Occurrence of Faceting for [110] Symmetric Tilt Boundaries in Cu Doped with Bi

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The faceting of the grain boundary in the binary Cu-Bi system was experimentally observed by transmission electron microscopy (TEM). For the observation, Cu bicrystals with $\Sigma 33$, $\Sigma 9$ and $\Sigma 11$ [110] symmetric tilt boundaries were doped with Bi at 1173 K for 120 h, and then homogenized at 1173 K for 48 h, followed by furnace cooling or water quenching. The misorientation angle between the [001] directions of the two single-crystals is 20.1°, 38.9° and 50.5° for the $\Sigma 33$, $\Sigma 9$ and $\Sigma 11$ boundaries, respectively. According to the TEM observation, the grain boundary is faceted markedly in the bicrystal with furnace cooling but barely in that with water quenching. Thus, the faceting takes place during furnace cooling but not during homogenization. The faceting was analyzed quantitatively on the basis of the inclination angle dependence of the boundary energy in Cu. The analysis yields that the contribution of the torque term to the faceting is important. Comparing the boundary diffusivities of Bi and Cu in Cu, we may expect that the mobility is much greater for the grain boundary with Bi than for that without Bi. As a result, the faceting during furnace cooling takes place considerably for the grain boundary with Bi but scarcely for that without Bi.

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1. Introduction

In many metals and alloys, faceting of the grain boundary occurs under suitable conditions.¹⁻⁷⁾ In order for the faceting of a grain boundary to take place spontaneously, the total boundary energy should be smaller for the faceted boundary than for the initially flat boundary. Special attention was focused on the faceting of the grain boundary in the binary Cu-Bi system by many investigators.⁸⁻²⁰⁾ Polycrystalline specimens of a Cu-Bi alloy containing 0.0115 mass% of Bi were used by Donald and Brown for observation of the faceting by transmission electron microscopy (TEM).¹⁰⁾ Their observation indicates that the faceting is attributed to the segregation of Bi on the grain boundary. The relationship between the faceting and the segregation was extensively observed by Ference and Balluffi.¹²⁾ According to their observation, the faceting takes place by the addition of Bi to the grain boundary, but the defaceting occurs by the removal of Bi from the grain boundary. As mentioned above, the total boundary energy has to be smaller for the faceted boundary than for the initially flat boundary. Thus, grain boundaries with small values of the boundary energy are formed due to faceting. In order to find the relationship between the characters of the faceted and initially flat boundaries, a Cu-Bi bicrystal with a $\Sigma 33$ [110] symmetric tilt boundary was used by Li *et al.*^{13,18)} Here, the misorientation angle between the [001] directions of the two single-crystal grains is equal to 160°. Their observation shows that the initially flat $\{118\}\{118\}$ boundary is faceted into the $\{114\}\{885\}$ and $\{334\}\{001\}$ boundaries. This means that the total boundary energy is smaller for the faceted $\{114\}\{885\}$ and $\{334\}\{001\}$ boundaries than for the flat $\{118\}\{118\}$ boundary. Unfortunately, however, there is no reliable information of the boundary energy for the $\{114\}\{885\}$ and $\{334\}\{001\}$ boundaries. Consequently, the driving force of the faceting could not be estimated quantitatively.^{13,18)}

The boundary energy in Cu was experimentally determined as a function of the misorientation angle for [100] twist boundaries by Mori *et al.*,²¹⁾ for [110] twist boundaries by Miura *et al.*,²²⁾ for [110] symmetric tilt boundaries by Monzen *et al.*,²³⁾ and for [100] symmetric tilt boundaries by Mori *et al.*²⁴⁾ On the other hand, the inclination angle dependence of the boundary energy in Cu was experimentally examined for $\Sigma 11$ and $\Sigma 9$ [110] asymmetric tilt boundaries with misorientation angles of 50.5° and 38.9°, respectively, in previous studies.^{25,26)} In those experiments, the equilibrium shape of silica particles formed on a grain boundary during annealing at an appropriate high temperature was observed by TEM, and then the boundary energy was evaluated from the equilibrium shape. Hereafter, this method is called the silica particle observation (SPO) method. The SPO method has no drawbacks which are inevitable in boundary grooving and tri-junction methods, and hence gives reliable information on the misorientation or inclination dependence of the boundary energy. According to the result of the $\Sigma 11$ [110] asymmetric tilt boundary at a temperature of $T = 1273$ K,²⁵⁾ deep cusps appear at the $\{111\}\{13, 13, 5\}$, $\{001\}\{667\}$ and $\{113\}\{113\}$ plane, and a shallow cusp exists at the $\{225\}\{441\}$ plane. In contrast, an only shallow cusp appears at the $\{7, 7, 10\}\{9, 9, 131\}$ plane in the case of the $\Sigma 9$ [110] asymmetric tilt boundary at $T = 1273$ K.²⁶⁾ On the basis of these experimental results for the boundary energy, the possibility of the faceting was quantitatively analyzed for the $\Sigma 11$ and $\Sigma 9$ boundaries.^{25,26)} According to the analysis, there are various combinations of the faceted planes with small values of the boundary energy for the $\Sigma 11$ and $\Sigma 9$ boundaries. Thus, an appropriate $\Sigma 11$ or $\Sigma 9$ boundary can be faceted during annealing of the Cu bicrystal at $T = 1273$ K. However, such faceting was not clearly recognized for the Cu bicrystal in previous studies.^{25,26)} Hence, the segregation of Bi on the grain boundary may be essentially important for sufficient growth of the faceting to visible extents. In order to confirm the validity of the analysis mentioned above, Cu bicrystals with different

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[110] symmetric tilt boundaries were doped with Bi, and then the faceting of the grain boundary was experimentally observed by TEM in the present study. The information of the boundary energy in Cu was used to analyze quantitatively the observation. On the basis of the analysis, the influence of the segregation was discussed from the viewpoint of the mobility of the grain boundary.

2. Experimental

Three different pure Cu bicrystals with a thickness of 3 mm and purity of 99.99% were prepared by a Bridgman technique with a graphite crucible in a manner similar to a previous study.²⁷⁾ In these bicrystals, the grain boundary is parallel to the [110] tilt axis, and the misorientation angle is equal to 20.1° ($\Sigma 33$), 38.9° ($\Sigma 9$) and 50.5° ($\Sigma 11$). As shown schematically in Fig. 1, the misorientation is defined as the angle θ between the [001] directions of the adjacent single-crystal grains. The orientation relationship between the adjacent grains was determined for each bicrystal by an X-ray reflection technique. However, only the bicrystals with deviations of θ smaller than 1° were used in the following experiment. Rectangular specimens with a size of 3 mm $\times$ 4 mm $\times$ 30 mm were cut from the bicrystal by spark erosion. In each specimen, the grain boundary is located at the center of and perpendicular to the sides with a length of 4 mm. Parallel flat surfaces with an area of 4 mm $\times$ 30 mm of the specimen were mechanically polished on 400–800 emery papers in order to reduce the thickness to 1.5 mm. After mechanical polishing, the specimen was chemically polished in an etchant consisting of 50 vol% of nitric acid and 50 vol% of distilled water. Owing to chemical polishing, the thickness of the specimen was reduced to 1.3 mm.

The mechanically and chemically polished specimen was inserted into a graphite case together with 9 g of pure Cu powders, 9 g of alumina powders and 0.1 g of pure Bi powders, and then isothermally annealed in a silica tube filled with a pure Ar gas at a temperature of $T = 1173$ K for a time of $t = 120$ h, followed by air cooling in the silica tube. The annealed specimen was cleaned in methanol with an

ultrasonic cleaner, and then dried completely. The cleaned specimen was encapsulated in an evacuated silica capsule, and then isothermally homogenized at $T = 1173$ K for $t = 48$ h. After homogenization, the specimen was cooled in different manners as follows: (A) quenching into ice water with breaking the capsule; (B) quenching into water without breaking the capsule; and (C) furnace cooling of one day. The cooling manners A, B and C are denominated coolings A, B and C, respectively.

Sheet specimens with a dimension of 1.3 mm $\times$ 4 mm $\times$ 3 mm were cut from the homogenized specimen by spark erosion. The sheet specimen was mechanically polished on 800–2000 emery papers in order to reduce the thickness to 200 μ m. After mechanical polishing, the specimen was chemically polished in an etchant composed of 20 vol% of nitric acid and 80 vol% of distilled water. Owing to chemical polishing, the grain boundary becomes visible. A disk specimen with a diameter of 3 mm was cut from the chemically polished sheet specimen by spark erosion. The thickness of the disk specimen was further reduced to 20 μ m by a conventional twin-jet electro-polishing technique at a voltage of 7 V using an etchant consisting of 20 vol% of phosphoric acid, 10 vol% of methanol and 70 vol% of distilled water with $T = 274$ – 283 K. After reduction of the thickness, the disk specimen was electrochemically polished at a voltage of 6.5 V in an etchant composed of 20 vol% of nitric acid and 80 vol% of methanol with $T = 223$ K. From the electrochemically polished specimen, a thin disk specimen was prepared by an ion milling technique using an Ar ion beam at accelerating voltages of 4–5 kV and at incident ion beam angles of 4 – 6° . The microstructure and the crystallography of the thin disk specimen were observed by transmission electron microscopy (TEM) at an accelerating voltage of 200 kV.

3. Results and Discussion

3.1 TEM observation

Typical bright-field (BF) images of the $\Sigma 11$ bicrystals before Bi-doping and after Bi-doping with cooling C are shown in Fig. 2(a) and (b), respectively. The incident electron beam is parallel to the [110] tilt axis of the bicrystal, and thus the grain boundary is in an edge-on position. As can be seen in Fig. 2(a), the grain boundary is flat before Bi-doping. The Miller indices of the initially flat boundary in the $\Sigma 11$ bicrystal are $\{332\}\{332\}$. On the other hand, after Bi-doping with cooling C, the grain boundary is faceted into various planes as indicated in Fig. 2(b). The faceted planes are also parallel to the [110] tilt axis, and hence in an edge-on position. According to the experimental result in a previous study,²⁷⁾ the segregation of Bi on the grain boundary occurs under the present Bi-doping conditions. Hence, the faceting is attributed to the segregation as mentioned in Sect. 1. However, the faceting of the grain boundary after Bi-doping was recognized for cooling C but not for coolings A and B. This means that the faceting occurs during furnace cooling after homogenization but not during homogenization.

From the BF image of the bicrystal with cooling C like Fig. 2(b), the inclination angle ϕ_i of the faceted plane i was measured as shown schematically in Fig. 3. Here, ϕ_i is the

Fig. 1 Cu bicrystal with a [110] symmetric tilt boundary. The misorientation is defined as the angle θ between the [001] directions of two single-crystal grains.

Fig. 2 Bright-field images of the $\Sigma 11$ bicrystals: (a) before Bi-doping; and (b) after Bi-doping with cooling C.

Fig. 3 Schematic drawing for faceted plane i with inclination angle ϕ_i and projected length l_i .

angle between the faceted plane i and the initially flat boundary. The probability p for appearance of the faceted plane i with $\phi = \phi_i \pm \Delta\phi$ is defined as

$$p = \frac{l_i}{\sum_{j=1}^n l_j}, \quad (1)$$

where l_i is the length of the faceted plane i projected on to the initially flat boundary and n is the number of the faceted planes. Here, ϕ_i is calculated by the relationship

$$\phi_i = (2i - 1)\Delta\phi \quad (2)$$

with $\Delta\phi = 1^\circ$. The dependencies of p on ϕ for the $\Sigma 11$, $\Sigma 9$ and $\Sigma 33$ bicrystals are shown in Fig. 4(a), (b) and (c),

Fig. 4 The probability p for appearance of faceted plane versus the inclination angle ϕ for boundaries of (a) $\Sigma 11$, (b) $\Sigma 9$ and (c) $\Sigma 33$.

respectively. According to the result of the $\Sigma 11$ bicrystal in Fig. 4(a), p takes peak values at $\phi = 8-14^\circ$. Thus, the faceted planes with $\phi = 8-14^\circ$ are formed most probably in the $\Sigma 11$ bicrystal. In the case of the $\Sigma 33$ bicrystal, such peak values of p appear at $\phi = 6-12^\circ$ as indicated in Fig. 4(c). On the other hand, peak values of p are split into two groups of $\phi = 2-4^\circ$ and $\phi = 14-18^\circ$ for the $\Sigma 9$ bicrystal in Fig. 4(b).

3.2 Boundary energy

As mentioned in Sect. 1, the inclination angle dependence of the boundary energy was experimentally determined for the $\Sigma 11$ and $\Sigma 9$ [110] asymmetric tilt boundaries in Cu by the SPO method in previous studies.^{25,26} The results of the $\Sigma 11$ ²⁵ and $\Sigma 9$ ²⁶ boundaries at a temperature of $T = 1273$ K are represented as open rhombuses with error bars in Fig. 5(a) and (b), respectively. In Fig. 5, the ordinate shows the relative boundary energy γ_B/γ_I , and the abscissa indicates the inclination angle ϕ . Here, γ_B is the boundary energy in Cu, and γ_I is the interfacial energy of the Cu/silica interface. In the case of the $\Sigma 11$ boundary, deep cusps appear at the $\{13, 13, 5\}\{111\}$, $\{667\}\{001\}$ and $\{113\}\{113\}$ planes, and a shallow cusp exists at the $\{441\}\{225\}$ plane. On the other hand, for the $\Sigma 9$ boundary, an only shallow cusp appears at the $\{7, 7, 10\}\{9, 9, 131\}$ plane. On the basis of the results in Fig. 5, the possibility of the faceting was quantitatively analyzed in previous studies.^{25,26} According to those analyses, the parameter f is defined as

$$f = \frac{2\gamma_B(\phi_i) \sin \phi_i}{\gamma_B(\phi_0) \sin 2\phi_i}. \quad (3)$$

Here, ϕ_i is the absolute value of the inclination angle, $\gamma_B(\phi_0)$ is the boundary energy of the initially flat boundary with $\phi = \phi_0 = 0^\circ$, and $\gamma_B(\phi_i)$ is that of the faceted plane i with $\phi = \phi_i$. The parameter f corresponds to the ratio of the total boundary energy before faceting to that after faceting relevant to the faceted plane i . The dependence of f on ϕ is calculated from eq. (3). The results of the $\Sigma 11$ ²⁵ and $\Sigma 9$ ²⁶ boundaries are represented as open squares in Fig. 4(a) and (b), respectively.

As indicated in Fig. 5, the boundary energy γ_B varies depending on the inclination angle ϕ . This means that torque terms may play important roles in the faceting.^{28,29} Taking the torque term into consideration, the boundary energy $\gamma_B^f(\phi_i)$ of the faceted plane i contributing to the faceting is expressed by the following equation:^{26,28}

$$\gamma_B^f(\phi_i) = \gamma_B(\phi_i) \pm \frac{\partial \gamma_B}{\partial \phi} \tan \phi_i. \quad (4)$$

Here, $\partial \gamma_B / \partial \phi$ is the derivative of γ_B at $\phi = \phi_i$. The sign of plus or minus on the right-hand side of eq. (4) is determined by the combination of the faceted plane i with the initially flat boundary.²⁶ Replacement of $\gamma_B(\phi_i)$ with $\gamma_B^f(\phi_i)$ in eq. (3) enables us to estimate the influence of the torque term on the faceting. Hereafter, the value of f obtained by the replacement is denoted by f_i . The dependencies of f_i on ϕ for the $\Sigma 11$ and $\Sigma 9$ boundaries are shown as open circles in Fig. 4(a) and (b), respectively.

As mentioned earlier, Fig. 5 shows the relative boundary energy γ_B/γ_I versus the inclination angle ϕ at $T = 1273$ K. Thus, the open squares and circles in Fig. 4 indicate the

Fig. 5 The relative boundary energy γ_B/γ_I versus the inclination angle ϕ of the [110] asymmetric tilt boundaries in Cu at 1273 K determined in previous studies: (a) $\Sigma 11$,²⁵ and (b) $\Sigma 9$.²⁶

dependencies of f and f_i on ϕ , respectively, calculated at $T = 1273$ K. On the other hand, the Bi-doping and the homogenization were carried out at $T = 1173$ K. Hence, the experimental data in Fig. 4 may correspond to the result at $T = 1173$ K. The boundary energy γ_B as well as the interfacial energy γ_I will vary depending on the temperature T . If the dependence of γ_B on T is not so dissimilar to one another for different values of ϕ at temperatures around 1200 K, however, f and f_i are insensitive to T . In such a case, the open symbols in Fig. 4 represent also the values of f and f_i at $T = 1173$ K. According to the result of the $\Sigma 11$ boundary in Fig. 4(a), both f and f_i are much smaller than unity at $\phi = 8-14^\circ$. This means that the total boundary energy considerably decreases due to faceting. Consequently,

Fig. 6 The relative boundary energy γ_B/γ_I of the $\Sigma 33$ [110] symmetric tilt boundaries in Cu at 1273 K determined by Monzen *et al.*²³⁾ shown as open rhombuses. An open circle indicates the estimation from eq. (3) using the value of γ_B/γ_I at $\phi = 0^\circ$ ²³⁾ and that of $f = 0.85$.

the faceting of the $\Sigma 11$ boundary occurs most probably at $\phi = 8\text{--}14^\circ$. In the case of the $\Sigma 9$ boundary in Fig. 4(b), however, f_I is smaller than unity but f is slightly greater than unity. Nevertheless, the faceting takes place most probably at $\phi = 2\text{--}4^\circ$ and $\phi = 14\text{--}18^\circ$. Therefore, the contribution of the torque term to the faceting is important. However, for the $\Sigma 9$ boundary, there is less information of the boundary energy at $\phi = 2\text{--}4^\circ$ and $\phi = 14\text{--}18^\circ$, and hence the peak values of p cannot be explained quantitatively only from the open circles in Fig. 4(b). Although there is no reliable information of the inclination angle dependence of the boundary energy for the $\Sigma 33$ boundary, the result in Fig. 4(c) implies that there exists an energy cusp around $\phi = 10^\circ$. Such an energy cusp may be approximately estimated as follows.

For the $\Sigma 33$ boundary, an asymmetric boundary with rather low Miller indices of $\{40, 40, 1\}\{221\}$ exists at $\phi = 9.0^\circ$. According to the open squares in Fig. 4(a), f takes values around 0.85 at $\phi = 8\text{--}14^\circ$ for the $\Sigma 11$ boundary. Thus, we assume that an energy cusp with $f = 0.85$ appears at $\phi = 9.0^\circ$ for the $\Sigma 33$ boundary. On the other hand, Monzen *et al.*²³⁾ reported $\gamma_B/\gamma_I = 0.384$ and 0.264 at $\phi = 0^\circ$ and 90° , respectively, for the $\Sigma 33$ boundary. Their values of γ_B/γ_I are shown as open rhombuses in Fig. 6. Using these parameters, we obtain $\gamma_B/\gamma_I = 0.322$ at $\phi = 9.0^\circ$ from eq. (3). This value of γ_B/γ_I is indicated as an open circle in Fig. 6. As previously mentioned, the contribution of the torque term to the faceting is important. In order to estimate the contribution, $\partial\gamma_B/\partial\phi$ in eq. (4) has to be calculated. Unfortunately, however, the calculation cannot be carried out reliably only from the open symbols in Fig. 6. Nevertheless, the present estimation indicates that the boundary energy of the $\Sigma 33$ boundary may considerably decrease with increasing inclination angle up to $\phi = 10^\circ$ like that of the $\Sigma 11$ boundary in Fig. 5(a) but unlike that of the $\Sigma 9$ boundary in Fig. 5(b).

3.3 Phase transformation of grain boundary

The faceting during cooling and the defaceting during heating in Al and Au were experimentally observed by Hsieh and Balluffi.⁵⁾ In their experiment, pure Al bicrystals with $\Sigma 11$ [110] and $\Sigma 3$ [111] asymmetric tilt boundaries and pure Au bicrystals with $\Sigma 3$ [111] asymmetric tilt boundaries were continuously heated and cooled on a hot stage in a transmission electron microscope. As to the $\Sigma 3$ boundary, the $\{110\}\{110\}$ boundary is faceted into the $\{112\}\{112\}$ planes at room temperature in both the Au and Al bicrystals. The faceted boundary becomes flat at $T = 0.54T_m$ and $0.89T_m$ during heating for the Al and Au bicrystals, respectively, and the flat boundary is faceted again during cooling. Here, T_m is the melting temperature of a pure metal. The faceting and the defaceting occur reversibly during repeated cooling and heating. As a consequence, the faceting and the defaceting are regarded as thermodynamic phase transformations of the grain boundary.^{5-7,20,30,31)} A mathematical method for the thermodynamic phase transformation is explained in detail in an ordinary textbook.²⁹⁾ Their observation⁵⁾ indicates that the transformation temperature T_t is slightly lower than $0.54T_m$ and $0.89T_m$ for the Al and Au bicrystals, respectively, with the $\Sigma 3$ boundary. As to the Al bicrystal with the $\Sigma 11$ boundary, the $\{667\}\{001\}$ boundary is faceted into the $\{113\}\{113\}$ and $\{441\}\{225\}$ planes during cooling. In this case, however, T_t is close to but lower than $0.96T_m$. Therefore, T_t remarkably varies depending on the material and the character of the grain boundary.

As mentioned in Sect. 1, the influence of the segregation of Bi on the faceting of the grain boundary in Cu was experimentally studied by Ference and Balluffi.¹²⁾ In their experiment, polycrystalline pure Cu specimens were isothermally annealed at $T = 823$ K for $t = 1.8$ ks in an atmosphere with a chemical potential of Bi slightly lower than that corresponding to the solubility of Bi in Cu. The annealed Cu specimen was heated on a hot stage in a transmission electron microscope. Bismuth atoms are added to the grain boundary due to annealing, but may be removed from the grain boundary owing to heating. During heating with a rate of 0.17 K/s, the faceted boundary in the annealed Cu specimen becomes round at $T = 448$ K, and then completely flat at $T = 498$ K. On the basis of this phenomenon, they concluded that Bi atoms began to diffuse out of the grain boundary at $T = 448$ K. Even by such diffusion, the segregation of Bi on the grain boundary may not vanish away completely at $T = 448$ K during heating with a rate of 0.17 K/s. Consequently, we can consider that T_t is equal to 448 K for the grain boundary in the binary Cu-Bi system. This value of T_t corresponds to $0.33T_m$, where $T_m = 1358$ K for Cu.³²⁾ The transformation temperature of $T_t = 448$ K is much lower than the eutectic temperature of $T_e = 544$ K in the Cu-Bi system.³²⁾ This means that the phase transformation of the grain boundary between the faceting and the defaceting occurs at solid-state temperatures in the Cu-Bi system.

According to the quantitative analysis of the boundary energy in Sect. 3.2, the faceting can spontaneously occur for the $\Sigma 11$ and $\Sigma 9$ boundaries during heating at temperatures around 1200 K. Hence, the faceting should be observed for the bicrystal with the $\Sigma 11$ or $\Sigma 9$ boundary homogenized at $T = 1173$ K regardless of the cooling rate. As mentioned in

Sect. 3.1, however, the faceting was clearly recognized only for the bicrystal with cooling C but not for those with coolings A and B. In order for the faceting to take place to a sufficient extent, the bicrystal should be heated for certain periods at temperatures slightly lower than T_l . This means that a large amount of the driving force is necessary for sufficient growth of the faceting. During such heating, each part of the initially flat grain boundary migrates by a certain distance towards the thermodynamically stable faceted plane in order to reduce the total boundary energy. In the present study, the homogenized bicrystal is cooled down to room temperature rapidly for coolings A and B but slowly for cooling C. Thus, the faceting with a certain extent is possible only in the bicrystal with cooling C. On the other hand, as shown in Fig. 5, the boundary energy in Cu was experimentally determined by the SPO method for the $\Sigma 11$ and $\Sigma 9$ [110] asymmetric tilt boundaries in previous studies.^{25,26)} In those experiments, the Cu bicrystal with silica particles precipitated on the grain boundary was degassed in vacuo at $T = 1273$ K for $t = 24$ h in order to remove oxygen segregated on the grain boundary, followed by furnace cooling. Hence, the cooling rate is close to each other between the SPO method and cooling C. Nevertheless, the faceting of the grain boundary in the Cu bicrystal was recognized clearly for cooling C but hardly for the SPO method. Thus, the segregation of Bi is necessary for the faceting of the grain boundary in Cu. This may yield that the boundary energy is varied by the segregation.

The influence of the segregation of Bi on the boundary energy of Cu at $T = 1293$ K was experimentally studied for $\Sigma 3$ and $\Sigma 9$ [110] asymmetric tilt boundaries by Straumal *et al.*²⁰⁾ According to their result, the relative boundary energy γ_B/γ_S is rather insensitive to the segregation for most of the boundaries. Here, γ_B and γ_S are the boundary and surface energies, respectively, of Cu. Therefore, the dependencies of γ_B/γ_l on ϕ for the $\Sigma 11$ and $\Sigma 9$ boundaries at $T = 1273$ K in Fig. 5 may be also insensitive to the segregation, though the absolute values of γ_B and γ_l can vary depending on the concentrations of Bi in the grain boundary and the interface, respectively. Since f and f_l in Fig. 4 are determined by the relative value of γ_B but not by the absolute value of γ_B , they are also insensitive to the segregation.

For reliable measurement of l_i by TEM, l_i should not be much smaller than $1\ \mu\text{m}$. In order to satisfy this criterion, each corner of the faceted boundary has to migrate by a distance of some hundreds nm. Such migration of the corner is realized by the rotation and the migration of the faceted plane. At a constant reaction time and a constant driving force, the migration distance of the grain boundary increases in proportion to the mobility of the grain boundary. Furthermore, the mobility is proportional to the boundary diffusivity across the grain boundary.²⁹⁾ The temperature dependence of the boundary diffusivity $s\delta D^b$ is usually expressed by the equation

$$s\delta D^b = s\delta D_0^b \exp\left(-\frac{Q^b}{RT}\right). \quad (5)$$

Here, s is the segregation factor, δ is the thickness of the grain boundary, D^b is the boundary diffusion coefficient, D_0^b and Q^b are the pre-exponential factor and the activation

Fig. 7 The boundary diffusivity P_X^{Cu} versus the melting temperature T_m of element X in the grain boundary of Cu calculated at $T = 448$ K from eq. (5) using the values of $s\delta D_0^b$ and Q^b reported by Kaur and Gust³³⁾ and by Divinski *et al.*³⁴⁾

enthalpy of D^b , respectively, and R is the gas constant. Values of $s\delta D_0^b = 1.05 \times 10^{-14} \text{ m}^3/\text{s}$ and $Q^b = 102.1 \text{ kJ/mol}$ are reported for Cu in Cu,³³⁾ and those of $s\delta D_0^b = 6.6 \times 10^{-12} \text{ m}^3/\text{s}$ and $Q^b = 102.8 \text{ kJ/mol}$ for Bi in Cu.³⁴⁾ For convenience sake, the values of $s\delta D^b$ for Cu and Bi in Cu are merely denoted by $P_{\text{Cu}}^{\text{Cu}}$ and $P_{\text{Bi}}^{\text{Cu}}$, respectively. Using the parameters mentioned above, $P_{\text{Cu}}^{\text{Cu}} = 1.31 \times 10^{-26} \text{ m}^3/\text{s}$ and $P_{\text{Bi}}^{\text{Cu}} = 6.82 \times 10^{-24} \text{ m}^3/\text{s}$ are calculated at $T = 448$ K from eq. (5). Thus, $P_{\text{Bi}}^{\text{Cu}}$ is 520 times greater than $P_{\text{Cu}}^{\text{Cu}}$. This means that the segregation of Bi on the grain boundary in Cu accelerates the migration of the grain boundary and thus the growth of the faceting. In order to actualize the faceting with the morphology like Fig. 2(b) also in the Cu bicrystal of Fig. 2(a), the furnace cooling should be carried out very slowly for a long period of 520 days.

Using the values of $s\delta D_0^b$ and Q^b reported for element X in Cu by Kaur and Gust,³³⁾ P_X^{Cu} was calculated at $T = 448$ K from eq. (5). The results of $X = \text{S, In, Zn, Ge, Ag}$ and Si as well as those of $X = \text{Bi}$ and Cu are shown as open circles in Fig. 7. In this figure, the ordinate indicates the logarithm of P_X^{Cu} , and the abscissa shows the melting temperature T_m of element X . Although the open circles are slightly scattered, P_X^{Cu} rather monotonically decreases with increasing melting temperature T_m . At a constant annealing temperature, the element with a low melting temperature is more mobile than that with a high melting temperature. Thus, P_X^{Cu} is greater for the former element than for the latter element. As shown in Fig. 7, P_{S}^{Cu} , $P_{\text{Zn}}^{\text{Cu}}$ and $P_{\text{In}}^{\text{Cu}}$ are much greater than $P_{\text{Cu}}^{\text{Cu}}$. Hence, the faceting of the grain boundary in Cu may be enhanced also by the segregation of S, Zn or In on the grain boundary. Unfortunately, however, reliable information is not available for the effect of the segregation of S, Zn or In on the faceting. On the other hand, the influence of K on the faceting of the (115) surface of Cu was experimentally studied by Schwenger and Ernst.³⁵⁾ Here, $T_m = 337$ K for $X = \text{K}$.

According to their result at $T = 340$ K, the (115) surface partially covered with K atoms is faceted into the (114) surface, but the clean (115) surface is not. Although the surface diffusivity of K in Cu was not known, they concluded that the growth of the faceting at $T = 340$ K was accelerated by the adsorption of K on the surface.³⁵⁾ Consequently, we may expect that the faceting of the grain boundary in Cu is expedited by the segregation of S, Zn or In.

4. Conclusions

In order to examine experimentally the faceting of the grain boundary in the binary Cu-Bi system, the Cu bicrystals with the $\Sigma 33$, $\Sigma 9$ and $\Sigma 11$ [110] symmetric tilt boundaries were doped with Bi at a temperature of $T = 1173$ K for a time of $t = 120$ h. Here, the misorientation angle between the [001] directions of the adjacent single-crystals is 20.1° , 38.9° and 50.5° for the $\Sigma 33$, $\Sigma 9$ and $\Sigma 11$ boundaries, respectively. As reported in a previous study,²⁷⁾ the segregation of Bi on the grain boundary proceeds during Bi-doping. After Bi-doping, the Cu bicrystals were homogenized at $T = 1173$ K for $t = 48$ h, and then cooled in different manners. The TEM observation indicates that the grain boundary is faceted clearly in the bicrystal with furnace cooling but scarcely in that with water quenching. This means that the faceting occurs during furnace cooling after homogenization but not during homogenization. The faceted plane appears most probably at $\phi = 8\text{--}14^\circ$ for the $\Sigma 11$ boundary, at $\phi = 6\text{--}12^\circ$ for the $\Sigma 33$ boundary, and at $\phi = 2\text{--}4^\circ$ and $\phi = 14\text{--}18^\circ$ for the $\Sigma 9$ boundary. Here, ϕ is the inclination angle between the faceted plane and the initially flat boundary. As pointed out by many investigators,^{5–7,20,30,31)} the faceting is regarded as a phase transformation of the grain boundary. According to the observation by Ference and Balluffi,¹²⁾ the transformation temperature of the faceting in the Cu-Bi system is close to 450 K. This temperature is much lower than the eutectic temperature of 544 K for the Cu and Bi solid-solution phases.³²⁾ Hence, the faceting in the Cu-Bi system takes place at solid-state temperatures. On the basis of the inclination angle dependence of the boundary energy in Cu,^{25,26)} the faceting was analyzed quantitatively. The analysis indicates that the contribution of the torque term to the faceting is important. Comparing the mobility between the grain boundaries with and without Bi, we may conclude that the segregation of Bi accelerates the rotation and the migration of the grain boundary during the phase transformation. Consequently, during furnace cooling of one day, the faceting occurs remarkably for the grain boundary with Bi but hardly for that without Bi.

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