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Precipitation kinetics of ordered γ′ phase and microstructure evolution in a Ni–Al alloy

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HIGHLIGHTS

- Kinetics of γ′ phase from nucleation to coarsening in Ni–Al alloy is studied.
- Non-stoichiometric ordered phase and initial cluster are quantitatively described.
- Time exponent of particle radius decreases from nucleation and growth to coarsening.
- Average aspect ratio of γ′ phase shows three stages with respect to average radius.

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ABSTRACT

The precipitation kinetics of ordered γ′ ($L1_2$-Ni_3Al) phase from nucleation and growth to coarsening in a Ni–Al alloy is studied by phase field simulation. The initial nucleation of the γ′ phase is quantitatively described by the variations of composition and order parameter profiles of the initial Al-enriched cluster, and the coarsening kinetics is clarified with the time exponent of the average particle radius of γ′ phase. The precipitation of the γ′ phase from the supersaturated γ solid solution goes through the non-stoichiometric ordered phase, stoichiometric ordered phase, growth and coarsening. The time exponent of the average radius of the γ′ phase with coherent equilibrium is smaller than that indicated by the Lifshitz–Slyozov–Wagner theory at the coarsening stage, and it decreases from 1.35 of the nucleation and growth stage to 0.22 of the coarsening stage. The peak of the particle size distribution decreases and the width of the particle size distribution increases as the aging progresses. As the average radius of the γ′ phase increases, the average aspect ratio of the γ′ phase undergoes a slowly increase to a fast increase from nucleation to growth stage, then goes into a relatively stable state at the coarsening stage.

1. Introduction

Nickel-based superalloys are the preferred structural materials in commercial and military jet engines and land-based gas turbines because of their excellent high-temperature properties [1–6]. In nickel-based superalloys, the coherent γ′ ($L1_2$-Ni_3X) phase embedded in the disordered γ (fcc-Ni) matrix, the coherent elastic strain energy, and the interactions between the γ′ phase and dislocations lead to a strengthening of the alloys. Therefore, the kinetics evolution of phases' size and the spatial distribution of the ordered γ′ phase during thermal aging and high-temperature service will affect the properties of nickel-based superalloys.

To study the phase transformation of the γ′ phase in nickel-based alloys, thermodynamic calculation of the phase diagram [7–16] and dynamic description of the growth and coarsening by simulation and experiments [17–19] have been conducted in past decades. Wendt [17] studied the decomposition of Ni-14 at.% Al during isothermal aging at 823 K using atomic probe field-ion microscopy (AP-FIM); the results showed that the particles grow in proportion to $t^{1/3}$ at later aging stages. Transmission electron microscopy (TEM) study of the coarsening behavior of the γ′ phase in elastically constrained Ni–Al–Ti alloys indicated that the average particle size increases in proportion to $t^{1/3}$ at first, after which the coarsening remarkably decelerates [18]. Vaithyanathan and Chen [19] investigated the coarsening of ordered intermetallic phase with coherency stress using a diffuse-interface phase field model; they demonstrated that the particle size distribution (PSD) of the intermetallic phase becomes broader as the volume fraction increases.

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In addition to the growth and coarsening, the nucleation of the γ′ phase, as a critical and extreme short-time phenomenon, has attracted much attention as well. Zhang [20,21] combined a diffusion-interface model with the minimax technique to predict the morphology of critical nuclei during solid-to-solid phase transformation in both two and three dimension; the results indicated that strong elastic interactions may lead to critical nuclei with a wide variety of shapes, including plates, needles, and cuboids with non-convex interfaces. The maximum composition within a critical nucleus can be either higher or lower than that of the equilibrium phase, while the morphology of an equilibrium phase may exhibit lower symmetry than the critical nuclei resulting from elastic interactions. Miyazaki [22,23] studied the critical nuclei sizes of the γ′ phase in a Ni–Al alloy with Al content ranging from 11.7 to 12.6 (at.%) using the macroscopic composition gradient method; the critical nucleus size shows a steep increase with decreasing composition in the vicinity of the phase boundary, whereas little composition dependence is revealed for the case when the composition is far from the phase boundary.

However, the previous studies focused on either growth and coarsening kinetics or the morphology of the γ′ phase at the nucleation stage. It is theoretically meaningful to study the precipitation microstructure and kinetics evolution of the ordered γ′ phase from nucleation to coarsening. As a process of atomic ordering and composition clustering, the initial nucleation and growth of the γ′ phase may present some novel properties. Besides, the coarsening time exponent are mostly by fitting the Lifshitz-Slyozov-Wagner (LSW) theory, the actual time exponent is expected for the coarsening kinetics.

Therefore, the present work studies the precipitation kinetics of the ordered γ′ phase from nucleation to coarsening with the verified thermodynamics parameters; the initial nucleation is detected by the variation of composition and order parameter profiles of the γ′ phase, the kinetics laws of growth and coarsening, particle size distribution (PSD) and average aspect ratio of the γ′ phase are also studied.

2. Model and method

The free energy F_{total} of a Ni–Al alloy can be expressed as the sum of the chemical free energy, the interfacial energy, and the elastic strain energy, which is expressed by the extended Cahn–Hilliard free energy function [24–27]:

$$F_{total} = \int_V \left[f + \frac{k_c}{2}(\nabla c)^2 + \sum_{i=1}^{3} \frac{k_\phi}{2}(\nabla \phi_i)^2 + f_{el} \right] dV, \tag{1}$$

where V is the volume of the system, ϕ_i is the long-range order (LRO) parameter field, c is the composition field of Al, f is the volume free energy density, which defines the basic thermodynamic properties of the system, and f_{el} is the elastic energy density. k_c and k_ϕ are the gradient energy coefficients of the composition and order parameters, respectively, which can be determined from the total interface energy.

The temporal evolution of the composition field can be described by the non-linear Cahn–Hilliard diffusion equation, while the spatial-temporal evolution of the LRO parameters can be obtained by solving the time-dependent Ginzburg–Landau equations [28]:

$$\frac{\partial c(\mathbf{r},t)}{\partial t} = \nabla \cdot \left[M_c \nabla \frac{\delta F_{total}}{\delta c(\mathbf{r},t)} \right] + \xi_c(\mathbf{r},t), \tag{2}$$

$$\frac{\partial \phi_i(\mathbf{r},t)}{\partial t} = -M_\phi \frac{\delta F_{total}}{\delta \phi_i(\mathbf{r},t)} + \xi_i(\mathbf{r},t) \quad (i = 1,2,3), \tag{3}$$

where M_c and M_ϕ are the chemical mobility and the interface mobility, respectively, and $\xi_c(\mathbf{r},t)$ and $\xi_i(\mathbf{r},t)$ are the random Langevin noise items [29], simulating fluctuations of composition and LRO parameters at the initial stage, respectively. The amplitude of noise item is chosen to be small enough to trigger the nucleation, and it will be removed when the system can develop automatically.

According to the sub-lattice model and the CALPHAD parameters [30,31], the Gibbs energy of the Ni–Al alloy can be expressed as follows [24–26]:

$$\begin{aligned} G = {} & cG_0^{Al} + (1-c)G_0^{Ni} + c(1-c)\Big[L_0 + L_1(2c-1) + L_2(2c-1)^2 \\ & + L_3(2c-1)^3\Big] + 4U_1c^2\sum_{i=1}^{3}\phi_i^2 + 12U_4(1-2c)c^2\sum_{i=1}^{3}\phi_i^2 \\ & - 48U_4c^3\phi_1\phi_2\phi_3 + (RT/4) \\ & \times \left\{ \begin{array}{l} [c(1+\phi_1+\phi_2+\phi_3)]\ln[c(1+\phi_1+\phi_2+\phi_3)]+ \\ [1-c(1+\phi_1+\phi_2+\phi_3)]\ln[1-c(1+\phi_1+\phi_2+\phi_3)]+ \\ [c(1-\phi_1-\phi_2+\phi_3)]\ln[c(1-\phi_1-\phi_2+\phi_3)]+ \\ [1-c(1-\phi_1-\phi_2+\phi_3)]\ln[1-c(1-\phi_1-\phi_2+\phi_3)]+ \\ [c(1-\phi_1+\phi_2-\phi_3)]\ln[c(1-\phi_1+\phi_2-\phi_3)]+ \\ [1-c(1-\phi_1+\phi_2-\phi_3)]\ln[1-c(1-\phi_1+\phi_2-\phi_3)]+ \\ [c(1+\phi_1-\phi_2-\phi_3)]\ln[c(1+\phi_1-\phi_2-\phi_3)]+ \\ [1-c(1+\phi_1-\phi_2-\phi_3)]\ln[1-c(1+\phi_1-\phi_2-\phi_3)] \end{array} \right\}, \end{aligned} \tag{4}$$

where G_0^{Al} and G_0^{Ni} are the Gibbs energy of pure Al and Ni, respectively, L_0, L_1, L_2, and L_3 are the interaction parameters of excess energy, U_1 and U_4 are the parameters of bond energy, R is the gas constant, and T is the absolute temperature. The chemical free energy density is given by$f = G/V_m$, where V_m is the mole volume.

According to equation (4), the chemical free energy of the γ phase can be obtained by setting all three order parameters ϕ_i (i = 1, 2, 3) to zero, while the chemical free energy of γ′ phase is calculated by minimizing the free energy. The chemical free energy curves of the γ phase and γ′ phase as a function of Al content X_{Al} at 1073 K are plotted in Fig. 1. The equilibrium compositions of the γ and γ′ phases at the stress-free state are X_{Al}^{γ} =0.141 and $X_{Al}^{\gamma'}$ = 0.222 (atom fraction), respectively. The typical free energy ΔG_0 for the γ to γ′ phase transformation is 173 Jmol^{-1} at 1073 K, where the two phases have the same free energy, as denoted by the arrow in Fig. 1.

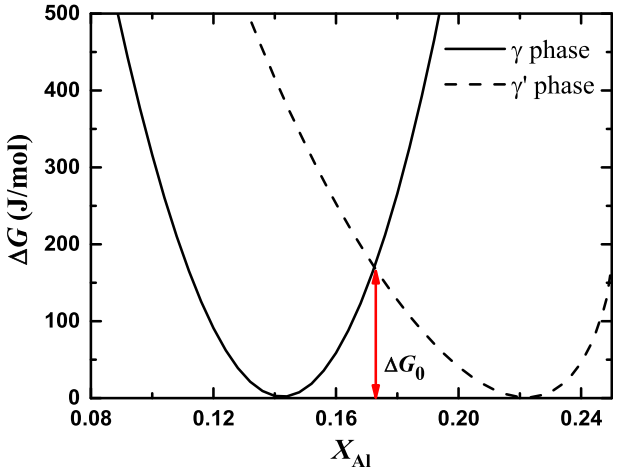

Fig. 1. Chemical free energy of the γ and γ′ phases in a Ni–Al alloy at 1073 K.