The Misfit Strain Energy Collapse during Precipitation in Solid Transformations

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Abstract. The misfit strain energy collapse (MSEC) which results in the dendritic or split γ′ precipitating particles during solid transformations in Ni-base alloys is discovered. Three parameters of the MSEC function, the MSEC delay, the MSEC rate, and the initial value of the MSEC function, are correlated to the persistence of the isothermal cooling, the rate during the continuous cooling, and the initial misfit strain during nucleation respectively. The MSEC point is the intersection of the two crystal lattice parameters $a_{\gamma'}(T)$ and $a_{\gamma}(T)$ of the two different phases.

1. Introduction
The microstructural misfit strain energy theory derived by A. G. Khachaturyan [1-2] reveals that the elastic strain energy of the microstructure depends on the misfit strain between the precipitates and the matrix during phase transformations in solids, but it does not point out when and how the elastic strain energy takes place. Considering the temperature is successively changed in different stage of aging during continuous cooling, the phenomenon of misfit strain energy collapse (MSEC) might occur accompanying with the variation of the structure during precipitation. The so-called MSEC refers to the opinion that the misfit strain energy varies successively during aging but not suddenly at beginning of nucleation.

2. The temperature dependent elastic strain energy
The temperature dependent total elastic energy may be expressed by
\[ E^e_l = \int_V C_{ijkl}(c,T)\varepsilon_{ij}^e(r,T)\varepsilon_{kl}^e(r,T)d^3r. \] (1)
If the applied strain is not taken into account, which means that $\varepsilon_{kl}^e = 0$, and the elastic constant is considered to be homogeneous, i.e. $\Delta C_{ijkl}(T) = 0$, the temperature dependent total elastic energy of the aging system may then be obtained
\[ E^e_l = \int_V B(n,T)|\Delta c(g,t)|^2 d^3r. \] (2)
The inhomogeneous part of $B(n,T)$ in Eq. (2) may be given by
\[ \Delta B(n,T) = B(n,T) - B(0,T) = \frac{4(c_1^T+2c_2^T)^2 n_T^2 \Delta}{c_1^T(c_1^T+c_2^T+2c_4^T)} [\varepsilon_0^e(T)]^2. \] (3)
With the definition
\[ \Delta E^e_l = \frac{1}{2} \int \left[ B(n,T) - B(0,T) \right]|\Delta c(g,t)|^2 \frac{d^2g}{(2\pi)^3}, \] (4)
and substituting Eq. (3) into Eq. (2) and combining Eq. (1), the simplified inhomogeneous part of the temperature dependent total misfit strain energy may then be obtained.

3. Temperature dependent elastic strain energy for modelled Ni-Ai-Si alloys
With the linear assumption the lattice constants of $\gamma$ and $\gamma'$ in the modeled Ni-base alloys may be given by

$$a_{\gamma,\gamma'} = a_0 + a_1 T + a_2 T^2,$$

where $a_i = (1 - x) a_i^{\text{Ni-Al}} + x a_i^{\text{Ni-Si}}$. The coefficients $a_i$ are listed in Table 1.

### Table 1. The coefficient $a_i$ of crystal lattice parameters of $\gamma'$ and $\gamma$ in modeled Ni-base alloy abiding by the linear rule.

| Ni-17.7at.%Al | Ni-12.4at.%Al-5.54at.%Si | Ni-18.47at.%Si |
|----------------|---------------------------|----------------|
| $a_0$ (nm)     | 0.35628                   | 0.35091       |
| $a_1 \times 10^6$ (nm/K) | 6.16199                | 4.71791       |
| $a_2 \times 10^{10}$ (nm/K$^2$) | -11.32198              | 7.58328       |

The inhomogeneity of the temperature dependent misfit strain energy $\Delta E^e_l(T)$ is given in Eq. (3), in which the temperature dependent misfit strain $\varepsilon^c_0(T)$ is a function of the temperature. With the assumption of the homogeneous temperature, the heat treatment regime may be simplified by function $T(t)$.

The temperature dependent misfit strain $\varepsilon^c_0(T)$ may be changed to the proximate form

$$\varepsilon^c_0(T) = \frac{2}{c_{\gamma'}(T) - c_{\gamma}(T) a_{\gamma'}(T)} \frac{a_{\gamma}(T) - a_{\gamma'}(T)}{a_{\gamma'}(T) + a_{\gamma}(T)}$$

For convenience in the following discussion, the concentration of $\gamma$ and $\gamma'$ are assumed to be the concentration at room temperature, i.e. $c_{\gamma} = c_{\gamma}(T)_{T=300K}$ and $c_{\gamma'} = c_{\gamma'}(T)_{T=300K}$. The intersecting point at $T_c = 1242.16K$ in Figure 1 (b) is the critical point at which the misfit strain changes from negative to positive. Figure 2 indicates that the temperature dependent misfit strain $\varepsilon^c_0(T)$ changes along with the variation of the aging temperature $T$. The temperature dependent misfit strain in Figure 2 (a) satisfies

$$\varepsilon^c_0(T) > 0 \quad (T < T^i_c),$$

Where $T^i_c = 1499.22K$ is the imaginary misfit strain collapse point. In this situation, if the temperature of starting aging $T_s$ below the real misfit strain collapse point $T^r_c$, the quenching do not passes by $T^r_c$. Otherwise, the quenching passes by $T^r_c$. For the situation in Figure 2 (c),

$$\varepsilon^c_0(T) < 0 \quad T \in [T^r_c, T_s],$$

which means that the temperature dependent misfit strain is always negative during the whole quenching procedure.
Figure 2. The temperature dependent misfit strain $\varepsilon^0_c(T)$. (a) Ni-17.70at.%Al, (b) Ni-12.40at.%Al-5.54at.%Si, (c) Ni-18.47at.%Si.

It should be noted that, the temperature dependent misfit strain $\varepsilon^0_c(T)$ demonstrated in Figure 2 (c) for the modeled Ni-18.47at.%Si alloy is always less than zero throughout the whole period of the heat treatment. The temperature dependent elastic constants for Ni-Al alloys selected from Prikhodko's work [3-4] are listed in Table 2.

Table 2. The coefficients $c_i$ in temperature dependent elastic constant $C_{ij}(T)$ of Ni-Al-Si alloys.

|        | Ni-17.7at.%Al | Ni-12.4at.%Al-5.54at.%Si | Ni-18.47at.%Si |
|--------|---------------|---------------------------|----------------|
| $C_{11}$ | $c_{0}$ (GPa) | $c_{1}$ (GPa/K) | $c_{0}$ (GPa) | $c_{1}$ (GPa/K) |
|        | 245.965       | -0.0372                  | 246.070        | -0.0407       |
|        | 157.869       | -0.0086                  | 161.910        | -0.0121       |
|        | 128.758       | -0.0326                  | 124.920        | -0.0338       |

The coefficient error of Ni-11.17at.%Si, Ni-12.0at.%Al-5.54at.%Si and Ni-18.47at.%Si demonstrated in Table 2 is in control. The temperature dependent elastic constants of $C_{11}$, $C_{12}$ and $C_{44}$ are given by the form in Figure 3 (a), (b) and (c) respectively [3-4].

Figure 3. The temperature dependent elastic constants $C_{ijkl}(T)$. (a) Ni-17.70at.%Al, (b) Ni-12.40at.%Al-5.54at.%Si, (c) Ni-18.47at.%Si.

4. Conclusions
The MSEC is characterized by the MSEC point which is the intersection of the temperature dependent crystal lattice parameters $a_{\gamma}'(T)$ and $a_{\gamma}(T)$ of different phases. If the quenching passes by the MSEC point, the MSEC point is termed as the real MSEC point. Otherwise, if the quenching do not passes by the MSEC point, the MSEC point is termed as the imaginary MSEC point. Not all pairs of $a_{\gamma}'(T)$ and $a_{\gamma}(T)$ intersects at some point. If $a_{\gamma}'(T)$ and $a_{\gamma}(T)$ intersects at the imaginary MSEC point, e.g. $T_s < T_c^i$ in Ni-17.70at. %Al alloy, the misfit strain at the temperature of starting aging is not zero. If $a_{\gamma}'(T)$ and $a_{\gamma}(T)$ intersects at the real MSEC point, e.g. $T_s \geq T_c^r$ in Ni-12.40at. %Al-5.54at.%Si alloy, the misfit strain at the temperature of starting aging might be approximate to zero. So that if the misfit strain is approximate to zero at $T_s$, the generation of the crystal nucleus need not
overcome the misfit strain energy barrier, furthermore the growth of the nucleus is only controlled by the interfacial energy, which is the reason of the dendritic morphology. The misfit strain energy may increase or decrease along with the decline of the aging temperature during quenching, which is the reason why the dendritic particles split into octet of cube.

5. Reference
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