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Theoretical estimation of the effect of interfacial energy on the mechanical strength of spinodally decomposed alloys

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New "interfaces" are produced on the slip plane when a crystal with continuous composition fluctuation arising from spinodal decomposition is deformed by slip. In this work, the energy of such "interfaces" is evaluated for both modulated and mottled structures, and their effects on slip behaviour are discussed. It is concluded that the contribution of this "interfacial energy" is large enough to account for the age-hardening concomitant with spinodal decomposition.

1. Introduction

Some supersaturated solid solutions have been reported to show rapid increase in the mechanical strength during the early stage of spinodal phase decomposition. According to a theory developed by Cahn on the age-hardening of spinodally decomposed alloys [1], such hardening has been accounted for by the interaction of dislocations with internal stress fields arising from the fluctuation of lattice spacing. However, it seems to be uncertain whether or not the fine stress fields, produced at the early stage of ageing, act as an effective obstacle to dislocation motion, because the wavelength of the stress field may be too small to bend dislocations along its potential valley. It has, in fact, been reported in some papers that Cahn's prediction gives too small a yield strength to account for the experimental values [2, 3]. In such fine microstructures, the interfacial energy on the slip plane may be more effective than the internal stress in hindering dislocation motion.

In the present work, the force on dislocations caused by the change of interfacial energy associated with the dislocation glide has been quantitatively derived.

2. Morphology of microstructures produced by spinodal decomposition

Microstructures in spinodally decomposed alloys are morphologically classified into two types. According to Cahn's theory on spinodal decomposition [4], the change of composition fluctuation with ageing can be expressed as a result of increase or decrease of the amplitude of each Fourier component:

$$C = C_0 + \sum_{\beta} A_\beta \exp [R(\beta)\, t] \cdot \cos (\beta \cdot r) \tag{1a}$$

$$R(\beta) = -M\beta^2 (f_0'' + 2\eta^2 Y_{\langle hkl \rangle} + 2K\beta^2) \tag{1b}$$

where C_0 is an average composition of the alloy, A_β is an initial amplitude of the Fourier component whose wavenumber is β, r is a distance in the crystal, t is the ageing time. $R(\beta)$ is a so-called amplification factor, M the mobility of solute atoms, f_0 the free energy of the supersaturated solid solution, $Y_{\langle hkl \rangle}$ is an elastic modulus in the $\langle h\,k\,l \rangle$ direction and K is a gradient energy having a positive value for the alloy exhibiting phase separation. η is the partial derivative of the lattice parameter a, with respect to the solute concentration c, $(1/a)\,(\partial a/\partial c)$. Being positive, the elastic energy term $2\eta^2 Y_{\langle hkl \rangle}$ in Equation 1b always restrains the spinodal decomposition, so that the decomposition tends to occur along the direction with minimum $Y_{\langle hkl \rangle}$. Since $Y_{\langle hkl \rangle}$ is minimum along the three orthogonal $\langle 1\,0\,0 \rangle$ directions in most cubic structure alloys, the periodic zone arrangement aligned with the three cubic directions

should be formed when η is fairly large. Such microstructure is called a "modulated structure". On the other hand, if the alloy has either isotropic elasticity or small η, spinodal decomposition produces a random zone arrangement, because $R(\beta)$ is independent of crystallographic direction. This microstructure is called a "mottled structure". In the next section, the dragging force on dislocations due to the interfacial energy is derived theoretically for both types of microstructure.

3. Dragging force on dislocations in the modulated structure

3.1. Face-centred cubic lattice

Consider the case where a single sinusoidal composition wave, the wavenumber and amplitude of which are β and $A/3$ respectively, appears along each cubic direction [1 0 0], [0 1 0] and [0 0 1] to dominate the morphology of microstructure. The concentration of solute atoms at any point in the conventional (X, Y, Z) co-ordinates is expressed by Equation 2:

$$C(X, Y, Z) = C_0 + A(\cos\beta X + \cos\beta Y + \cos\beta Z)/3. \quad (2)$$

In order to simplify the calculation, the (X, Y, Z) co-ordinates are rotated to new (x, y, z) co-ordinates, which are defined as follows: the x-axis is in the $[\bar{1}\,1\,0]$ direction, i.e. the slip direction in the fcc lattice; the y-axis is in the $[\bar{1}\,\bar{1}\,2]$ direction, perpendicular to the Burgers vector and laid on the slip plane (1 1 1); and the z-axis is in the [1 1 1] direction normal to the slip plane. Solute concentration at a point (x, y, z) in the new co-ordinates is described by Equation 3:

$$C(x, y, z) = C_0 + A\{2\cos\beta(y/\sqrt{6} - z/\sqrt{3}) \cos(\beta x/\sqrt{2}) + \cos\beta(2y/\sqrt{6} + z/\sqrt{3})\}/3. \quad (3)$$

Suppose N dislocations with Burgers vector $\boldsymbol{b}$ have passed on a slip plane. Then a difference in concentration, ΔC_N, is created between the two opposing atomic planes just above and below the glide plane, as given in Equation 4:

$$\Delta C_N(x, y, z) = C(x, y, z) - C(x - N\boldsymbol{b}, y, z) = -(4/3)A\cos\beta(y/\sqrt{6} - z/\sqrt{3}) \sin[\beta(x - N\boldsymbol{b}/2)/\sqrt{2}] \sin(\beta N\boldsymbol{b}/2\sqrt{2}). \quad (4)$$

An interfacial energy γ per unit area of the slip plane is expressed as a sum of the chemical interfacial energy and the elastic strain energy. The former is concerned with a short-range force related to the binding energy of atom-pairs across the slip plane [5], while the latter is a long range force resulting from the misfit in lattice spacing [6]. Thus

$$\gamma = \{2U_E \nu n_s + k\mu\eta^2\}(\Delta C_N)^2 \quad (5)$$

where U_E is the interchange energy of atom-pairs defined by $U_E = U_{AB} - (U_{AA} + U_{BB})/2$ (U_{ij} is the binding energy between i and j atoms), ν the co-ordination number, n_s the number of atoms per unit area of the interface, μ the shear modulus and k is a constant related to the shape of the solute-rich region. Since the interfacial energy, γ, is proportional to $(\Delta C_N)^2$ as shown in Equation 5, the change in interfacial energy, $\Delta\gamma_N$, induced by the motion of Nth dislocation is given by Equation 6:

$$\Delta\gamma_N \propto (\Delta C_N)^2 - (\Delta C_{N-1})^2 = \boldsymbol{b}\,\mathrm{d}(\Delta C_N)^2/\mathrm{d}(N\boldsymbol{b}) = (2\sqrt{2}/9)A^2\beta\boldsymbol{b}\{\sin(\beta N\boldsymbol{b}/2\sqrt{2})\}\{1 - \cos\beta(2y/\sqrt{6} - 2z/\sqrt{3})\}\{\cos(\beta N\boldsymbol{b}/2\sqrt{2}) - \cos(\beta(2x - 3N\boldsymbol{b}/2)/\sqrt{2})\}. \quad (6)$$

As can be seen from this equation, $\boldsymbol{b}\mathrm{d}(\Delta C_N)^2/\mathrm{d}(N\boldsymbol{b})$ is a periodic function with periodicity of $\sqrt{2}\pi/\beta$ in the x-direction and $\sqrt{6}\pi/\beta$ in the y-direction. Consequently, the stress for dislocation motion can be evaluated from an energy balance equation over a segment of $\sqrt{2}\pi/\beta$ long for a screw dislocation and $\sqrt{6}\pi/\beta$ long for an edge dislocation. Equating the change of interfacial energy to the work done by the applied shear stress, τ, during the glide of the Nth screw dislocation over a distance Δy or the glide of the Nth edge dislocation over a distance Δx, the following two equations can be derived:

$$\tau\boldsymbol{b}(\sqrt{2}\pi/\beta)\Delta y = \{2U_E\nu n_s + k\mu\eta^2\} \Delta y\int_0^{\sqrt{2}\pi/\beta} \boldsymbol{b}(\mathrm{d}(\Delta C_N)^2/\mathrm{d}(N\boldsymbol{b}))\,\mathrm{d}x \quad (7a)$$

(for a screw dislocation)

$$\tau\boldsymbol{b}(\sqrt{6}\pi/\beta)\Delta x = \{2U_E\nu n_s + k\mu\eta^2\} \Delta x\int_0^{\sqrt{6}\pi/\beta} \boldsymbol{b}(d(\Delta C_N)^2/\mathrm{d}(N\boldsymbol{b}))\,\mathrm{d}y \quad (7b)$$

(for an edge dislocation).

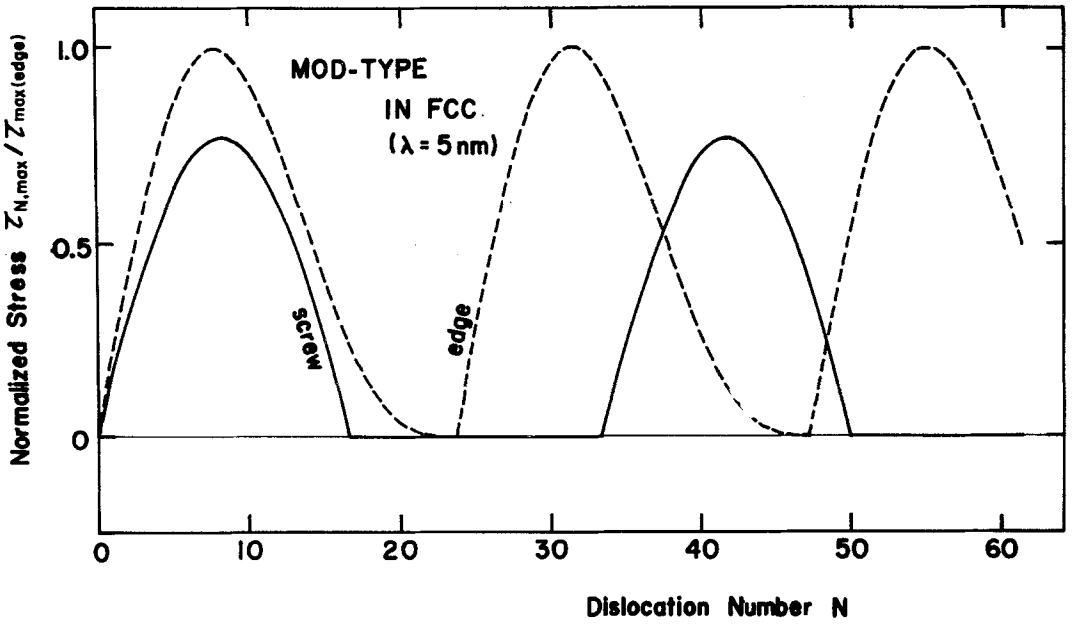

Figure 1 Stress for dislocation motion in a modulated structure plotted against the number of dislocations emitted by the source (f c c).

Substituting Equation 6 into Equation 7, the dragging stress due to the change of interfacial energy can be expressed as

$$\tau = (\sqrt{2}/9)A^2\beta\{2U_E\nu n_s + k\mu\eta^2\}\sin(\beta Nb/2)\{1 - \cos\beta(2y/\sqrt{6} - 2z/\sqrt{3}) \quad (8a)$$

(for a screw dislocation)

$$\tau = (2\sqrt{2}/9)A^2\beta\{2U_E\nu n_s + k\mu\eta^2\}\sin(\beta Nb/2\sqrt{2})\{\cos(\beta Nb/2\sqrt{2}) - \cos(\beta(2x - 3Nb/2)/\sqrt{2})\} \quad (8b)$$

(for an edge dislocation).

Since the stress, τ, is a function not only of a number of dislocations, N, but also the position of the dislocation, i.e. y and z in Equation 8a and x in Equation 8b, the Nth dislocation receives its maximum dragging at different positions in the crystal. In Fig. 1, the maximum dragging stress, $\tau_{N,\max}$, for the Nth dislocation is plotted against the number of dislocations, N, for the case $\lambda = 2\pi/\beta = 5$ nm. The ordinate is normalized by the peak value of $\tau_{N,\max}$ for an edge dislocation. $\tau_{N,\max}$ varies periodically with N. It should be noted here that the peak stress for a screw dislocation differs from that for an edge dislocation only by a factor of 1.3. Therefore, based upon the present hardening model, similar mobilities are predicted for both components in f c c metals, in contrast to the theory by Cahn [1]. This will be further discussed in Section 5. Analytical expression of the peak stress, τ_{max}, can be obtained by substituting $N = (4n + 1)\pi/\beta b$ and $y = \sqrt{6}(2n + 1)\pi/2\beta + 2z(n = 0, 1, 2, 3, \ldots)$ for a screw dislocation, and $N = 2\sqrt{2}(6m + 1)/3\beta b$ and $x = \sqrt{2}(3m + n + 1)/\beta$ or $N = 4\sqrt{2\pi}(3m + 2)/3\beta b$ and $x = \sqrt{2\pi}(3m + n + 2)/\beta$ ($n = 0, 1, 2, 3, \ldots$, $m = 0, 1, 2, 3, \ldots$) for an edge dislocation:

$$\tau_{max} = (4\sqrt{2\pi}/9)\{2U_E\nu n_s + k\mu\eta^2\}A^2\lambda^{-1} \quad (9a)$$

(for a screw dislocation)

$$\tau_{max} = (\sqrt{6\pi}/3)\{2U_E\nu n_s + k\mu\eta^2\}A^2\lambda^{-1} \quad (9b)$$

(for an edge dislocation).

It is worthwhile to note that τ_{max} is proportional to the square of amplitude, A^2, and inversely proportional to the wavelength, λ.

3.2. Body-centred cubic lattice

Similar expressions for the dragging force of slip dislocations in b c c lattice can be obtained in the same manner as above, by choosing new co-ordinates so that the x-, y- and z-axes are

parallel to $[\bar{1}\,1\,1]$, $[1\,\bar{1}\,2]$, perpendicular to the slip direction $[\bar{1}\,1\,1]$, and $[1\,1\,0]$ normal to the slip plane, respectively. The dragging stress, τ, for the Nth dislocation at a point (x, y, z) is given by

$$\tau = (2\sqrt{3}/27)\,\pi\,\{2U_{\mathrm{E}}\nu n_{\mathrm{s}} + k\mu\eta^2\}\sin(\beta Nb/\sqrt{3})\,\{2(\cos(\beta z/\sqrt{2}))^2 + 2\cos(\beta z/\sqrt{2})\cos(3\beta y/\sqrt{6}) + 1/2\}A^2\lambda^{-1} \quad (10a)$$

(for a screw dislocation)

$$\tau = (2\sqrt{3}/27)\,\pi\,\{2U_{\mathrm{E}}\nu n_{\mathrm{s}} + k\mu\eta^2\}\sin(\beta Nb/\sqrt{3})\,\{2(\cos(\beta z/\sqrt{2}))^2 + 1/2\}A^2\lambda^{-1} \quad (10b)$$

(for an edge dislocation).

It is evident from Equation 10 that $\tau_{N,\max}$ is a function of z, i.e. the position of the slip plane in the crystal, in contrast to the case of the fcc lattice derived above (see Equation 8). In this case, therefore, instead of plotting $\tau_{N,\max}$ against N, as shown in Fig. 1, it is necessary to plot $\tau_{N,\max}$ against z for the Nth dislocation which satisfies the condition $\sin(\beta Nb/\sqrt{3}) = 1$ in order to determine the maximum dragging stress $\tau_{\max}$. The plot obtained is shown in Fig. 2, where the ordinate is normalized stress with units of $\{2U_{\mathrm{E}}\nu n_{\mathrm{s}} + k\mu\eta^2\}A^2\beta$. It is interesting to note that the stress for a screw dislocation is always higher than that for an edge dislocation except in the case $\cos(\beta z/\sqrt{2}) = 0$.

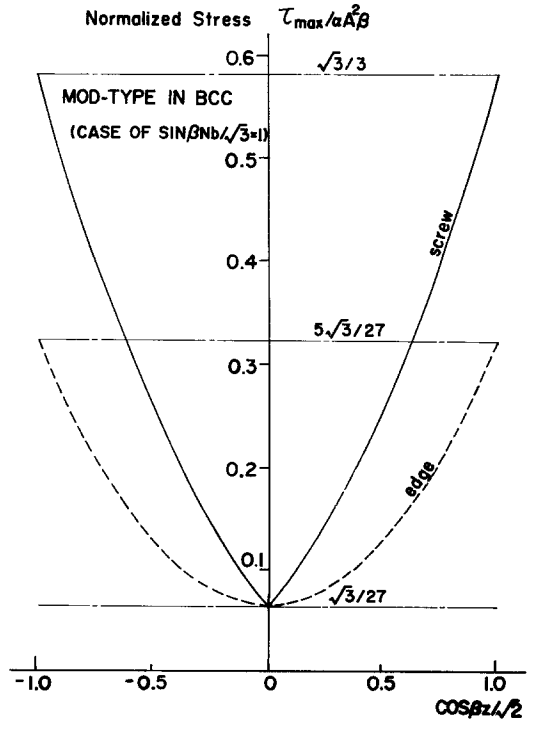

Figure 2 Stress for dislocation motion in a modulated structure plotted against the position of the slip plane (b c c). $\alpha = 2U_{\mathrm{E}}\nu n_{\mathrm{s}} + k\mu\eta^2$.

4. Dragging force on dislocations in the mottled structure

In general, the microstructure produced by spinodal decomposition in a material which is either isotropic or for which there is no significant elastic-energy contribution, is given by a superposition of sinusoidal composition waves of a fixed wave number β_{m} (wave number of Fourier component receiving maximum amplification) but random in direction, phase angle and amplitude [4]. Namely, the composition at a point (x, y, z) is expressed

$$C(x, y, z) = C_0 + \sum_i A_i \cos\{\beta_{\mathrm{m}}(u_i x + v_i y + w_i z) + \phi_i\}, \quad (11)$$

where u, v and w are directional cosines of a component wave vector, and A and ϕ are the corresponding amplitude and phase angle, respectively. To obtain a composition variation representative of the mottled structure, a sum of 100 random sine waves was computed after Cahn [4], using a Gaussian distribution for the amplitudes and a flat one for the phase angles, and is hereafter taken as an analytical expression of solute concentration at a point (x, y, z).

Then, let us take a co-ordinate so that the x-, y- and z-axes are parallel to the direction of Burgers vector, perpendicular to the Burgers vector but contained on the slip plane, and normal to the slip plane, respectively. The energy balance equation for a screw dislocation is given by

$$\tau bL\Delta y = \{2U_{\mathrm{E}}\nu n_{\mathrm{s}} + k\mu\eta^2\}\,\Delta y \int_0^L b\{\mathrm{d}(\Delta C_N)^2/\mathrm{d}(Nb)\}\,\mathrm{d}y, \quad (12)$$

where L is the length of dislocation segment, and ΔC_N is

$$\Delta C_N = C(x, y, z) - C(x - Nb, y, z)$$

as before (Equation 5). Since the composition variation in the mottled structure is essentially isotropic by definition, as mentioned above, this equation is valid for all crystal structures having

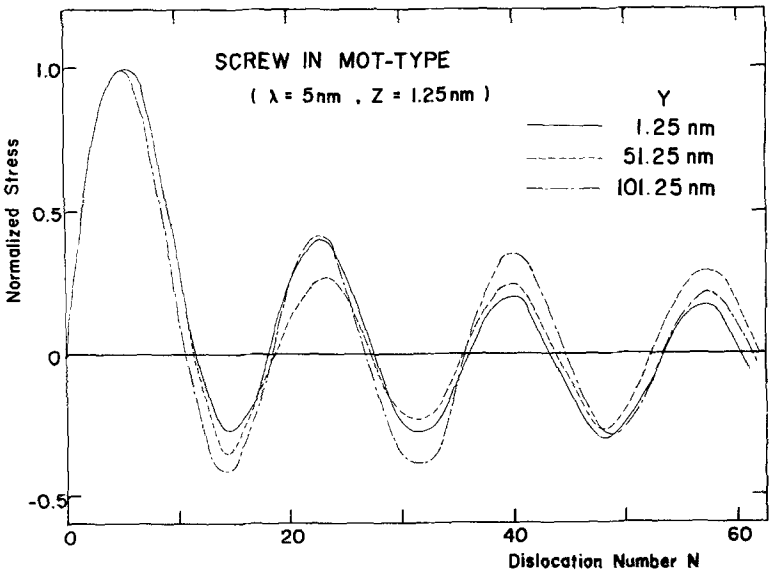

Figure 3 Stress for motion of screw dislocations in a mottled structure plotted against the number of dislocations emitted by the source (on an arbitrarily chosen slip plane of $z = 1.25$ nm).

different slip systems. Fig. 3 shows normalized critical shear stress, τ_N/τ_{max}, for the Nth dislocation in a mottled structure with $\lambda_m(=2\pi/\beta_m)$ of 5 nm, evaluated from Equation 12. In the evaluation, the integration in Equation 12 was taken over a long segment L of dislocation, 100 times as large as λ_m. The curves in Fig. 3 correspond to the dragging stresses for dislocations at three different positions on an arbitrarily chosen slip plane $z = 1.25$ nm, which are 50 nm apart, i.e. at $y = 1.25$, 51.25 and 101.25 nm, respectively. It is evident from the figure that in all cases only dislocations with numbers clustered about $N = 5$ receive maximum dragging while others are less affected. It follows that the subsequent dislocations around $N = 5$ can glide quite easily as long as they remain on the original slip plane without making any cross-slip. Extension of the calculation to edge dislocations gives essentially the same results as those shown in Fig. 3.

From these theoretical considerations, the deformation process in alloys having a fine mottled structure produced by spinodal decomposition, for example Fe–Cr and Al–Zn alloys, is predicted as follows; once the applied stress reaches a critical level to emit a given number of dislocations from a source (the number is a function of λ_m and is 5 for the case $\lambda_m = 5$ nm as mentioned above), subsequent dislocations are easily multiplied from the source and tend to continue to glide along the original slip plane because of the reduced dragging on it. This proceeds until work-hardening on the

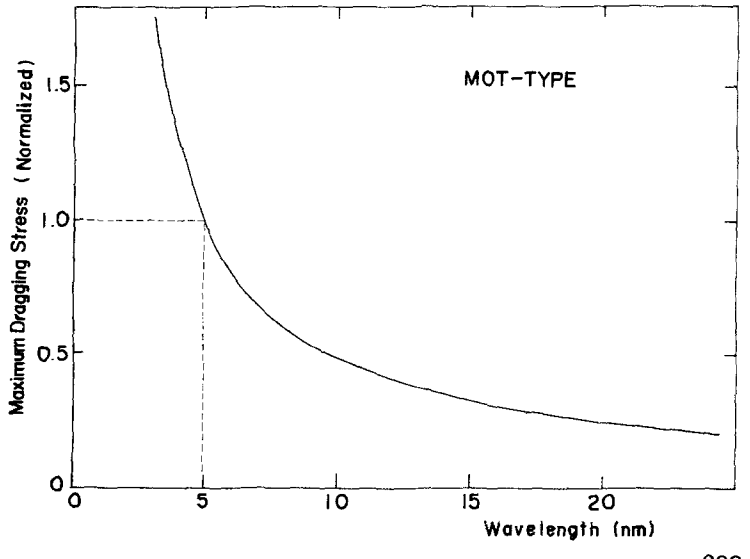

Figure 4 Maximum dragging stress plotted against wavelength of a mottled structure.

slip plane dominates the flow stress. Thus, coarse slip bands are generally expected to be formed in this type of alloy.

Finally, effect of λ_m on τ_{max} is investigated, based upon Equation 12 and the results obtained are shown in Fig. 4. In this figure, normalized critical stress $\tau_{max}/\tau_{max}(\lambda_m = 5\,nm)$ is plotted against λ_m, where $\tau_{max}(\lambda_m = 5\,nm)$ is the maximum dragging stress encountered in a mottled structure with $\lambda_m = 5\,nm$. It is noted that the dragging stress increases with decreasing λ_m, and is therefore most effective for structures with small λ_m. This is in qualitative agreement with results on modulated structures described in Section 3.

5. Comparison with some experimental results

The propriety of the theory is discussed below. At first the dragging force is quantitatively evaluated. The interfacial energy of a coherent particle has been reported to be between 0.2 and 0.4 $J\,m^{-2}$ for many alloys, for instance 0.25 to 0.30 $J\,m^{-2}$ for a Cu–Co alloy [7], 0.322 $J\,m^{-2}$ at the (1 1 0) interface and 0.370 $J\,m^{-2}$ at the (2 1 1) interface for an Fe–Cr alloy [8]. As an exception, extremely low energies, 0.01 to 0.03 $J\,m^{-2}$, have been reported for the $L1_2$ ordered γ' phase such as Ni_3Al and Ni_3Si particles in Ni–Al [7, 9] and Ni–Si alloys [10] by experimental investigations on the Ostwald ripening for these particles. The particles have a cuboid shape whose surfaces, {1 0 0} planes, are in contact with the {1 0 0} planes of the matrix. Therefore, the like atom-pairs are in high probability at the interface of the (1 0 0) matrix plane and the (2 0 0) plane of the γ' cube. This is proposed as one reason why the $L1_2$ particles show such small interfacial energies [7]. However, in the case where the γ' particles are sheared by the dislocations having a usual Burgers vector in fcc, $a/2\langle 1\,1\,0\rangle$, as is the case in the present work, a new interface is produced on the (1 1 1) plane, so that the interfacial energy may not be so small, but in the order of the usual value. Assuming the interfacial energy to be $\gamma = \{2U_E\nu n_s + k\mu\eta^2\}A^2 = 0.3\,J\,m^{-2}$ and the Taylor factor $\bar{m} = 3$, the increment of yield stress due to the interfacial energy can be approximately evaluated from Equation 9b for fcc polycrystallines having a modulated structure. Fig. 5 represents the calculated increments against wavelength, λ. It is clear from this figure that the interfacial energy does not have such a small effect on the yield stress as suggested by Cahn [1], but makes a fairly large contribution to the yield stress in fine modulated structures, particularly those whose wavelength is less than several nanometers. Such a fine composition wave is usually produced at the early stage of ageing on spinodal decomposition.

Fig. 6 is a transmission electron micrograph, taken from a foil which was prepared from a Ni–40 at. % Cu–5.5 at. % Si single crystal aged at 773 K for 6.0×10^3 sec and then elongated until the end of stage I in the stress–strain curve. Structural changes with ageing in this alloy system have already been reported previously [11, 12], where the periodic microstructures resulting from spinodal decomposition have been clearly found in a range of Ni–Cu–Si (Ni–40 at. % Cu–3 to

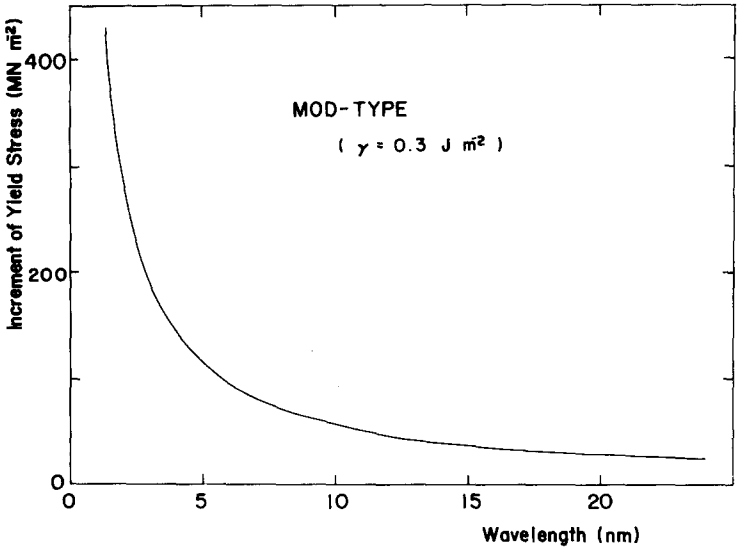

Figure 5 Increment of yield stress plotted against the wavelength of a modulated structure.

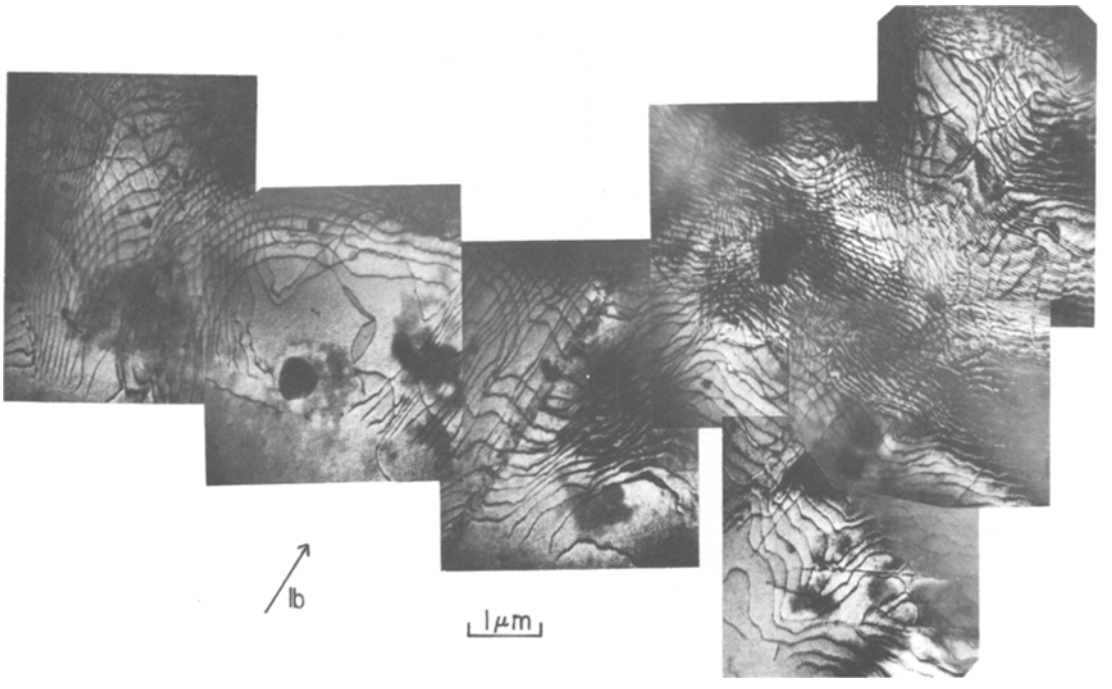

Figure 6 Dislocations in a modulated structure of Ni–37.8 at .% Cu–5.6 at .% Si alloy aged for 6.0×10^3 sec at 773 K.

12 at.% Si) alloys. The foil was cut parallel to the primary slip plane (1 1 1).

Many dislocations multiplied from a Frank–Read source are semi-circular in shape, showing that the mobility of a dislocation is not so different between the screw and edge components. If the magnitude of the dragging force for the edge component is much larger (over five times), than that for the screw component, as given in Cahn's theory [1], then the screw dislocations move a greater distance than the edge components. This theoretical inference, however, is inconsistent with the dislocation configuration seen in Fig. 6. On the other hand, the dragging force resulting from the interfacial energy shows little difference between the screw and edge components, therefore the mobilities should be almost the same, which explains the experimental finding in Fig. 6.

6. Conclusions

Influence of the interfacial energy on the yield stress of the spinodally decomposed alloy was investigated. The results obtained are as follows:

(1) An increment in the yield stress, resulting from the effect of interfacial energy is proportional to the square of the amplitude and to the inverse of the wavelength for the morphologically anisotropic structure (modulated structure). Equations obtained for the f c c crystal are

$$\tau = (4\sqrt{2\pi}/9)\{2U_E\nu n_s + k\mu\eta^2\}A^2\lambda^{-1}$$

(for a screw dislocation)

$$\tau = (\sqrt{6\pi}/3)\{2U_E\nu n_s + k\mu\eta^2\}A^2\lambda^{-1}$$

(for an edge dislocation).

Strengthening due to this effect may be in priority for the fine modulated structure formed at an early stage of ageing. The dragging forces for screw and edge dislocations are little different in the f c c crystal, whereas in the b c c crystal, screw dislocations always receive a higher dragging force than edge dislocations at all placed except at specified slip planes.

(2) In the morphologically isotropic microstructure (mottled structure), a specified numbered dislocation (5th dislocation for the case λ_m = 5.0 nm) receives maximum dragging force, and the other dislocations are not dragged so strongly. Consequently, the sources which once produced this critical number of dislocations can subsequently easily continue to multiply. This may introduce coarse slip into the mottled structure and result in the stress concentration at a grain boundary or inclusion interface.

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