Diffusion of Copper in Nanocrystalline Al-7.8 at%Ti-0.3 at%Fe Alloy Prepared by Mechanical Alloying

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The powder of supersaturated solid solution of Al-7.8 at%Ti-0.3 at%Fe with a nanocrystalline structure was prepared by mechanical alloying, and it was compacted to columnar shape material at low temperature by application of high pressure of 3 GPa. Diffusion of copper was studied in this compacted nanocrystalline material using an ion mass microanalyzer. The interfacial diffusion coefficient of copper in the nanocrystalline materials is fairly higher than the volume diffusion coefficient of copper in aluminum, and the activation energy of the interfacial diffusion is quite small when compared with that of volume diffusion of copper in aluminum. The characteristic of the interfacial diffusion implies that the interface in the nanocrystalline materials of this research should have a very loose structure.

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I. Introduction

Mechanical alloying techniques can produce new phases, amorphous structure, nanocrystalline materials and supersaturated alloys, which cannot be obtained by usual ingot making methods⁽¹⁾⁻⁽⁵⁾. In these techniques, a mixture of different kinds of metal powder is mechanically alloyed near room temperature by compression, friction and shearing due to collision and rub of balls⁽⁶⁾, and the large mechanical energies thrown into the powder particles are stored in forms of defects, dislocations, nanocrystalline interface^{†††} and so on. We guess that such defects and interfaces would promote the mechanical alloying process by enhancing reactions in or between the powder particles. However, it has not been sure if such enhanced reactions exist and contribute to the

promotion of mechanical alloying processes even at low temperatures.

Since diffusion along the interfaces of nanocrystalline materials synthesized by a gas-condensation and high pressure compacting techniques has been reported to be very rapid⁽⁷⁾, it is of great interest if this type of rapid diffusion is enough to enhance the chemical reactions during mechanical alloying when the mechanical alloyed powder has the nanocrystalline structure. However, the investigation on diffusion in nanocrystalline materials prepared by a mechanical alloying technique has not been reported yet so far as we know. As a first step, a research on diffusion in such nanocrystalline materials is worthwhile to elucidate the above possibility of enhancement. Some limitations are found in the basic researches and the industrial applications of mechanically alloyed powder because the shape of alloys prepared by mechanical alloying technique is powder itself. Therefore, some consolidation techniques have been required to compact the mechanical alloyed powder without losing typical structure and properties of nanocrystalline. Among them, the high pressure technique which utilizes the pressures of the order of GPa can make good compacts; the large deformation of powder by high pressure breaks oxidation films on the surface of powder particles, considerably increases fresh contact areas between powders and crushes voids lying between powder particles. Furthermore, the high pressure makes it possible that the compacts of mechanically alloyed powder will retain its typical properties even after the sintering⁽⁸⁾ because the ultra-high pressures of the order of GPa are expected to

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†††† Being distinguished from a grain boundary between the ordinary grains, an interface between nanocrystals is, particularly, referred to as "a nanocrystalline interface" or only "interface", because it is thought that there should be differences in the structure and properties between the nanocrystalline interface and the ordinary grain boundary. Diffusion along the grain boundaries is called "grain boundary diffusion", and diffusion along the interface between nanocrystals "interfacial diffusion".

significantly retard the precipitation, recrystallization, grain growth and so on, and to also rise the temperatures of such phenomena⁽⁹⁾.

Aluminum-rich alloys in the Al-Ti system have the good properties of heat-resistance when fine precipitates of the metastable Al₃Ti phase are densely dispersed in the aluminum matrix. One of the present authors has elaborately studied the mechanical alloying process of the mixture of aluminum and titanium powder, and reported that the supersaturated nanocrystalline aluminum-rich Al-Ti alloy powder can be obtained by this technique⁽³⁾. The purposes of this research are to make the supersaturated nanocrystalline powder of aluminum-rich alloy in the Al-Ti system by mechanical alloying, to compact it at a lower temperature under the high pressure of 3 GPa, and to determine the interfacial diffusion coefficient of copper in the compacted nanocrystalline materials. Here, the copper element is one of the important elements for aluminum alloys.

II. Experimental Procedure

99.85 mass%Al powder 32 μm in average diameter and 99.5 mass%Ti powder 13 μm in average diameter were mixed to the composition of Al-6 at%Ti in a gloved box filled with argon gas. This mixed powder is referred to as MIX material, here. Subsequently, 10 g of the MIX material and 238 g of stainless steel mill-balls 4 mm in diameter were put into a stainless steel mill-pot with 2 ml of methyl alcohol for lubrication, and then the lid was tightly put on the mill-pot with a rubber O-ring. The mill-pot was taken out of the gloved box, and set to a high energy planetary ball-mill equipment. The mechanical alloying was carried out in the condition of the milling power of 150N and milling time of 216 ks. After mechanical alloying, the mill-pot was put back into the gloved box, and then the mechanically alloyed powder was put out of the mill pot. Immediately, this powder was preformed into disks 4 mm in diameter and 2.5 mm in height by pressing of 380 MPa using the piston and cylinder of tool steel and pressing machine set in the gloved box. This disk is referred to as MA material. Thus, the MA material was prepared without exposing to air.

In order to compact the MA materials by high pressure, a couple of MA materials was put into a cubic high pressure cell, as shown in Fig. 1. The MA materials were covered with a BN capsule which has the good lubricity and thermal stability. The cubic pyrophyllite {Al₂Si₄O₁₀(OH)₂} serves as pressure medium and self-gasket. The high pressure cell was set in a high pressure equipment which consists of a 12MN pressing machine and high pressure blocks having the six tungsten carbide (WC) anvils. This high pressure equipment was designed to transform a press generated by the press machine to six presses by the six WC anvils. These six WC anvils press the high pressure cell on its six planes, and generate a hydrostatic and high pressure in the cell. The pressure was calibrated with the transition pressure of bismuth

Fig. 1 High pressure cell.

I-II(2.55 GPa), bismuth II-III(2.7 GPa) and thallium II-III(3.67 GPa) at room temperature. Under the high pressure of 3 GPa, the MA materials were heated with a carbon heater by passing the electric current. The temperature was measured by a thermocouple put near the MA materials, and it was calibrated using the method similar to Hanneman and Strong's method⁽¹⁰⁾. These MA materials which were compacted at 673 and 733 K for 3.6 ks under high pressure of 3 GPa are referred to as MA-36 and MA-37 materials, respectively. Some of MA and MA-36 materials were annealed at 673 to 773 K for 3.6 ks under 0.1 MPa of argon: the MA material annealed at 673 and 773 K for 3.6 ks under 0.1 MPa are referred to as MA-06 and MA-07 materials, respectively, and the MA-36 material annealed at 773 K and 0.1 MPa for 3.6 ks is done to as MA-36-07 material.

The density of MA-36 material was measured by Archimedian's principle using the aluminum single crystal disk of same size for the calibration. The lattice parameter and grain size of MIX, MA, MA-36, MA-37 and MA-36-07 materials were measured by the X-ray diffraction (XRD) method using monochromatic X-ray of Cu K α line and Scherrer's relation⁽¹¹⁾:

$$L = \lambda / \beta \cos \theta \quad (1)$$

where L is the crystalline size, λ the wave length of X-ray radiation, β the integral width of the diffraction peak, and θ the diffraction angle. The curves of differential scanning calorimetry (DSC) for the MA, MA-36 and MA-37 materials were measured at the heating rate of 10 K/min under an argon gas flow. The MA-36 and MA-37 materials were ground and polished using Al₂O₃ powder of 0.05 μm , and then they were observed by a scanning electron microscope (SEM). The ratio of the section area of porosities to the whole area was micrographically evaluated from the scanning electron micrographs by a special computer program. The composition of MA materials was measured by an energy dispersive X-ray spectroscopy (EDX).

An aluminum single crystal was made by cutting from 5N-aluminum ingot whose grains were largely grown by annealing at 873 K for 160 ks under 0.1 MPa. Copper of 99.99% was deposited by vacuum evaporation at 1.6×10^{-3} Pa into 9 nm in thickness on the polished surface

of the aluminum single crystal, MA-36 and MA-36-07 materials. The aluminum single crystal, MA-36 and MA-36-07 materials deposited with copper were diffusion-annealed at low temperatures of 373 to 573 K for 0.9 ks to 7.2 ks under the argon gas flow in an electric furnace in order to diffuse the copper element into the inner part of the materials.

In order to obtain the diffusion profiles of copper in the materials, the intensities of secondary-ion signal of ^{63}Cu (isotopic abundance: 69.1%) and the total secondary-ions signals were measured from the surface by in-depth profiling with an ion mass microanalyzer (IMMA). In this measurement, the 10 keV Ar^+ primary ions were used, the voltage of the secondary ion was 3 keV, the diameter of the ion beam was 0.5 mm, and the ion current was $0.25 \mu\text{A}$. The depths of the sputtered craters on the surface of materials by the Ar^+ ion sputtering were measured by a surface rough meter in order to examine the uniformity and flatness of the sputtered craters and to obtain the sputtering rates. The following equation shows the relation between the atomic fraction of copper and the ratio of the ion intensity of secondary-ion signal of ^{63}Cu to that of the total ions⁽¹²⁾:

$$C_{\text{Cu}} = \frac{I_{\text{Cu}}/K_{\text{Cu}}}{\sum (I_j/K_j)} \quad (2)$$

where C_{Cu} is the atomic fraction of copper, I_j the intensity of secondary-ion signal of element j , and K_j the ionization rate of element j . Since $K_{\text{Al}} \cong K_{\text{Ti}} \cong K_{\text{Cu}}$ holds for aluminum, titanium and copper elements, eq. (2) becomes simple as:

$$C_{\text{Cu}} = I_{\text{Cu}} / (I_{\text{Al}} + I_{\text{Ti}} + I_{\text{Cu}}) = I_{\text{Cu}} / I_{\text{T}} \quad (3)$$

From this relation of eq. (3), the ^{63}Cu ion intensity I_{Cu} was converted into the atomic fraction of copper.

When a very thinly deposited copper on the surface of materials penetrates inside, the interfacial and volume diffusion coefficients can be evaluated from the diffusion profiles by the following two methods⁽⁷⁾⁽¹³⁾⁽¹⁴⁾. The interfacial diffusion coefficient was evaluated by one of analysis methods for the grain boundary diffusion because such analysis can be mathematically applied to the interfacial diffusion. At low temperatures, the interfacial diffusion coefficients are higher than the volume diffusion ones, and the interface width satisfies the following equation when the diffusion time is short:

$$D_1 \gg I_v \quad (4)$$

$$2(D_v t)^{0.5} \leq \delta_1 \quad (5)$$

where D_1 is the interfacial diffusion coefficient, D_v the volume diffusion coefficient, t the diffusion time, and δ_1 the interface width. In this case, the diffusion profile is presented as follows⁽⁷⁾:

$$C(x, t) = C_0(2\delta_1/g)(\pi D_1 t)^{-0.5} \exp(-x^2/4D_1 t) \quad (6)$$

where C_0 is the concentration at $t=0$, and g is the diameter of nanocrystals. On the other hand, the diffusion profile of the volume diffusion in a single crystal is

presented as follows⁽¹³⁾:

$$C(x, t) = \frac{M}{(\pi D_v t)^{0.5}} \exp(-x^2/4D_v t) \quad (7)$$

where M is the total amount of diffusion element. By plotting the diffusion profiles of the logarithm of Cu concentration versus the square of diffusion distance, the D_1 and D_v were evaluated from the gradient of the linear part of plots using (6) and (7) equations.

III. Results and Discussion

Figure 2 shows the X-ray diffraction patterns of various kinds of materials. The MIX material exhibits the sharp peaks of X-ray diffraction of pure aluminum and titanium because of no reaction between the powder particles as shown in Fig. 2(a). On the other hand, the titanium peaks disappear from the MA materials as shown in Fig. 2(b), and only the broad aluminum peaks which shift towards higher diffraction angles are observed. According to the concentration measurement by the EDX, the composition of MA material was Al-7.8 at%Ti-0.3 at%Fe. The higher concentration of titanium in MA material than the initial one is ascribed to sticking of aluminum powder on the balls and walls of the mill-pot, while the iron of 0.3 at%Fe in the MA material was introduced from the stainless steel ball and wall. The nickel and chromium elements of stainless steel must be also contained, but they were not detected because of their lower concentrations. According to equilibrium state bi-

Fig. 2 X-ray diffraction patterns; (a) MIX, (b) MA, (c) MA-06, (d) MA-07, (e) MA-36, and (f) MA-37 materials.

nary diagrams⁽¹⁵⁾⁽¹⁶⁾, the aluminum solid solution in the Al-Ti system has the maximum solid solubility of 0.7 at%Ti, and it is in equilibrium with the DO₂₂-type Al₃Ti phase⁽¹⁵⁾. On the other hand, the maximum solid solubility of iron in aluminum is about 0.04 at%Fe in the Al-Fe system, and the aluminum solid solution equilibrates with the Al₃Fe phase⁽¹⁶⁾. Although the contents of titanium and iron in the MA material are over their equilibrium solid solubilities reported by phase diagrams⁽¹⁵⁾⁽¹⁶⁾, yet no peaks of such binary non- and equilibrium phases were observed in the XRD measurement of the MA material as mentioned above. Table 1 lists the lattice parameters and grain diameter determined by the XRD measurements for various materials. The lattice parameter of MA material is 0.4037 nm. This is quite smaller than 0.4049 nm of pure aluminum. The large decrease in the lattice parameter of MA material is mainly ascribed to the large supersaturation of titanium in aluminum, since the dissolution of the titanium atoms into aluminum solid solution is reported to decrease the lattice parameter⁽¹⁷⁾. The grain diameter of MA material is 14 nm. So, a nanocrystalline structure with grain size of 14 nm is formed in the MA material. Thus, it follows that the MA material is the nanocrystalline face-centered-cubic structure aluminum solid solution supersaturated with elements of 7.8 at%Ti and 0.3 at%Fe, which are about 10 times larger than their maximum solid solubilities in aluminum.

As shown in Fig. 2(d), the peaks for the DO₂₂-Al₃Ti phase are distinctly observed in addition to those of Al phase by the XRD measurement of MA-07 material. When compared with the peaks in Fig. 2(c) and (d), the peaks of the DO₂₂-Al₃Ti phase in the MA-06 are fairly smaller than those in MA-07 one because of lower annealing temperature. Furthermore, it is to be noted that their peaks in MA-37 material are smaller than in MA-07 one in spite of the same annealing temperature and the time, as shown in Fig. 2(d) and (f). This indicates that the high pressure considerably retards the precipitation of DO₂₂-Al₃Ti phase. As listed in Table 1, the crystal sizes of the MA-36 and MA-37 materials are 22 and 18 nm, while the grain size of MA material is 14 nm. Thus the slight grain growth occurs in the former two, however, the nanocrystalline structure of the MA-36 and MA-37 materials steadfastly remains in spite of the heating at more than 673 K for 3.6 ks under 3 GPa. The diameter of nanocrystals in the MA-36-07 material becomes only about twice larger than that of MA materials by the additional annealing at 773 K and 0.1 MPa for 3.6 ks. Thus,

the slight grain growth in nanocrystalline materials suggests that high pressure also decreases the grain growth rate and the nanocrystalline structure might be essentially stable even at the high temperatures.

Figure 3 shows the DSC curves of MA, MA-36 and MA-37 materials. The DSC curves of MA and MA-36 materials exhibit an exothermic peak near 700 K, while no peak is observed in the MA-37 material. As listed in Table 1, the lattice parameters of MA-37 and MA-36-07 materials are larger than that of MA material, and they are equal to that of pure aluminum. This means that the DO₂₂-Al₃Ti phase plentifully precipitates from the aluminum solid solution of MA material through such a annealing at 773 K under 0.1 MPa and then the titanium contents in aluminum solid solutions of the MA-37 and MA-36-07 materials become near zero. Judging from the results of the XRD and DSC measurements, the precipitation of DO₂₂-Al₃Ti phase occur near about 700 K.

As shown in Fig. 2(b) and (e), the shape of XRD curve of MA-36 is quite similar to that of MA material and the peaks of DO₂₂-Al₃Ti phase in the MA-36 material are difficult to be recognized. Furthermore, the lattice parameter of 0.4034 nm of the MA-36 material is approximately equal to the 0.4037 nm of the MA material as listed in Table 1. Therefore, the MA-36 material retains the almost same structure of the MA material because the compacting temperature of 673 K at the high pressure is lower than the precipitation temperature of about 700 K and the high pressure suppresses change in the structure of the supersaturated solid solution.

The density of the MA-36 material was measured, and it was converted to the relative density using the theoretical density of single crystal which were evaluated from above lattice parameters and the alloy concentration measured by the EDX method. The relative density of the MA-36 material was 98%. This value is in good agree-

Table 1 Crystal sizes and lattice parameters.

Materials	Crystal size nm	Lattice parameters nm
MA	14	0.4037
MA-36	22	0.4034
MA-36-07	18	0.4049
Single Al	33	0.4049
	—	0.4049

Fig. 3 DSC curves; (a) MA, (b) MA-36 and (c) MA-37.

Fig. 4 Depth-profile of intensity of secondary-ion signal of ^{63}Cu ion and total elements in the MA-36 material diffusion-annealed at 473 K and 0.1 MPa for 3.6 ks.

ment with the result of the SEM observation which reveals that the ratio of the section area of the porosities to the whole of the polished MA-36 material is less than about 1%. On the other hand, the relative density of interfaces in a nanocrystalline material is reported to be about 75%⁽⁷⁾. If a nanocrystalline material consists of the cubic nanograins in volume of $20 \times 20 \times 20 \text{ nm}^3$ and the interface of 0.7 nm in width with relative density of 75%, the relative density of such an assumed nanocrystalline material is evaluated to be 97.5%, which is in good agreement with the experimental one of 98%. Thus, the MA-36 material used for the diffusion experiments is a well compacted one under the high pressure of 3 GPa.

Figure 4 shows an example of plots of the intensity of secondary-ion signal of ^{63}Cu , I_{Cu} , and total intensity, I_{T} , obtained by the IMMA versus sputtering time for the MA-36 materials annealed at 473 K and 0.1 MPa for 3.6 ks. Both the I_{Cu} and I_{T} steeply fall off in the beginning of sputtering and then gradually decline with increasing time of sputtering. Figure 5 shows an example of the shape of the sputtered crater on the surface of the MA-36 material by being sputtered for 10.2 ks. The diameter of this crater is 0.5 mm and its depth is 4 μm . Although the bottom of crater seems to be rugged due to the reduced scale of abscissa of figure, the bottom is considerably flat as a whole and there is no preferential sputtering. The depth of crater versus the sputtering time is shown in Fig. 6. There exists a linear relationship between the sputtering time and the depth of crater. Using it, the sputtering time can be converted to the distance from the surface, x . Figure 7 shows an example of the plots of the logarithms of $I_{\text{Cu}}/I_{\text{T}}$ versus x^2 according to eqs. (6) and (7). The plots

Fig. 5 Shape of the crater sputtered for 10.2 ks on MA-36 material diffusion-annealed at 473 K and 0.1 MPa for 3.6 ks.

Fig. 6 Relation between sputtering time and the depth of sputtered craters.

of logarithms of $I_{\text{Cu}}/I_{\text{T}}$ have the gentle curve near the surface, and then they show the linear part. In the deep inside, the plots also depart from the linear line. The initial departure from linear line is ascribed to the oxidation, contamination and so on, while the departure in the deep part is mainly attributable to the increasing error due to the increasing depth of the crater and the error induced by approaching the limit of measurement. From the gradient of linear part of plots, the interfacial diffusion coefficients of Cu, $D_{\text{I}}(\text{Cu})$, in the MA-36 and MA-36-07 materials were determined by using eq. (6), and the volume diffusion coefficient of Cu, $D_{\text{V}}(\text{Cu})$, in aluminum single crystal was done using eq. (7).

Figure 8 shows the $D_{\text{I}}(\text{Cu})$ in MA-36 material vs. reciprocal temperature, and for comparison it also ex-

Fig. 7 The logarithms of concentration profile of Cu in MA-36 material diffusion-annealed at 473 K and 0.1 MPa for 3.6 ks versus squared diffusion distance.

hibits the $D_I(\text{Cu})$ in the MA-36-07 material, the $D_V(\text{Cu})$ in aluminum single crystal and the extrapolated line from the $D_V(\text{Cu})$ in aluminum determined at high temperature above 673 K⁽¹⁸⁾. The $D_V(\text{Cu})$ in aluminum single crystal of this research is in vicinity of the extrapolated line of the $D_V(\text{Cu})$ in aluminum measured at high temperatures in spite of the dissimilarities of the experimental methods. Their values are recognized to be consistent with each other. When being compared at 473 K, the $D_I(\text{Cu})$ is largest among the diffusion coefficients. Especially, the $D_I(\text{Cu})$ in MA-36 material is by about four times larger than the $D_I(\text{Cu})$ in MA-36-07 material. The MA-36 material is the supersaturated aluminum solid solution of the nanocrystalline 22 nm in diameter, while the MA-36-07 material is the nanocrystalline of 33 nm in diameter with the great amount of Al_3Ti precipitates. Therefore, the lower value of $D_I(\text{Cu})$ in MA-36-07 material is probably ascribed to the change in the structure and components of interfaces due to the higher temperature annealing.

The $D_I(\text{Cu})$ in MA-36 material satisfies the Arrhenius-type equation⁽¹⁹⁾:

$$D_I(\text{Cu}) = D_{I0}(\text{Cu}) \exp\left(\frac{-Q_I}{RT}\right) \quad (8)$$

where $D_{I0}(\text{Cu})$ is the frequency factor for interface diffusion, Q_I the activation energy for interface diffusion, R the gas constant, and T the absolute temperature. Table 2 lists the experimental values of $D_{I0}(\text{Cu})$ and Q_I evaluated by eq. (8), also including the diffusion data by other researchers⁽⁷⁾⁽¹⁸⁾⁽²⁰⁾⁽²¹⁾. In Table 2, the data on interfacial

Fig. 8 Temperature dependence of diffusion coefficients of Cu element in various materials; ● in MA-36 material, ▲ in MA-36-07 material, ■ in single crystal of aluminum, and — extrapolated line from volume diffusion coefficient in single crystal of aluminum at higher temperatures.

diffusion of copper and silver in a nanocrystalline material of copper prepared by a gas-condensation and high pressure compacting methods were obtained by Horváth using the radioactive tracer and ion-beam sputtering methods⁽⁷⁾, and the data of $D_V(\text{Cu})$ and $D_V(\text{Ag})$ in copper single crystal were determined at high temperature by the radioactive tracer method⁽²⁰⁾⁽²¹⁾. It is to be noted that the values of Q_I and $D_{I0}(\text{Cu})$ are considerably smaller than those for the volume diffusion, Q_V and D_{V0} , respectively. Although the value of Q_I in the MA-36 material cannot be directly compared with the value of Q_V for copper diffusion in aluminum, the value of Q_I/Q_V is about 0.28. This value is quite similar to the Q_I/Q_V of 0.29 for copper diffusion in copper and 0.18 to 0.38 for silver diffusion in copper.

In general, the empirical relations have been appreciated between the melting points of pure elements and activation energies for volume, grain boundary, surface and liquid diffusion as follows⁽²²⁾:

$$Q_V = 146T_m \quad (9)$$

$$Q_G = 90T_m \quad (10)$$

$$Q_S = 55T_m \quad (11)$$

$$Q_L = 25T_m \quad (12)$$

where T_m is the melting point, and Q_G , Q_S and Q_L are the activation energies for grain, surface and liquid diffu-

Table 2 Activation energies and preexponential factors.

Matrix	Diffusion elements	Interfacial diffusion		Ref.	Volume diffusion		Ref.
		Q (kJ/mol)	D_0 (m ² /s)		Q (kJ/mol)	D_0 (m ² /s)	
Al-Ti-Fe	Cu	34.8	2.4×10^{-12}	(*)	—	—	
Al	Cu	—	—		126	1.5×10^{-5}	(18)
Cu	Cu	61.7	3×10^{-9}	(7)	211	7.8×10^{-5}	(21)
Cu	Ag	34.7 ~ 74.2	$4 \times 10^{-13} \sim 3 \times 10^{-7}$	(7)	195	6.1×10^{-5}	(20)

(*): present work

sion, respectively. The ratios of the activation energies to the Q_v are calculated from eqs. (9) to (12):

$$Q_G/Q_v = 0.62 \quad (13)$$

$$Q_s/Q_v = 0.38 \quad (14)$$

$$Q_L/Q_v = 0.17. \quad (15)$$

Among them, it should be noted that the Q_G strongly depend on the properties of grain boundaries⁽²³⁾: for grain boundaries made up of dissociated dislocation and twist boundaries,

$$Q_G/Q_v = 0.6 \sim 0.8 \quad (16)$$

and for grain boundaries made up of undissociated dislocation or high angle boundaries,

$$Q_G/Q_v = 0.4 \sim 0.5. \quad (17)$$

Furthermore, diffusion on a twist boundary is pointed out to be 10 or 100 times slower than on the tilt boundary even for the same misorientation between two grains. Since the lower activation energy will translate to a higher value of diffusion coefficient, the activation energy of diffusion on the twist boundary may be higher than that on the tilt boundary⁽²³⁾. On the other hand, although the frequency factors are more sensitive to experimental errors than activation energies⁽²³⁾, the experimental values of frequency factors gather around the magnitudes of about 1×10^{-5} m²/s for volume diffusion⁽²⁴⁾, about 6×10^{-6} m²/s for grain boundary diffusion⁽²⁵⁾, about 1×10^{-7} m²/s for surface diffusion⁽²³⁾ and 1×10^{-14} m²/s for liquid diffusion⁽²²⁾. There seems to be the tendency that the activation energies and frequency factors for diffusion in more open structures are smaller.

When compared with the ratios in eqs. (13) to (17), the experimental value of Q_i/Q_v is in the vicinity of the following values: 0.4 to 0.5 for diffusion on grain boundaries made of undissociated dislocation or high angle boundaries, 0.38 for surface diffusion and 0.17 for liquid diffusion. The frequency factors of interface diffusion listed in Table 2 are also in the vicinity of those of grain boundary, surface and liquid diffusion. The ratios in eqs. (13) to (17) and the magnitude of frequency factors indicate that if there is a more open space in the nanocrystalline interfaces than in a grain boundary, some of the atoms will be able to jump with a lower activation energy than if the atoms are more tightly packed. In other words, the structure of nanocrystalline interface should be more open than that of grain boundaries such as a

high angle boundary, while less open than that of liquid.

The extrapolated value of $D_i(\text{Cu})$ at 300 K is about equal to the value of the $D_v(\text{Cu})$ in the aluminum single crystal at about 510 K, and it is 10^9 times larger than the extrapolated value at 300 K of the $D_v(\text{Cu})$ in the aluminum single crystal. At the 510 K, a solid aluminum alloy can sufficiently react with other materials⁽²⁶⁾, or diffusion-type transformations of aluminum alloys can occur quickly⁽²⁷⁾. As the volume fraction of the interfaces is comparable with the volume fraction of the crystalline component in nanocrystalline materials, the diffusion flux along the interfaces is huge even at low temperatures due to the quite rapid interfacial diffusion. Therefore, reactions rate-controlled by diffusion should be able to contribute to the mechanical alloying even at temperatures near the room temperature when materials have the nanocrystalline structures during mechanical alloying.

IV. Conclusions

The supersaturated alloy powder of Al-7.8 at%Ti-0.3 at%Fe with a nanocrystalline structure was made by mechanical alloying. This powder was well compacted by sintering at 673 K for 3.6 ks under the high pressure of 3 GPa, and the relative density of the compact was 98%. The interfacial diffusion of copper in the compact was investigated by the IMMA method. The interfacial diffusion coefficient of copper (m²/s) satisfies the following Arrhenius equation:

$$D = 2.4 \times 10^{-12} \exp \{ -34.8 \text{ (kJ/mol)} / RT \}.$$

The ratio of activation energy for the interfacial diffusion to that for volume diffusion is about 0.28. This low value indicates that there is more open space in the nanocrystalline interfaces than in ordinary grain boundaries. The interfacial diffusion coefficient at 300 K in the compact of this research is 10^9 times larger than the volume diffusion coefficient in aluminum single crystal at the same temperature. This value is sufficiently huge to enhance reactions in the nanocrystalline material.

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