Influence of Structural Modulation on Yield Strength of Ni-10 at. % Ti Alloy.

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The isothermal growth of the modulated structure and the structural dependence for the yield stress of aged Ni-10 at. % Ti alloy were investigated with X-ray diffraction method and tensile test. The results obtained are as follows: (1) In early stage of aging, Ni-10 at. % Ti alloys have the modulated structures, the wave length and the amplitude of which increase continously with aging. (2) The growth of the modulated structures in Ni-10 at. % Ti alloys are controlled by the rate of diffusion of Ti in Ni-Ti solid solution. (3) Experimental results of the yield stresses of the alloys in early stage of aging seem to support Cahn's theory, in which the yield stress is given by an interaction between a dislocation and the periodic internal stress field due to the compositional modulation give the strength.

1. Introduction

There have been few reports⁽²⁾ on relation between the mechanical properties and the structural modulation of Ni-Ti alloy, concentrations of Ti in the solid solution of which change periodically⁽¹⁻⁴⁾.

Cahn⁽⁵⁾ researched theoretically a yield stress of a modulated structure alloy from an interaction between a dislocation and and an internal stress field due to a periodic distribution of solute atoms. According to this theory, the yield stress of the modulated structure alloy is proportional to a wave length and a square of an amplitude of the modulation if a dislocation cut through the strain field in the alloy.

Ben Israel et al⁽³⁾ investgated experimentally an influence of the amplitude obtained from Curei-point on the yield strength of Ni-10 at. % Ti alloy. Carpenter⁽¹⁾ attempted an explanation of a relationship between age-hardening and wave length, obtained from side bands of X-ray diffraction, of the modulated structures in aged Au-Pt alloys. These investigtions, however, may be not enough to explain the age-hardening mechanism of the alloys, since increments of the wave lengths and the amplitudes during aging are not independent.

In this present work, the wave length and the amplitudes are obtained experimentally from the profile analysis of X-ray diffraction and the influence of the both on the yield strength of Ni-10 at. % Ti alloys aged at 500~800°C are investigated.

2. Experimental methods

Ni-10 at. % Ti alloys, prepared from 99.9 % Nickel and 99.8 % sponge Titanium powder in a vacuum furnace, were forged, rolled to 1.5 mm in thickness and drawed to 0.55 mm in diameter. These specimens were aged at 500~800°C for various time after homoginized at 850°C for 1 hr and drop-quenched.

X-ray diffractions were carried out on condition as follows ; X-ray : CuKα, Voltage : 38 Kv, Current ;20 mA, Scanning speed : 1/16°/min., Receiving slit : 0.1 mm and G-M counter.

Tensile test was carried out at room temperature and the strain rate of tensile test was 1.7×10^{-4}/sec.

3. Experimental results

(1) Structural changes in aging

The structural changes of Ni-Ti alloy has been reported already⁽²,³,⁶⁾. The super-saturated solid solution of the alloy was decomposed to two phases ; a Ti rich zone and a poor zone in early stage of aging. The Ti rich zone transform to a meta-stable fcc Ni_3Ti phase continously and finally to a stable intermetallic compound, hcp Ni_3Ti phase, while the Ti poor zone become the matrix phase.

In early stage of the aging for Ni-10 at. % Ti alloy, a satelite reflection, that is, a side band, was recognized⁽²⁾. It is considered that the Ni-10 at. % Ti alloy in this stage of aging have a"modulated structure", because appearence of the side band is caused by the modulation of the lattice spacing due to the periodic distribution of the solute atoms in the solid solution(7,8). Modulated structures were also recognized in the observaton by the transmission electron microscope(2,3).

Fig. 1 shows several X-ray diffraction profiles, (200) of Ni-10 at. % Ti alloys aged at 600°C for various time. The Ni-Ti alloys as-quenched shows a sharp X-ray reflection pattern taken from a face centred cubic lattice, while the alloys aged the weak diffraction peak on the each side of the main peak, that is, the side band. The side bands move towardes the main peak and these intensities increase with aging of the alloys as shown in Fig. 1.

On further aging, a diffraction peack of a fcc intermediate phase (lattice constant, 3.580 Å) appear on the low angle side of the main peak. This indicates that the modulated structure changs to the intermediate phase.

(a) Wave length of the modulated structure

The wave lengths of the structure are calculated from difference of diffraction angle, $\Delta\theta$, between the main peak and the side band. According to Daniel and Lipson(7), a wave length in unit cell, Q, of the modulated structure, in which solute atoms distribute in sinusoidal, is given as follow ;

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

, where θ is Bragg angle of the main peak and h, k, l are Miller indexs of the main peak. Eig. 2 shows changes of the wave length of the Ni-10.1 at. % and Ni-9.7 at. % Ti alloys aged at 550°C, 600°C and 650°C for various time. The wave lengths increase in proportional to 3rd power of aging time, $t^{1/3}$

(b) Amplitude of the modulation

Various types of the distribution of solute atoms in the modulated structure have been proporsed(7,8,9). In these, Daniel and Lipson(7) model, that is, the sinusoidal distribu-

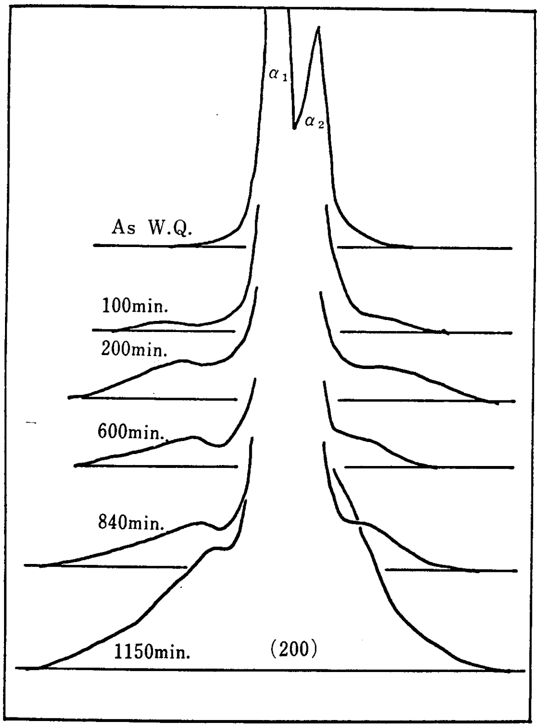

Fig. 1 X-ray diffraction patterns of Ni-10. 2 at. % Ti alloy quenched and annealed at 650°C for variuos time.

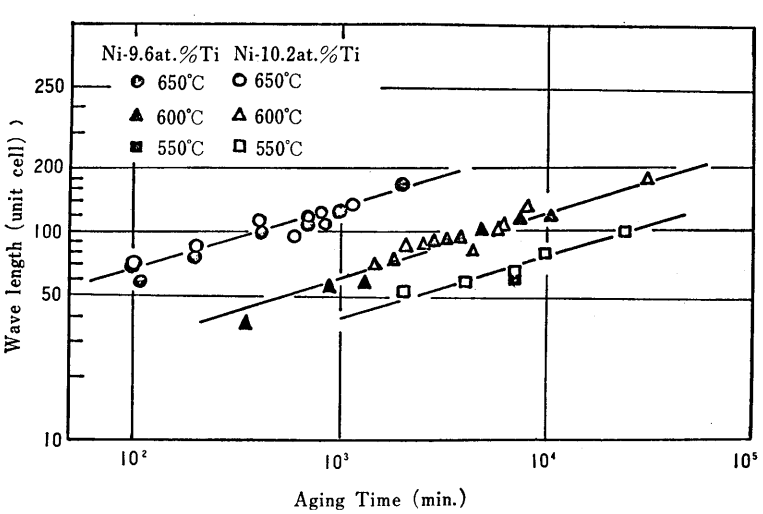

Fig. 2 Logarithmic plot of growth of wave length in modulated structure of Ni-10 at. % Ti alloy.

tion of the solute atoms, is said to be most suitable by many workers(10,11,13).

According to Guinier(13), the fluctuations of X-ray scattering factor, f_n, and of position of n atom, x_n, are given by (2a) and (2b).

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

$$x_n = na - (Ld/2\pi)\cos(2\pi ua/L) \qquad (2b)$$

L is a wave length in Å, d is an amplitude of the lattice constant and fg is an amplitude of X-ray scattering factor. From these equations, ratio of diffraction intensity, of a side band, $I_{h\mp a/L}$, to a main peak, I_h, are given as follow(13);

$$I_h : I_{h\mp a/L} = 1 : [g/2 \pm Ld(h \mp a/L)\ (2a^2)^{-1}]^2 \quad (3)$$

Assuming that the fluctuations of the X-ray scattering factor and the lattice constant are proportional to concentration of the solute atom in the solid solution, the amplitude of concentration, A(c), is given in an equation(4).

$$A(c) = \frac{-2\sqrt{I_S}}{-(f_{Ni} - f_{Ti})/100\,f + (Lg/a^2)(h - a/L)} \quad (4)$$

, where f_{Ni}, f_{Ti} and f are X-ray scattering factor of Ni, Ti and Ni-Ti alloy respectively. The amplitude of the modulated structure obtained from ratio of the intensities I_S in the Ni-10 at.% Ti alloys aged at 550°C,600°C

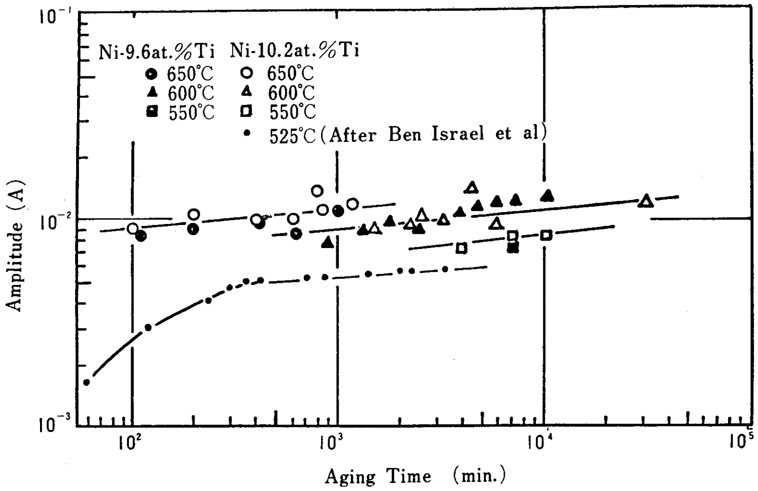

Fig. 3 Log-log plot of the amplitudes of the modulated structure against aging time.

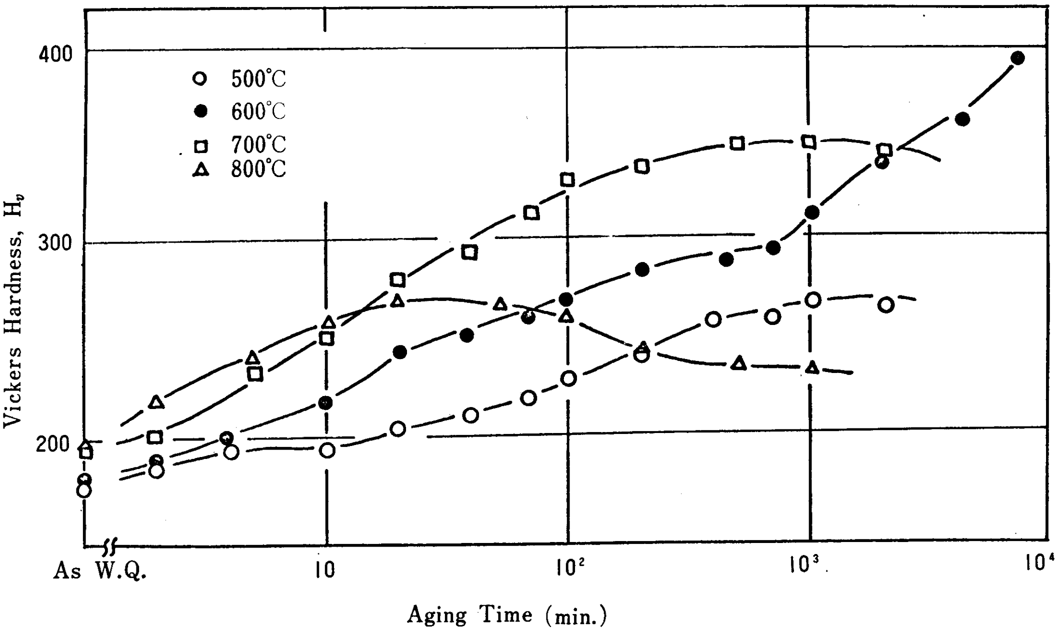

Fig. 4 Hardness change of Ni-10.2 t % Ti alloy with aging time.

and 650°C for various time are shown in Fig. 3. In Fig. 3, the fluctuation of the concentration of the solute atoms are not used, but the fluctuation of the lattice constant are used.

(2) Hardness

Fig. 4 shows change in Vicker's hardness of Ni-10.2 at. % Ti alloys during aging at 500~800°C for various time. Hardening in early stage of aging are due to the structural modulation, since in this stage only side bands are recognized. Softening on overaging is thought to be due to precipitation of a precipitates, η -phase(4,14).

(3) Yield stresses

The stress-strain curves of the Ni-10 at. % Ti alloys do not show clear yield phenomena such as yield dropping but a smooth parabola. The yield strengths of the aged alloys are considerably high in comparison of the as-quenched alloy, but the alloys are not brittle. Changes of the yield strength (0.1 % strain proof stress) with aging for Ni-9.6 at. % Ti alloys aged at 550, 600 and 650°C are shown in Fig. 5.

4. Disussion

(1) Structural modulation in early stage of aging.

It has not been evident that the formation-mechanism of the modulated structure is either a Nucleation-growth or a Spinodal decomposion, nevertheless there has been many reports in Cu-Ni-Fe,(12,15) Pt-Au(16) and Ni-Al(17) alloys.

Growth of the wave length is able to be indicated often as follow ;

$$L^m - L_0^m = K(t - t_0) \qquad (5)$$

· where L is the wave length of the modulated structure, t is aging time and m, K are constats. Slopes of the straight lines in Fig. 2 give m=3. Ardell et al(17) reported m=3 for growth of the wave length in Ni-6.7 wt. % Al modulated structure alloy. When the precipitates coagulate on a mechanism of Ostward growth(18,19,20), that is, small precipitate particles solute into the matrix and re-precipitate on the interface of large particles of the precipitates, the rate of growth are said to be proportional to $t^{1/3}$. Therefore, the growth of the modulated structure in this Ni-10 at. % Ti alloys in the present work may be also explained by the Ostward growth. There have been, however, many reports in which m is not equal to 3. For instance, Cu-5 at. % Ti alloy(21), of which aging processes are similiar to the Ni-10 at. % Ti alloy in the present work, shows m=3. In Au-Pt alloy(16), m is changed from3.2 to 9.3 with variation of Pt content. In Fe-Ni-Ti side band alloy(22), m is 2, and further there is a report(2) in which m is 6.6 for Ni-Ti alloy being same alloy-system in the present work. Therefore, it is thought to be too haste to conclude that a mechanism of growth of the modulated structure in Ni-10 at. % Ti alloy is the Ostward growth.

Fig. 6 shows changes of the wave lengths in Ni-10 at. % Ti alloys as a function of $t^{1/3}$. Three straight lines converge to the wave length, zero, and so it is anticipated that the critical size of the embryo is very small. These phenomenon is not contradictory to reports(2,3), in which Ni-Ti alloy decomposes

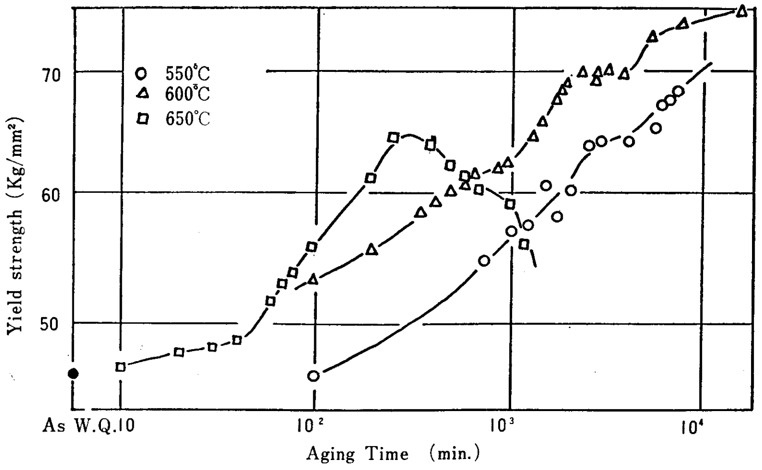

Fig. 5 Yield strength of Ni-9. 6 at. % Ti alloy aged at 550°C~650°C for variuos time.

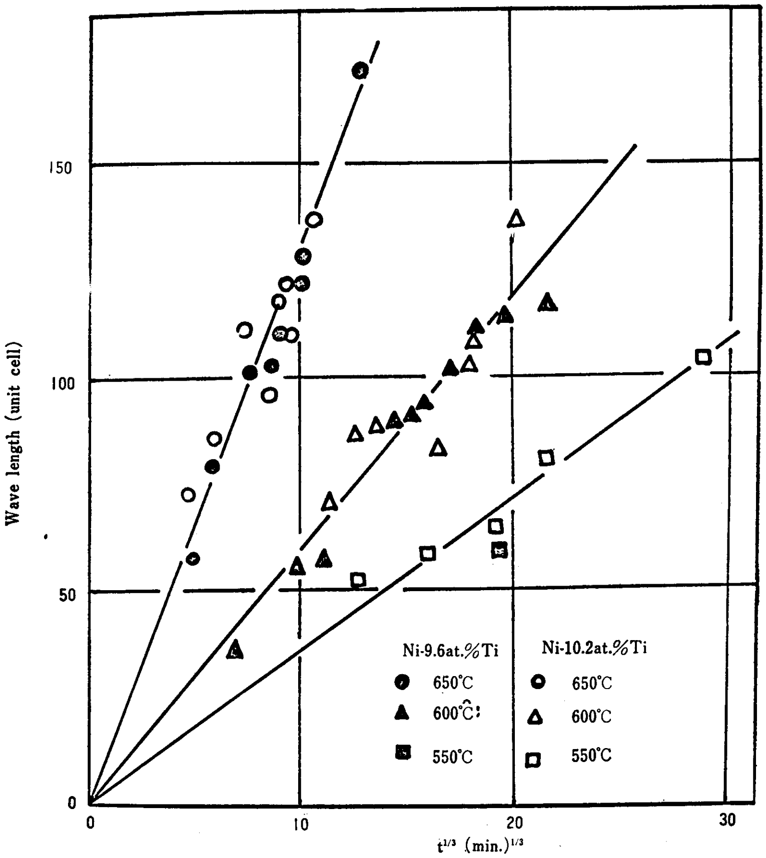

Fig. 6 Increment of wave lenght as a function of $t^{1/3}$.

spinodally to two phases.

Maximum amplitude obtained experimentally is 0.013 Å as shown in Fig. 3. This value is not equal to difference of lattice constant, 0.022 Å, between the super-saturated solid solution, 3.558 A, and the intermediate phase γ', 3.580 Å. Therefore, the maximum amplitude obtained experimentally does not reach to Ti concentration in γ' phase. In our investigation of Cu-5 at. % Ti alloy, the maximum amplitude obtained experimentally is about equal to the difference of the lattice constant between the super-saturated solid solution and the intermediate phase(21). Continous transition of the modulated structure to the intermediate phase in the Cu-5 at. % Ti alloy is able to be observed with X-ray diffraction method. In Ni-10 at. % Ti alloy of the present work, however, the growth of the amplitude of the structural modulation is slower than that of the wave length as shown in Fig. 2 and 3, and so that before the amplitude grow up to the Ti concentration of the intermediate phase, the wave length reach to the size on which the side bands are able not to be observed, because of overlaping of the side band and the main peak.

An activation energy, 61.4 Kcal/mol, for growth of wave length is calculated from the relation between aging time up to 100 unit cells of the wave length and reciprocal aging temerature. The energy for the growth of amplitude is also same values. These values are equal to the activation energy for the diffusion of Ti in Ni-Ti solution, 61.4 Kcal/mol obtained by Swalin et al(23) Therefore, the growth of the modulated structure is thought to be controlled by rate of the volume diffusion of Ti atoms.

(2) Structural modulation and yield stress

Age-hardening in early stage for Ni-10 at. % Ti alloys are due to the structural modulation. Theoretical analysis of the yield stress have come through Cahn(5), and experimental investigations have carried out by Ben Israel et al(3), and Carpenter(1), but these investigations supported to Cahn's theory insufficiently.

According to Cahn(5), sinusoidal distribution of solute atoms in a modulated structure is given as follw ;

$$C-C_0=A(L)\sin(2\pi x/L) \qquad (6)$$

, where C is concentration of solute atoms, C_0 is average concentration of solute atoms, A(L) is amplitude of the modulaiton when the wave length is L, and x is distance along <100>. A dislocation in a modulated structure experiences a force shown in equation (7) from the internal stresses due to the sinusoidal distribution of solute atoms.

$$\mathbf{b}\sigma\mathbf{n}=\sqrt{2/3}\ A\varepsilon bE\ \sin(2\pi y'/\sqrt{6}L)\sin \times(2\pi x'/\sqrt{2}L) \qquad (7)$$

, where σ is in internal stress, **n** is unit vector in the slip plane, **b** is a Burger's vector, E is a Young's modulus, $\varepsilon=(1/a)(da/dc)$ (a is a lattice constant), and x' and y' are distance along [110] and [112] respectively. Working out the equation(7), yield stress is given as an equation(8), when $A\varepsilon EL/2\pi T<1$ (T ; line tension of a dislocation), that is, a dislocation shear the stress field.

$$J=(A^2\varepsilon^2E^2Lb)/(6\sqrt{6}\pi T) \text{ for a screw dislocation,} \qquad (8\,a)$$

$$J=(A^2\varepsilon^2E^2Lb)/(2\sqrt{2\pi}T) \text{ for an edge dislocation.} \qquad (8\,b)$$

Fig. 7 shows changes of the yield stress (0.1 % proof stress) as a function of A^2L for Ni-10 at. % Ti alloy aged at 600°C for various time. The yield stresses are proportional to A^2L in short time of aging and the slope of the straight line is nearly equal to that of Cahn's theoretical. Therefore, it is considered that the experimental results in early stage of aging support Cahn's theory(5). In later stage, however, the experimental results do not support Cahn's theory. As shown in Fig. 7, The increment of the yield stresses are delayed on A^2L, 80~100 and after the 'delaying point' the yield stresses increase slowly. The amplitudes in the lattice modulation at the delaying point are 0.009~0.01 Å. As the lattice constant of Ni-Ti solid solution increase 3.33×10^{-3} Å with 1 at. % Ti, the amplitudes at the delaying point are 2.7 ~3.0 at. % Ti. Therefore, the concentration of Ti in the Ti rich region is 12.3~12.6 at. % Ti and in poor region is 6.6~6.9 at. % Ti, because average concentration of Ti in this alloy is 9.6 at. % Ti. This concentration of Ti in the poor region is nearly equal to the solibility limit of Ti in the Ni solid solution at aging temperature 550~650°C on the Ni-Ti phase diagram. Therefore, the amplitudes are able to grow symmetrically in the rich regions till the amplitudes reach to the delaying point. After the delaying point, however, the amplitudes in the poor region are able to grow no longer and the increment of amplitude keep on only in the rich region. Concequently the sinusoidal distribution of Ti atoms tend to chage a rectangular distribution. In this case, supplying of Ti atoms for increment of the amplitude in the rich region must be carried from the skirts of the rich regions because the concentration of Ti in the poor region decrease no longer. Therefore, volume fraction of the Ti rich region decrease with aging. Theories of yield stress for this case, have been reported by many

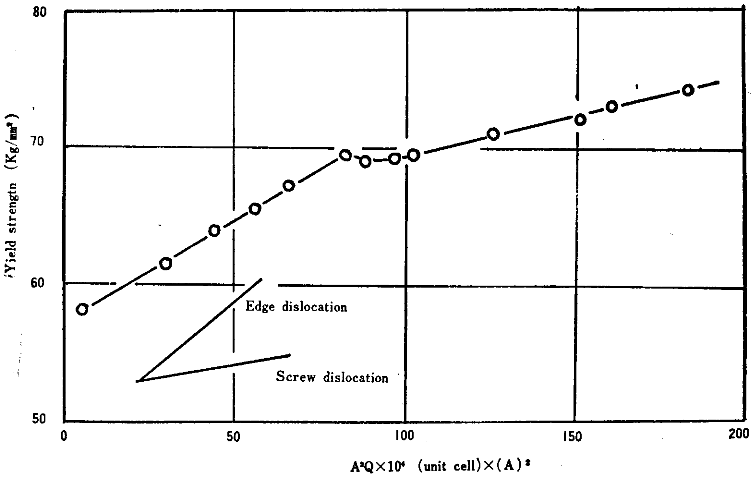

Fig. 7 Relation between A^2Q and yield strength for Ni-9.6 at. % Ti alloy aged at 600°C. Q=wave length, and A=amplitude in Å.

workers[24,25] and in these theories the yield stresses are a function of the volume fraction of the precipitates. It is considered that the yield stresses of Ni-10 at. % Ti alloys in the present work decrease with aging after the delaying point, if considering these phenomena from a stand point of only volume fraction of the precipitates. Actually, the yield stresses may increase slightly for the increment of the interface energy between the Ti rich region and matrix, and also the increment of the shear modulus of the rich region.

5. Conclusion

The isothermal growth of the modulated structure and the structural dependence for the yield stress of aged Ni-10 at. % Ti alloy was investigated with X-ray diffraction mehod and tensile test. The results obtained are as follows:

(1) In early stage of aging, Ni-10 at. % Ti alloys have the modulated structures, the wave length and the amplitude of which increase continously with aging.

(2) The growth of the modulated structures in Ni-10 at. % Ti alloys are controlled by rate of the diffusion of Ti in Ni-Ti solid solution.

(3) Experimental results of the yield stresses of Ni-10 at. % Ti alloy in early stage of aging seem to support Cahn's theory, in which an interaction beween a dislocation and the periodic internal stress field due to the compositional modulation.

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