Influence of Structural Modulation on the Yield Stress of Copper-5at% Titanium Alloy*

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The growth of the modulated structure during isothermal aging and the influence of the growth on the yield stress of aged Cu-5 at% Ti alloy was investigated. The wave lengths and amplitudes of the modulated structure were obtained from angular distances between the side band and the matrix reflections and from the ratio of reflection intensities of the side band to the main reflection, respectively. The results obtained are as follows : (1) In the early stages of aging, Cu-5 at% Ti alloys have a modulated structure, the wave length and the amplitude of which increase continuously with aging. (2) Experimental results of the yield stresses of the alloys in the early stages of aging seem to support Cahn's theory based on an interaction between a dislocation and the sinusoidal internal stress fields due to the compositional modulation. In the later stages of the structural modulation, the yield stress is smaller than Cahn's theoretical values. This disagreement is considered to be caused by the change of the structure from the sinusoidal to rectangular distributions.

(Received October 26, 1970)

I. Introduction

In our understanding of the decomposition of super-saturated solid solutions, there have been two types ; nucleation-growth and spinodal decomposition⁽¹⁾. Age-hardening of the former alloys containing precipitates have been investigated by many workers^{(2)~(4)} and the mechanisms of strengthening have become clear. There have been, however, very few reports on mechanical properties of the alloys containing structural modulation which may be formed by a spinodal decomposition^{(1) (5)~(7)}.

Cahn⁽⁷⁾ obtained theoretically the yield stress of a modulated structure alloy from the interaction between a dislocation and an internal stress field due to periodic distribution of solute atoms in the matrix. Israel et al.⁽⁸⁾ investigated experimentally the influence of amplitudes on the yield stress for a Ni-Ti alloy, and Carpenter⁽⁹⁾ made an attempt to explain the relationship between age-hardening and wave lengths of modulated structures in Au-Pt alloys. It has been known that the wave length and the amplitude of the modulated structure in many alloys increase simultaneously during aging⁽¹⁾. Therefore, these investigations are thought to be not adequate to explain the hardening mechanism of the alloys because of the negligence of the concurrent influence of the wave length and the amplitude on the yield stress.

In the present work, the influence of the wave lengths and the amplitudes, obtained from profile analysis of side bands, on the yield stress of a Cu-5 at% Ti alloy of the modulated structure are investigated.

II. Experimental Method

Cu-4.7 at% Ti alloy, prepared from 99.99% copper and 99.8% sponge titanium powder in a vacuum induction furnace, were annealed at 890°C for 10 hr, and forged, rolled to 0.3 mm in thickness or drawn to 0.55 mm in diameter at room temperature. The specimens

Fig. 1 Cu-Ti phase diagram. Full line after Saito et al.⁽¹⁰⁾ and dotted line after Saarivirta et al.⁽¹¹⁾

- * This paper was originally published in Japanese in J. Japan Inst. Metals, **34** (1970), 1184.
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were aged at temperatures ranging from 350° to 450°C in vacuum (10^{-4}) after being homogenized at 890°C for 3hr and drop-quenched in ice brine. Figure 1 shows a Cu-Ti phase diagram. The Ti content in the specimen was determined from a lattice constant, 3.637 Å, of the super-saturated solid solution, using a relationship between the lattice constant and the concentration of Ti in Cu-Ti solid solution (Fig. 2). X-ray diffraction analysis was carried out on the following condition; X-ray: CuK α , voltage: 40kV, current: 20mA, scanning speed: 1°/16/min, receiving slit: 0.1mm, and the G-M counter. Tensile testing was carried out at room temperature at a strain rate of 1.7×10^{-4} /sec. 0.01% strain proof stress was used as the yield stress.

Fig. 2 Copper solid solution lattice spacing as a function of composition at room temperature.
 Δ : Trzebiatowski et al. ⁽¹²⁾ $\blacktriangle$: Simon ⁽¹³⁾
 $\circ$: Segmüller ⁽¹⁴⁾ $\bullet$: Heubner et al. ⁽¹⁵⁾

III. Experimental Results and Discussion

1. Structural changes in aging

Figure 3 shows several X-ray diffraction profiles (200) of Cu-5at% Ti alloys aged at 450°C for various times.

Fig. 3 X-ray diffraction patterns of Cu-5at% Ti alloys quenched and aged at 450°C for various times.

An alloy in the as-quenched state shows sharp X-ray diffraction profiles taken from a face-centred cubic lattice as shown in (a), but the alloy aged at 450°C for 100min shows weak diffraction peaks on both sides of the matrix main peak, that is to say "side band" (b). It is considered that the Cu-5at% Ti alloy in this stage of aging have a "modulated structure" because the appearance of the side band is caused by the modulation of the lattice spacing due to the periodic distribution of solute atoms in a solid solution ^{(16)~(20)}.

With the advance of aging, the diffraction angles of the side bands move towards the main peaks continuously and the intensities increase. On further aging, the side bands become extinct and weak diffraction peaks appear on the low angle side of the main peaks as shown in (c). This indicates that the Ti rich region in the modulated structure changes to an intermediate phase. Finally, diffraction peaks of a stable precipitate, Cu₃Ti(hcp), is recognized (d).

(1) Wave length of the modulated structure

Side bands of Cu-5at% Ti alloys aged at 400°C for various times are shown in Fig. 4. The wave length of the modulated structure is calculated from the difference of diffraction angle, $\Delta\theta$, between the main peak and the side band. According to Daniel and Lipson ⁽¹⁶⁾, the wave length in unit cell, Q , of the modulated structure, in which solute atoms are sinusoidally distributed, is given by the equation

$$Q = \frac{h \tan \theta}{\Delta\theta(h^2 + k^2 + l^2)} \quad (1)$$

where θ is the Bragg angle of the main peak and h, k, l are the Miller indices of the peak. The calculations were carried on the (200) peaks. Diffraction theory ⁽¹⁶⁾ suggests the appearance of a sharp reflection peak of a side band, but the side bands obtained experimentally have a considerable breadth as shown in Fig. 4.

Fig. 4 (200) side bands of Cu-Ti alloys aged at 400°C for various times.

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This contradiction may be caused by the existence of various wave lengths in the actual alloy. Figure 5 shows growth of the wave lengths for the Cu-5at% Ti alloy aged at 350°~450°C for various times. The higher the aging temperature, the wave lengths increase faster. The wave length of the Cu-5at% Ti alloy aged for 3 hr at 450°C is about 230 Å as shown in Fig. 5, and this length is nearly equal to a wave length 250 Å in a Cu-4at% Ti alloy aged at 450°C for 3 hr, obtained from the transmission electron microscopic observation by Saito et al.⁽¹⁰⁾

As slopes of the straight lines in Fig. 5 are 1/4, the wave lengths are proportional to $t^{1/4}$. Figure 6 shows wave lengths as a function of the quarter power of the aging time, $t^{1/4}$. The three straight lines converge on

Fig. 5 Logarithmic plot of growth of wave length.

Fig. 6 Wave length of modulated structure in Cu-5at% Ti alloy as a function of $t^{1/4}$.

the wave length, zero. The growth of wave lengths can often be expressed as follows^{(21)~(24)}:

$$L^m - L_0^m = K(t - t_0) \quad (2)$$

L is the wave length of a modulated structure after aging, L_0 is the initial wave length, t is aging time and m , K are constants. When precipitates coagulate on a

mechanism of the Ostwald growth, that is, small precipitate-particles dissolve into the matrix to reprecipitate on large precipitate particles, the rate of growth is said to be proportional to $t^{1/3}$ ⁽²⁵⁾. Whereas in a spinodally decomposed alloy such as Au-Pt alloy, the values of m are not constant. For instance, the values of m in the Au-Pt alloy⁽²³⁾ change from 3.2 to 9.3 with a variation of Pt content in the alloy. The growth rate of the wave length in Cu-5at% Ti alloy is slower than that of the Ostwald growth.

The activation energy for the growth of the modulated structure, calculated from the relation between aging time up to 30, 40 and 50 unit cells of the wave length and reciprocal aging temperature is 39.2 kcal/mol. This value is equal to an energy calculated from the growth rate of the amplitude of the modulated structure as mentioned later.

(2) Amplitude of the modulated structure

According to Guinier⁽²⁶⁾, fluctuations of the X-ray scattering factor, f_n , and the displacement of the lattice point, x_n , due to the sinusoidally structural modulation are given by eqs. (3a) and (3b), respectively.

$$f_n = f[1 + g \sin(2\pi na/L)] \quad (3a)$$

$$x_n = na - (Ld/2\pi) \cos(2\pi na/L) \quad (3b)$$

where L is a wave length in units of Å, d is an amplitude of a lattice constant, f is X-ray scattering factor of the super saturated solid solution, and fg is an amplitude of X-ray scattering factor in a modulated structure. From these equations, if ghd/a^2 is much smaller than 1 (h : the largest index in Miller indices of the main peak), the ratio of diffraction intensities of the side band, $I_{h \pm a/L}$, to the main peak, I_h , are given in eq. (4).

$$I_h : I_{h \pm a/L} = 1 : [g/2 \pm (Ld/2a^2)(h \mp a/L)]^2 \quad (4)$$

The largest value of ghd/a^2 in the present work is 4×10^{-3} for the alloy aged at 450°C for 500 min. If fluctuations of the X-ray scattering factor and the lattice constant are assumed to be proportional to the concentration of solute atoms in a solid solution*, g and d are shown as follows:

$$g = -(f_a - f_b)A(c)/100f \quad (5)$$

$$d = KA(c) \quad (6)$$

where f_a and f_b are the X-ray scattering factors of solvent, a and solute, b , respectively. $A(c)$ is the amplitude of compositional modulation (atomic percentage) and K is a constant. Substituting eqs. (5) and (6) for (4), the ratio of the diffraction intensities, I_s , of the side band to the main peak are given in eq. (7).

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* The increment of the lattice constant are proportional to Ti at% as shown in Fig. 2, and the influence of the Cu-Ti atom pair on the X-ray scattering intensity is neglected, because the atomic numbers of Cu and Ti are in close proximity. Further, changes of $\sin\theta/\lambda$ (λ : X-ray wave length) due to the phase modulation of the lattice spacing are small enough to be neglected.

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$$I_s = I_{h \mp a/L} / I_h = [A(c)^2 / 4] \{ - (f_a - f_b) / 100f \pm (L/a^2) K (h \mp a/L)^2 \} \quad (7)$$

Replacing L by Qa (Q : wave length in unit cell, a : lattice constant),

$$A(c) = \frac{2 \sqrt{I_s}}{-(f_a - f_b) / 100f \pm (Q/a) K (h \mp 1/Q)} \quad (8)$$

The amplitude of the lattice constant, d , is given from the Ti concentration-dependence of the lattice constant (Fig. 2).

$$d = 4.44 \times 10^{-3} A(c).$$

g is given from the X-ray scattering factors of Cu and Ti atoms:

$$g = -2.85 \times 10^{-3} A(c).$$

Therefore, eq. (8) is rewritten to the equation

$$A(\text{\AA}) = 3.638 \sqrt{I_s} / (Q - 1.67). \quad (9)$$

In eq. (9), the amplitude of the lattice modulation, $A(\text{\AA})$, is used instead of the amplitude of the compositional modulation, $A(c)$.

Figure 7 shows the amplitudes of the modulated structure, $A(\text{\AA})$, calculated from the ratios of the intensities of the Cu-5at% Ti alloy aged at 350°, 400° and 450°C. Slopes of the straight lines are about 1/4, that is, A is proportional to $t^{1/4}$. Figure 8 shows the relationship between the amplitudes and $t^{1/4}$. Three straight lines converge on the zero amplitude in the same way as in

Fig. 7 Amplitudes of modulated structures for Cu-5at% Ti alloys aged at 350°~450°C for various times.

Fig. 8 Plot of the amplitude against $t^{1/4}$.

case of the wave length shown in Fig. 5. Therefore, the growth of both of the wave length and the amplitude start from a very small size.

If the solute rich region in the modulated structure transforms to the intermediate phase continuously, the maximum amplitude obtained experimentally should be equal to the difference of the lattice constant between the intermediate phase and the super-saturated solid solution. The experimentally obtained maximum amplitude is 0.027 Å as shown in Fig. 7. This value is nearly equal to the difference of the lattice constant, 0.030 Å, between the super-saturated solid solution, 3.637 Å and the intermediate phase, 3.667 Å, as shown in Fig. 11. Therefore, it is considered that the rich regions change to the intermediate phase, when the amplitude of the modulated structure reach 0.027~0.030 Å.

An activation energy for growth of the modulated structure, calculated from the relation between the aging time up to 0.023 Å of the amplitude and the reciprocal aging temperature, is 39.3 kcal/mole, which is equal to the activation energy, calculated from the growth of the wave length as mentioned above. Although the activation energy for the diffusion of Ti in Cu-Ti solid solution has not been investigated, this value may be equal to an activation energy for the diffusion of Ti in Cu-Ti solid solution, because the activation energies for the diffusion of various atoms in Cu are 38~46 kcal/mol.

(3) Relation between yield stress and structural modulation

The yield stress (0.01% strain proof stress) for Cu-5 at% Ti alloy aged at 350°~450°C for various times are shown in Fig. 9. Increments of the hardness in the early stages of aging are thought to be due to the structural modulation, because only the side bands are observed in the stages.

Theoretical analysis of the yield stress has been carried out by Cahn⁽⁷⁾. A sinusoidal distribution of solute atoms in a modulated structure is given as follows:

$$C - C_0 = A(L) \sin(2\pi x/L). \quad (10)$$

Fig. 9 Changes of yield strength with aging time.

Here, C is concentration of solute atoms in the modulated structure, C_0 is average concentration of solute atoms, $A(L)$ is the amplitude of the modulation when the wave length is L , and x is the distance along $\langle 100 \rangle$. A dislocation in the modulated structure receives a force shown in an eq. (11), calculated from the internal stresses due to the sinusoidal distribution of solute atoms.

$$\sigma b n = \frac{\sqrt{2/3} A \epsilon b E \sin(2\pi y') / \sqrt{6} L}{\sin(2\pi x' / \sqrt{2} L)} \quad (11)$$

where σ is internal stress, n is unit vector, E is Young's modulus, $\epsilon = (1/a)(da/dc)$ (a is lattice constant), and x' and y' are the distances along $[1\bar{1}0]$ and $[112]$ respectively. Resolving eq. (11), the yield stress is given by eq. (12), when $A\epsilon EL/2\pi T$ is smaller than 1 (T : line tension of a dislocation), that is, a dislocation shears the stress field.

$$\tau = (A^2 \epsilon^2 E^2 L b) / (6 \sqrt{6} \pi T) \text{ for a screw dislocation,} \quad (12a)$$

$$\tau = (A^2 \epsilon^2 E^2 L b) / (2 \sqrt{2} \pi T) \text{ for an edge dislocation.} \quad (12b)$$

Figure 10 shows the change in the yield stress (0.01% proof stress) as a function of $A^2 L$. In the present work

Fig. 10 Relation between $A^2\lambda$ and yield strength for Cu-5at% Ti alloys. Full lines are given by Cahn's equations.

all $A\epsilon EL/2\pi T$ are smaller than 1 in the range of aging time. Two straight lines show Cahn's theoretical values. As shown in Fig. 10, experimental yield stresses increase parabolically against $A^2 L$. The yield stress in the early stages are nearly equal to the theoretical value predicted by Cahn. Therefore, it is considered that the experimental results in the early stages of aging support the Cahn's sinusoidal model. But in the later stages of structural modulation, especially over 45~50 unit cells of the wave length, the yield stress increases very slowly. The amplitude of the lattice modulation on the 45 unit cells of the wave length is 0.019 Å. As the increment of the lattice constant of Cu-Ti solid solution is 4.44×10^{-3} Å per at%Ti, the amplitude 0.019 Å corresponds to 4.2 at% Ti of the compositional amplitude. Therefore,

the Ti concentration of the Ti rich region is 8.9 at% Ti and that of the poor region is 0.5 at% Ti, because the average concentration of Ti in this alloy is 4.7 at% Ti. This concentrations of Ti in the poor region is nearly equal to the solubility limit of Ti into a Cu solid solution at aging temperatures 350°~450°C on the Cu-Ti phase diagram shown in Fig. 1. Therefore, the amplitudes are thought to be able to grow symmetrically in the Ti rich and poor regions until the wave length of the modulated structure reaches the 45 unit cell. After this aging time, however, the amplitude in the Ti poor region grows no longer and the increment of the amplitudes goes on only in the rich regions. Consequently, the sinusoidal distributions of Ti atoms tend to change to a rectangular distribution as reported by Guinier⁽¹⁹⁾. The validity of this consideration can also be inferred from the lattice constants of the intermediate phase and the matrix phase. The lattice constants of the intermediate phase and the matrix are 3.667 Å and 3.618 Å respectively, as shown in Fig. 11, corresponding to the concentrations of 11.5 at% Ti and 0.45 at% Ti respectively. These values are asymmetrical to the average concentration of Ti (4.7 at% Ti). It is considered that an asymmetrical distribution of Ti atoms in the alloy containing the intermediate phase also occurs on the modulated structure of the later stages, since the Ti-rich regions change to the intermediate phase continuously⁽²⁷⁾.

Fig. 11 The relation between $\sin^2\theta$ and lattice constants for Cu-5at% Ti alloys quenched and aged.

It may be necessary to investigate whether the experimental values of the amplitude of the modulated structure of the later stages are reliable or not, because eq. (9) should be applied to the side bands for the alloys containing the sinusoidal distribution of the solute atoms. The amplitudes obtained experimentally, however, are considered to be reliable from the fact that the yield stress is plotted on an extension line of the experimental values (Fig. 10) shown as a function of the product of the wave length and the square of the amplitude which is obtained from the lattice constant without application of eq. (9).

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Ti atoms necessary to increase the amplitude in the Ti rich region of the later stages of aging must be sought from skirts of the rich regions, because the concentration of Ti in the poor region decreases no longer. Therefore, in the later stages the volume fraction of Ti rich regions should decrease with increasing amplitude. The yield stress of the alloy, of which the compositional distribution of solute atoms is rectangular, has been explained by Mott-Nabarro's stress field theory⁽²⁸⁾ or Kelly-Nicholson's interfacial energy theory⁽²⁹⁾. In these theories yield stress is shown as a function of the volume fraction of the precipitates. Therefore, it is most likely that the yield stresses of Cu-5at% Ti alloy in the later stages should decrease with aging, as viewed these phenomena from the standpoint of the volume fraction in the Ti rich region. However, the yield stress of the actual alloy increases slightly as shown in Fig. 10. It is considered that this decrement of the yield stress is supplemented by an increment of the interfacial energy between the Ti rich region and the matrix and of the shear modulus in the Ti-rich region with the advance of aging.

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IV. Conclusions

The growth of the wave length and amplitude of the modulated structure during isothermal aging and the influence of the growth on the yield stress of aged Cu-5at% Ti alloy were investigated by the X-ray diffraction method and the tensile test.

The results obtained are as follows :

(1) In early stages of aging, Cu-5at% Ti alloys have a modulated structure, the wave length and the amplitude of which increase continuously with the advance of aging.

(2) The yield stress of the alloy in the early stages of aging increase at a rate nearly proportional to the product of the wave length and the square of the amplitude, $\lambda^2 L$. Therefore, experimental results seem to support Cahn's theory based on the interaction between a dislocation and the sinusoidal internal stress field due to the compositional modulation. In the later stages of the structural modulation, however, the yield stress is lower than Cahn's theoretical values. This disagreement is considered to be caused by the change of the structure from a sinusoidal to a rectangular distribution of the solute atoms.

Acknowledgment

The authors are indebted to Mr. M. Niwa for his continued cooperation in the experimental work.