Diffusion Distances of the Constituent Atoms in the Metallurgical Phenomena Such as Recovery, Recrystallization, Grain Growth, and Aging in Aluminum and Copper Alloys

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It is known that metallurgical phenomena such as recovery, recrystallization, grain growth, and aging are due to the diffusion of constituent atoms in materials. The heat treatments that cause these phenomena are conducted defining both time and temperature. In the diffusion process, it is the diffusion distance that is defined by both time and temperature. Therefore, the authors surmise that there must be a relationship between the change of material properties as a result of heat treatment and the diffusion distances of constituent atoms. Under this assumption, diffusion distances of constituent atoms at recovery, recrystallization, grain growth, and aging in aluminum and copper alloys were examined. As a result, it was found that these phenomena take place at the fixed diffusion distances peculiar to the materials and phenomena. Therefore, the relationship between time and temperature was decided in terms of the fixed diffusion distances. In this respect, empirically used "normalized annealing time" turns out to mean the diffusion distance.

Keywords aging, diffusion distance, grain growth, normalized annealing time, recovery, recrystallization

1. Introduction

In metals, metallurgical phenomena such as recovery, recrystallization, grain growth, and aging are caused by heat treatment. Furthermore, it is said that these phenomena are controlled by the diffusion of constituent atoms. Here, the diffusion distances between constituent atoms in the aluminum (Al) and copper (Cu) alloys in heat treatments were calculated and compared and related with each metallurgical phenomenon.

2. Diffusion

In general, diffusion coefficient D is expressed by the following equation:

$$D = D_0 \exp(-Q/RT)$$

where D_0 is the frequency factor; Q is the activation energy of diffusion; and R is the gas constant.

Next, diffusion distance l is expressed by the following equation:

$$l = \sqrt{Dt}$$

where t is time.

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Table 1 shows the diffusion data of constituent atoms in the Al and Cu alloys used here.[1]

3. Anneal Softening and Diffusion Distance of Cu-Ag Alloy

Figure 1(a) and (b) shows the anneal softening curves of the 24% cold-worked material and 52% cold-worked material of Cu-0.2%Ag alloy based on oxygen-free Cu, respectively.[2] Figure 1(c) and (d) shows the diffusion distances of Ag and Cu atoms derived at the softening beginning points of the softening curves of the 24% cold-worked material and 52% cold-worked material of Cu-0.2%Ag alloy, respectively.

From these figures, the diffusion distances of Ag atoms at the softening beginning point in the 24% cold-worked material

Table 1 Diffusion Data of Elements in Al and Cu Matrices

Matrix Metal	Diffusion Element	D_0/m$^2 \cdot$ s^{-1}	Q/kJ $\cdot$ mol^{-1}	Measurement Temperature, T/K
Aluminum	Cu	1.5×10^{-5}	126	623 ~ 903
	Mg	1.24×10^{-4}	131	667 ~ 928
	Zn	1.77×10^{-5}	117	438 ~ 918
Copper	Be	6.6×10^{-5}	196	973 ~ 1348
	Ag	6.1×10^{-5}	195	728 ~ 1337
	Cr	3.4×10^{-5}	195	999 ~ 1338
	Ti	6.9×10^{-5}	196	973 ~ 1283
	Zn	3.4×10^{-5}	191	878 ~ 1322
	Cu	7.8×10^{-5}	211	971 ~ 1334

D_0, frequency factor; Q, activation energy

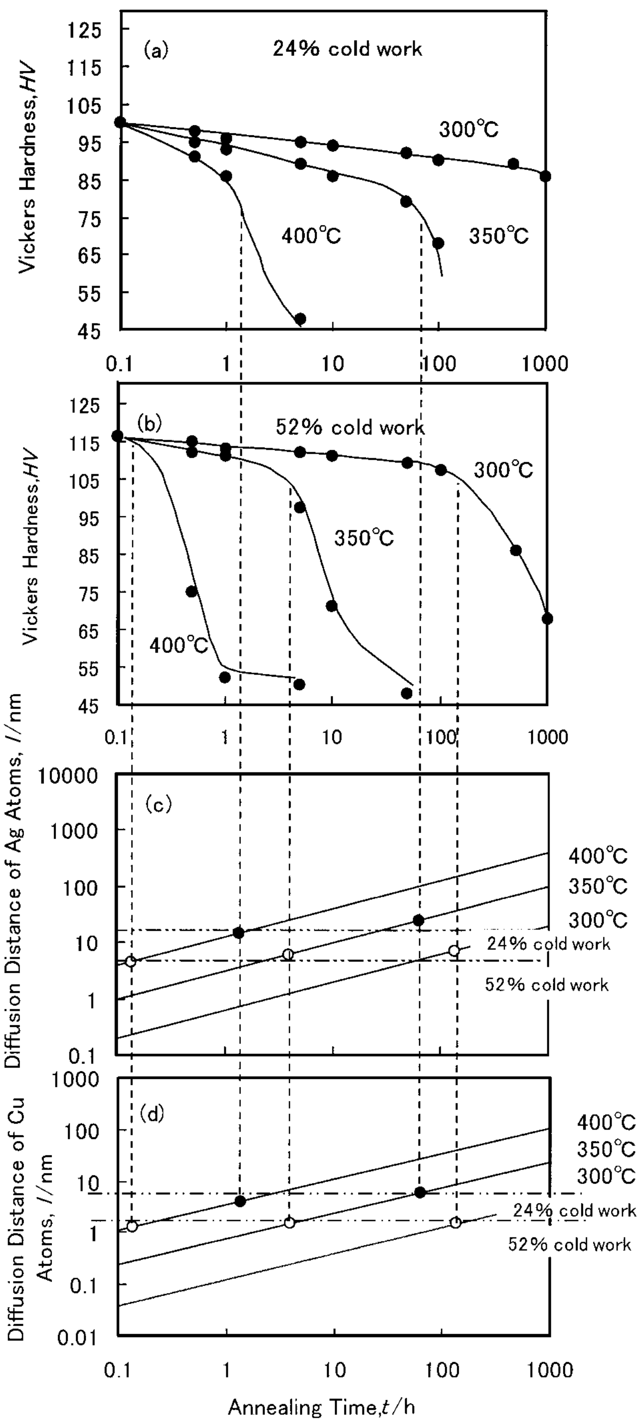

Fig. 1 Hardness of an oxygen-free Cu-0.2%Ag alloy in its isothermal annealing process and diffusion distances of Ag/Cu atoms. **(a)** Hardness of 24% cold-worked material; **(b)** hardness of 52% cold-worked material; **(c)** diffusion distances of Ag atoms; and **(d)** diffusion distances of Cu atoms

and 52% cold-worked material of Cu-0.2%Ag are 20 nm and 5 nm, respectively, irrelevant to time and temperature. Diffusion distances of Cu atoms under the same conditions are 5 nm and 1 nm, respectively, irrelevant to time and temperature.

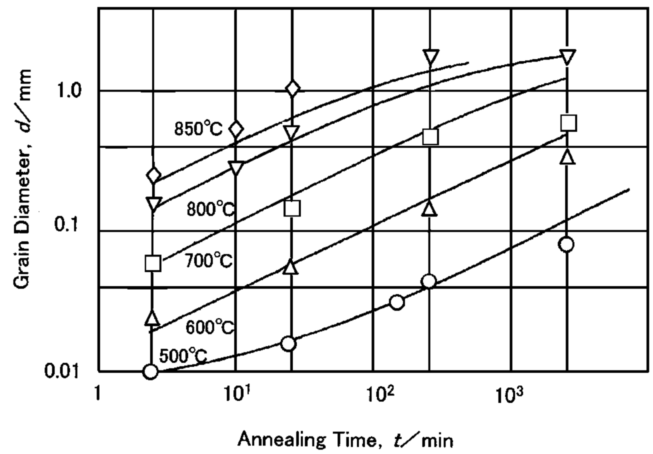

Fig. 2 Isothermal grain growth curves of Cu-35%Zn brass

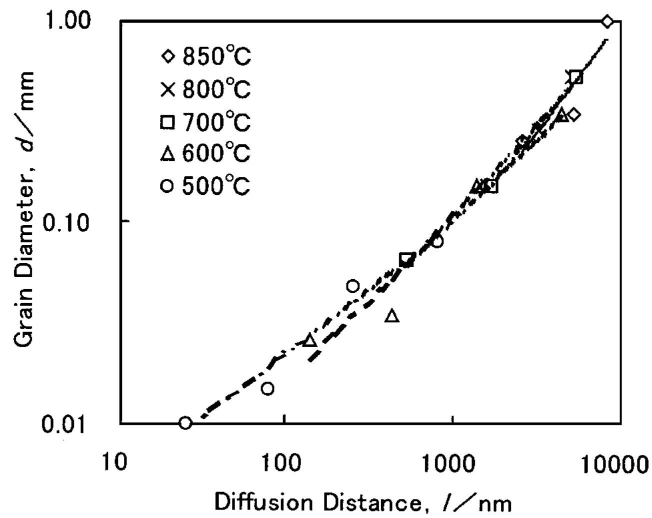

Fig. 3 Grain growth related to diffusion distances of Zn atoms in Cu-35%Zn brass

It is well known but not well interpreted that even the small addition of Ag, although the diffusion velocity of the Ag atom is larger than that of the self-diffusion of Cu, raises the softening temperature of copper.

The result of Fig. 1 shows that Ag atoms must diffuse at much longer distances than Cu and that this is the reason for the high softening temperature of Ag-bearing Cu. Moreover, anneal softening is supposed to occur at the fixed diffusion distance irrelevant to time and temperature.

4. Grain Growth and Diffusion Distance of Cu-35%Zn Brass

Figure 2 shows the relationship between the grain growth and annealing time of Cu-35%Zn brass as a parameter of temperature.[3]

In brass, Zn content mainly controls the recrystallization characteristics; therefore, here the diffusion distances of Zn atoms are considered. Annealing times, which are needed to get each grain size at each annealing temperature, were taken from Fig. 2, from which diffusion distances were calculated. Figure 3 shows the relationship between grain size and diffusion distance. As is shown, most points fall on the same line. In this case, the fixed grain size is supposed to occur at the fixed diffusion distance.

5. Age Hardening and Diffusion Distance of Al-Cu Alloys

Age-hardening curves of Al-Cu alloys, which contain 2 through 4.5% Cu at 130 and 190 °C are shown in Fig. 4(a) and (b), respectively.[4] Two straight lines in Fig. 4(c) show the diffusion distances versus aging time at 130 and 190 °C, respectively. Diffusion distances corresponding to the maximum hardness points at each aging temperature are plotted on these two straight lines.

In this case, diffusion distances of Cu atoms are supposed to be nearly 100 nm irrelevant to aging temperature and time. Small differences in the diffusion distances between 130 °C-aged material and 190 °C-aged material may be due to the subtle difference of the precipitates.[5]

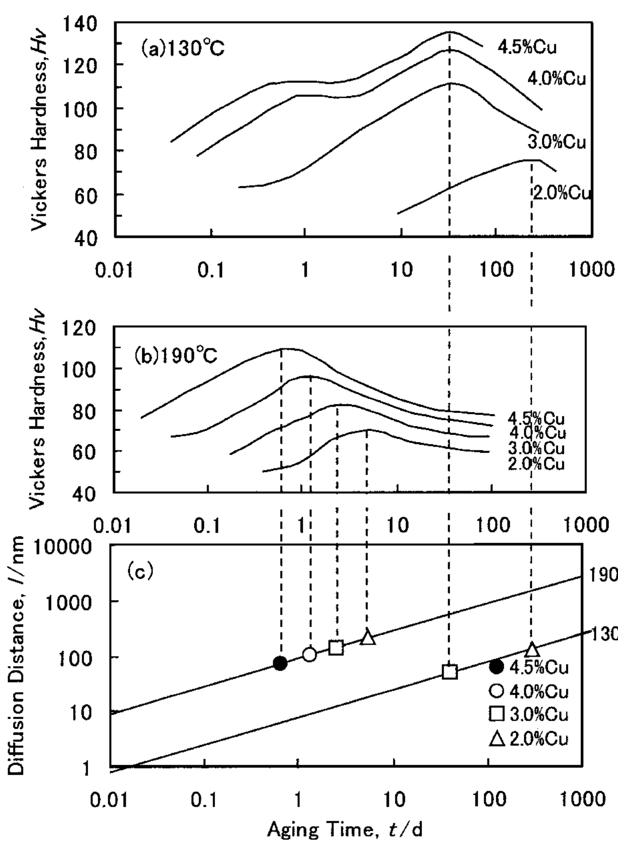

Fig. 4 Age-hardening curves and diffusion distances of Cu atoms for Al-Cu alloys. **(a)** Age-hardening curves at 130 °C; **(b)** age-hardening curves at 190 °C; and **(c)** diffusion distances of Cu atoms

6. Age Hardening and Diffusion Distance of Al-Cu-Mg Alloys

Figure 5(a) shows the aging curves of Al-3.15%Cu-0.52Mg alloy at the temperature ranging from 130-260 °C.[6] Straight lines in Fig. 5(b) show the diffusion distances of Cu and Mg atoms versus aging time as a parameter of aging temperature, respectively. Diffusion distances of Cu and Mg atoms corresponding to the maximum hardness points at each aging temperature are plotted on these straight lines, respectively. In this case, diffusion distances of Cu and Mg atoms are supposed to be nearly 100 nm irrelevant to aging temperature and time. Age-hardening precipitates called GPBs in these alloys are said to contain both Cu and Mg atoms,[6] which is consistent from the viewpoint of diffusion distance.

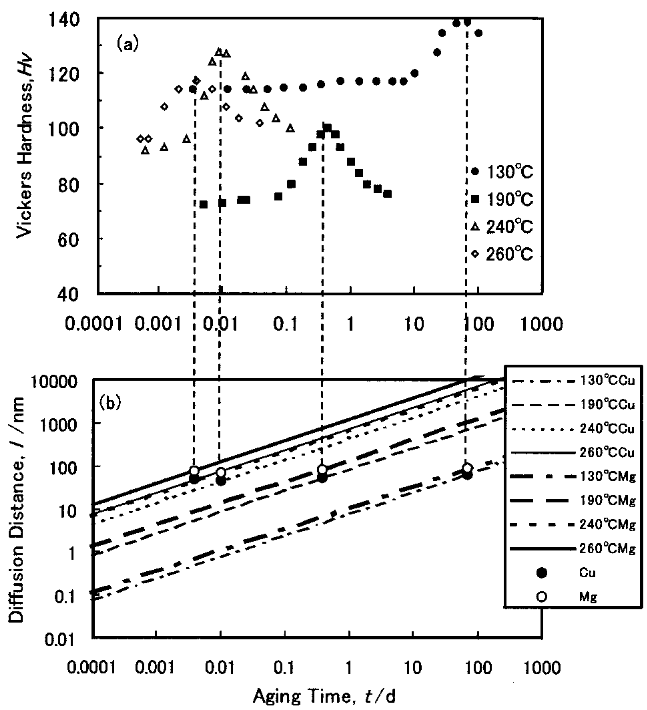

Fig. 5 Age-hardening curves and diffusion distances of Mg and Cu atoms for Al-3.15%Cu-0.52% Mg alloy. **(a)** Age-hardening curves at the indicated temperature; **(b)** diffusion distances of Cu and Mg atoms

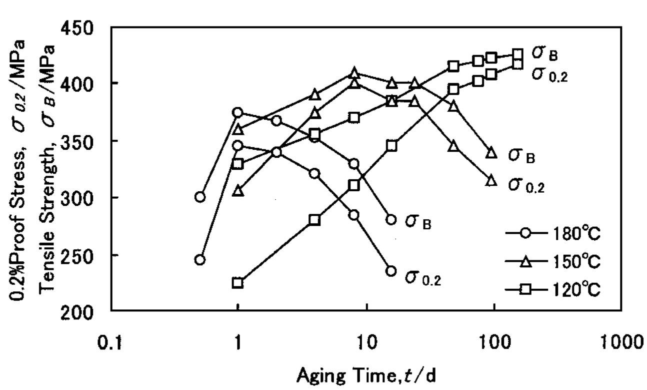

Fig. 6 Age-hardening curves of Al-6%Zn-1.5%Mg alloy

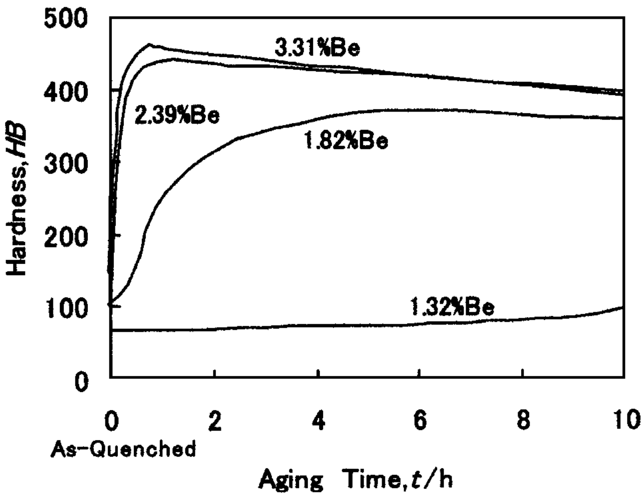

Fig. 7 Age-hardening curves at 350 °C of Cu-Be alloys with different Be contents quenched from 800 °C

Table 2 Diffusion Distances of Zn and Mg Atoms in Al-6%Zn-1.5%Mg Alloy Corresponding to the Maximum Hardness in Three Aging Curves

Aging Temperature, *T*/°C	Aging Time at Maximum Hardness, h	Diffusion Distance of Zn, nm	Diffusion Distance of Mg, nm
120	(100)	(42)	(13)
150	10	47	17
180	1	45	19

Table 3 Diffusion Distances of Be Atoms Corresponding to the Maximum Hardness in the Aging Curves of Four Cu-Be Alloys

Be Concentration, mass %	Aging Time at Maximum Hardness, h	Diffusion Distance of Be, nm
1.32	…	…
1.82	6	7
2.39	1	3
3.31	1	3

7. Age Hardening and Diffusion Distance of Al-Zn-Mg Alloys

Figure 6 shows the age hardening curves of Al-6%Zn-1.5%Mg alloy at the aging temperature ranging from 120-180 °C.[7] Diffusion distances of Zn and Mg atoms corresponding to the maximum hardness points at each aging temperature are shown in Table 2. Diffusion distances at 120 °C aging are obscure because clear maximum hardness points are not obtained. In both cases of 150 and 180 °C aging, diffusion distances of Zn atom are commonly 50 nm and those of Mg atoms are commonly 20 nm. The composition of precipitates is supposed to be $MgZn_2$ and it is consistent from the viewpoint of diffusion distance.

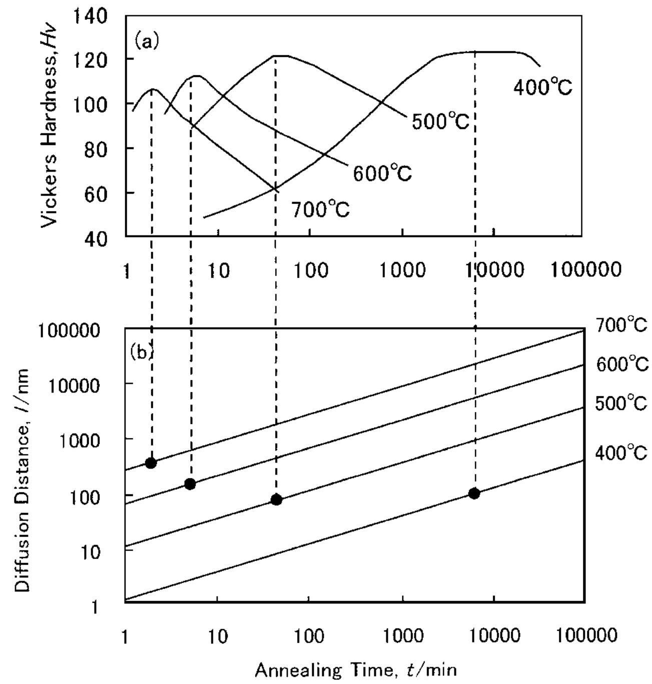

Fig. 8 Age-hardening curves and diffusion distances of Cr atoms for Cu-0.6%Cr alloy. **(a)** Age-hardening curves at the indicated temperatures; **(b)** diffusion distances of Cr atoms

8. Age Hardening and Diffusion Distance of Cu-Be alloys

Figure 7 shows the aging curves of Cu-Be alloys containing from 1.32-3.31% Be aged at 350 °C.[8] Table 3 shows the diffusion distances that are obtained from the maximum hardness points of each Be content. From this result, it is recognized that in Cu-Be alloys the maximum hardness is obtained at the diffusion distance of only a few nanometers. It shows that γ intermediate phase particles with the composition of CuBe are finely dispersed in the matrix.

9. Age Hardening and Diffusion Distance of Cu-Cr Alloys

Figure 8(a) shows age hardening curves of Cu-0.6%Cr alloy aged at the temperature ranging from 400-700 °C.[9] Straight lines in Fig. 8(b) show the diffusion distances at each aging temperature and diffusion distances corresponding to each maximum hardness point are plotted on these straight lines. Diffusion distances corresponding to the maximum hardness point distribute around 100 nm. These diffusion distances are much longer than those of Cu-Be alloys.

10. Age Hardening and Diffusion Distance of Cu-Ti Alloys

Figure 9 shows age hardening curves of Cu-5.8%Ti alloy aged at the temperature ranging from 204-538 °C.[10] The aging

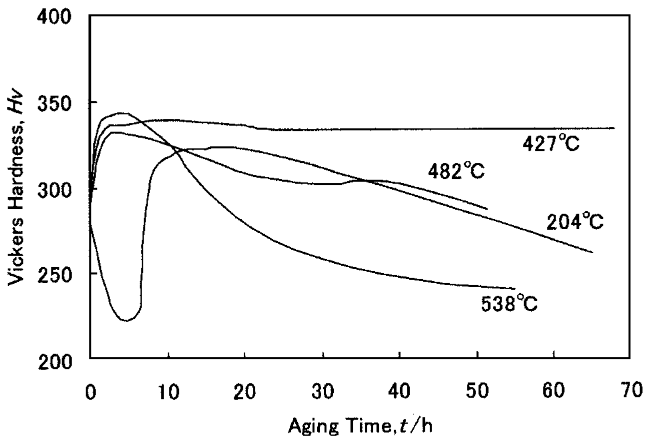

Fig. 9 Age-hardening curves of Cu-5.8%Ti alloy

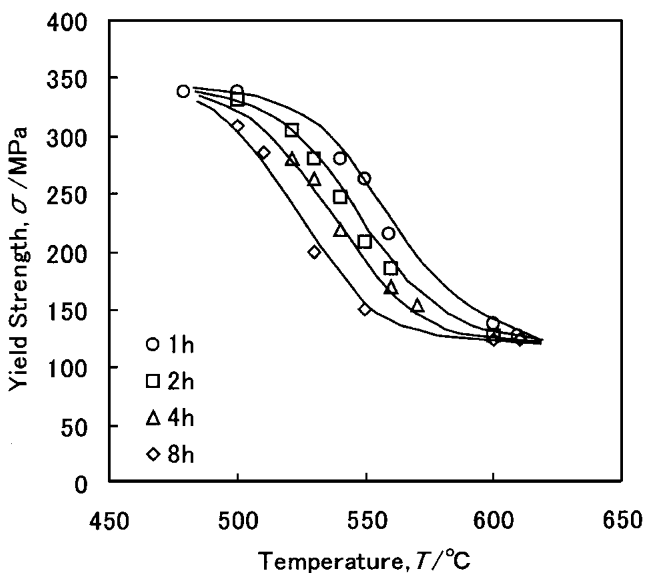

Fig. 10 Dependence of the 400 °C yield strength of Zircaloy-4 cladding tubes cold worked by 63.4% on annealing temperature

curves are a little more complicated than those of Cu-Be and Cu-Cr alloys; Table 4 shows the diffusion distances obtained from the maximum hardness point at each age hardening curve.

The diffusion distance at 204 °C aging is extremely small, less than 1 nm, and it is considered that such a small diffusion distance owes to a special case of aging such as the formation of GP zone. Moreover, at higher aging temperatures, the diffusion distance increases as the aging temperature increases, which is different from the cases of other alloys mentioned above. It is considered that the precipitation mechanism varies with aging temperature and it leads to the variation of diffusion distance.

11. Critical Diffusion Distance and Its Meaning

From the results above, it is supposed that if the material is fixed, any metallurgical phenomenon occurs at the fixed dif-

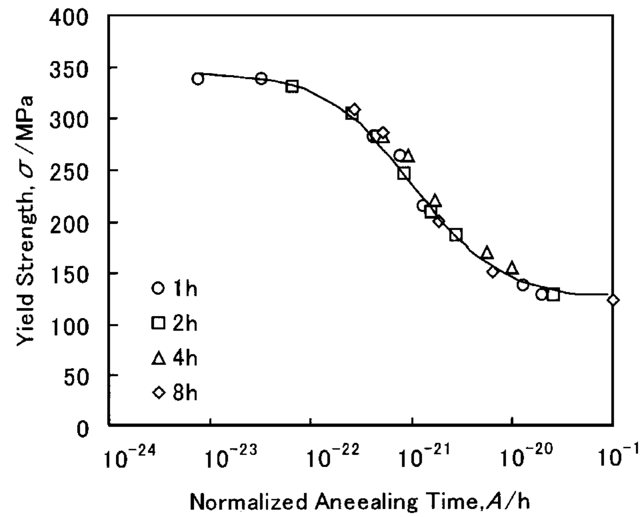

Fig. 11 Dependence of the 400 °C yield strength on the normalized annealing time, *A*, corresponding to Fig. 10

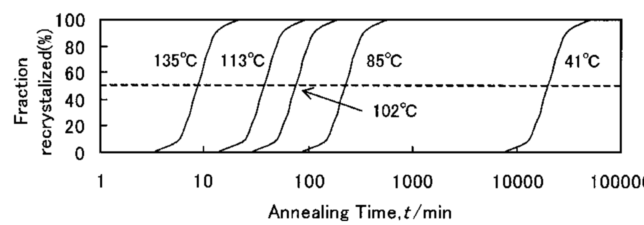

Fig. 12 Isothermal recrystallization curves of high purity Cu cold-worked by 98%[12]

Table 4 Diffusion Distances of Ti Atoms in a Cu-5.8%Ti Alloy Corresponding to the Maximum Hardness in the Aging Curves

Aging Temperature, *T*/°C	Aging Time at Maximum Hardness, h	Maximum Hardness, *Hv*	Diffusion Distance of Ti, nm
204	15	320	0.0358
427	10	340	77
482	4	330	165
538	4	340	486

fusion distance of the constituent atoms, corresponding to the phenomenon. This diffusion distance can be called the "critical diffusion distance" peculiar to each phenomenon.

The square of diffusion distance is expressed as follows:

$$l^2 = Dt = D_0 \exp\left(-\frac{Q}{RT}\right) \cdot t$$

The term

$$\exp\left(-\frac{Q}{RT}\right) \cdot t$$

is Sherby-Dorn parameter, which is empirically defined and also referred to as "normalized annealing time A."[11]

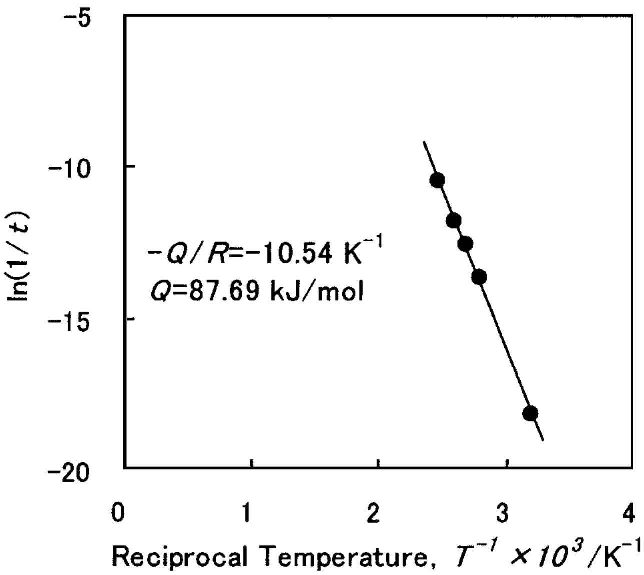

Fig. 13 Relation between ln (1/*t*) and reciprocal temperature, where *t* is the annealing time in minute needed for fraction recrystallized of 50% in Fig. 12, and *T* is the annealing temperature in Kelvin

Figure 10 shows the annealing curves of 400 °C yield strength of Zircaloy as a parameter of time. Using normalized annealing time A, annealing curves are summarized into one curve as is shown in Fig. 11.

In this way, from the equation above, empirically used normalized annealing time turns out to mean the diffusion distance of the alloying elements in Zircaloy. Namely, heat treatment responses in metals and alloys can be described in terms of diffusion distance uniformly through metals and alloys.

Until now, diffusion distances at recovery, grain growth, and age hardening were obtained from the known diffusion data, but inversely now activation energy Q will be obtained from the diffusion distances as follows.

Figure 12 shows isothermal recrystallization curves of high purity copper.[12] In this case also, for instance, the diffusion distances at 50% recrystallization can be assumed equal throughout any temperatures.

Namely,

$$\sqrt{Dt} = k = const.$$

and

$$Dt = k^2$$

$$D_0 \exp\left(-\frac{Q}{RT}\right) \cdot t = k^2$$

therefore

$$\exp\left(-\frac{Q}{RT}\right) = \frac{k^2}{D_0}\frac{1}{t}$$

$$-\frac{Q}{RT} = \ln\frac{k^2}{D_0} + \ln\frac{1}{t}$$

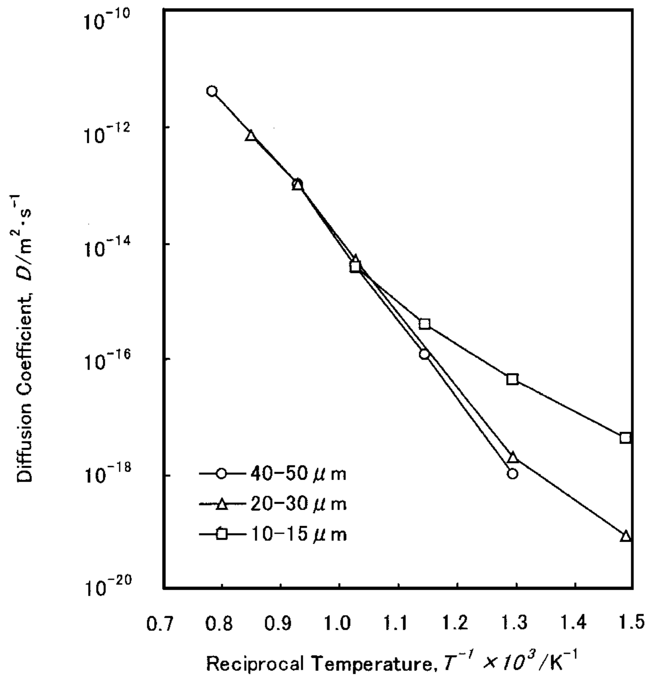

Fig. 14 Self-diffusion coefficient of Cu with different grain sizes obtained from sintering data

By reading the annealing times at 50% recrystallization rate at each annealing temperature and plotting 1/*t* versus 1/*T* from each time and temperature, Fig. 13 was obtained. Every point falls well on the same straight line, so the equation above is proven to be valid.

The value of activation energy *Q* that is obtained from the slope of the line in Fig. 13 is 86 kJ/mol. This value is smaller than the nominal one of the self-diffusion of Cu atom (211 kJ/mol). But as is shown in Fig. 14, it is noted that the self-diffusion of Cu increases remarkably at lower temperatures.[13] The values of self-diffusion data obtained from the diffusion coefficients ranging from 400-700 °C for the grain size 10-15 μm in Fig. 14 are 90.7kJ/mol as *Q* and 7.7×10^{-11} m^2/s as D_0.

This value of *Q* coincides well with the one obtained from the recrystallization curves of Fig.12.

12. Conclusions

Diffusion distances of constituent atoms at recovery, recrystallization, grain growth, and aging in Al and Cu alloys were examined. As a result, it was found that these phenomena take place at the fixed diffusion distances peculiar to the materials and phenomena.

It has been proven that the values of diffusion distances take approximately 10 nm for recovery, 20 nm for the fine grain recrystallization of 10 μm grain size, 1000 nm for the coarse grain recrystallization of 100 μm grain size, 100 nm for the most age hardening with the exception of 10 nm for the peculiar alloys.

These diffusion distances can be called the "critical diffusion distance" peculiar to material and phenomenon. Therefore, the relation between time and temperature in the metallurgical phenomena such as recovery, recrystallization, grain growth, and aging is to be decided by the values of critical diffusion distances.

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