater 39:1603
9. Kiselev AN, Sarrazit F, Stepantsov EA, Olsson E, Claeson T, Bondarenko VI, Pond RC, Kiselev NA (1997) Phil Mag A 76:633

10. Sarrazit F, Pond RC, Kiselev NA (1998) Phil Mag Lett 77:191
11. Straumal B, Polyakov S, Bischoff E, Mittemeijer E (2004) Z Metallkd 95:939
12. Straumal BB, Polyakov SA, Chang L-S, Mittemeijer EJ (2007) Int J Mater Res (former Z Metallkd) 98:451
13. Gottsein G, Shvindlerman LS (1999) Grain boundary migration in metals: thermodynamics, kinetics, applications. CRC Press, Boca Raton, p 467
14. Koo JB, Yoon DY (2001) Metall Mater Trans A 324:69
15. Mendelev MI, Srolovitz DJ, Shvindlerman LS, Gottstein G (2002) Interface Sci 11:234
16. Straumal BB, Sursaeva VG, Polyakov SA (2001) Interface Sci 9:275
17. Straumal BB, Rabkin E, Sursaeva VG, Gornakova AS (2005) Z Metallkd 96:161
18. Straumal BB, Sursaeva VG, Gornakova AS (2005) Z Metallkd 96:1147
19. Sursaeva VG, Gornakova AS, Straumal BB, Shvindlerman LS, Gottstein G (2008) Acta Mater 56 (in press)
20. Bruggeman GA, Bishop GH, Hart WH (1972) In: Hsun Hu (ed) The nature and behaviour of grain boundaries, Plenum, New York, pp 83–122
21. Nye JF (2004) Physical properties of crystals. Clarendon Press, Oxford, p 329
22. Wulff GV (1895) Isvestia Warsz Univ 7:1; (1896) 9:1 (in Russian)
23. Wulff G (1901) Z Krystallogr 34:449 (in German)
24. Straumal BB (2003) Grain boundary phase transitions. Nauka publishers, Moscow, p 327 (in Russian)
25. Rabkin E (2005) J Mater Sci 40:875
26. Mullins WW (1956) J Appl Phys 27:900