

Site occupation evolution of alloying elements in L_{12} phase during phase transformation in $Ni_{75}Al_{7.5}V_{17.5}$

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Abstract: Correlation between site occupation evolution of alloying elements in L_{12} phase and growth of DO_{22} phase in $Ni_{75}Al_{7.5}V_{17.5}$ was studied using microscopic phase field model. The results demonstrate that the growing process of DO_{22} phase can be divided into two stages. At the early stage, composition in the centre part of L_{12} phase almost remains unchanged, and the nucleation and growth of DO_{22} phase is controlled by the decrease of interface between L_{12} phases. At the late stage, part of V for growth of DO_{22} phase is supplied from the centre part of L_{12} phase and mainly comes from Al sublattice, the excess Ni spared from the decreasing L_{12} phase migrates into the centre part of L_{12} phase and occupies the Ni sublattices exclusively, while the excess Al mainly occupies the Al sublattice. At the late stage, the growth of DO_{22} phase is controlled by the evolution of antisite atoms and ternary additions in the centre part of L_{12} phase.

Key words: nickel based superalloys; $Ni_{75}Al_{7.5}V_{17.5}$ alloy; phase transformation; micro-phase field; grain growth; antisite defect

1 Introduction

Site occupation behavior of alloying elements (including site preference of ternary alloying elements and antisites of constituent elements) in intermetallic compounds and their effects on physical property are subjects of not only great practical interests but also fundamental theoretical interests [1,2]. Site preference of alloying elements can be affected by changing temperature [3,4], composition [5,6], or magnetism [7]. The performance of alloy is strongly influenced by site preference of ternary additions and antisite atoms. CHIBA et al [8] found that when the ternary addition preferentially substitutes Ni on the face centered sites in Ni_3Al , the ductility of Ni_3Al can be improved significantly. Studies also demonstrate that site preference of alloying elements affects the solute segregation strongly [9,10]. However, to our best knowledge, attention has not been paid to the correlation between site occupation evolution of alloying elements

and phase transformation. An understanding of the site occupation behavior of alloying elements during phase transformation is extremely useful in order to control the microstructure and to improve the physical properties of alloys.

The phase transformation in $Ni_{75}Al_xV_{25-x}$ alloys during aging process has been studied extensively both experimentally and theoretically. Most of the studies are focused on kinetics of phase separation and microstructure evolution [11–13]. The atomic ordering and composition clustering process were studied by PODURI and CHEN [14] and HOU et al [15], and LI et al [16] investigated the coarsening behaviors of L_{12} and DO_{22} in $Ni_{75}Al_xV_{25-x}$ alloys systematically. Few studies are focused on the correlation between the behavior of interfaces and phase transformation in $Ni_{75}Al_xV_{25-x}$ alloys [17–19]. However, the mechanism and kinetics of phase transformation between L_{12} and DO_{22} still need further understanding. In this work, site occupation behavior of alloying elements in L_{12} phase during phase transformation from L_{12} to DO_{22} in $Ni_{75}Al_{7.5}V_{17.5}$ was

studied, and their correlation was discussed. To our best knowledge, few studies have been carried out to study the kinetics of phase transformation by investigating the site occupation evolution of alloying elements at atomistic scale using a numerical simulation method. And understanding the correlation between site occupation behavior of alloying elements and growth of the second phase would make us know the kinetics of phase transformation better.

2 Microscopic phase-field model

The microscopic phase-field model describes the evolution of site occupation probability from the non-equilibrium distribution to an equilibrium one. It is firstly proposed by KHACHATURYAN [20] and developed by PODURI and CHEN [14] for the ternary alloy system. Equations for ternary alloy systems are written as:

$$\begin{cases} \frac{dP_A(r,t)}{dt} = \frac{1}{k_B T} \sum_{r'} \left[L_{AA}(r-r') \frac{\partial F}{\partial P_A(r',t)} + \right. \\ \left. L_{AB}(r-r') \frac{\partial F}{\partial P_B(r',t)} \right] \\ \frac{dP_B(r,t)}{dt} = \frac{1}{k_B T} \sum_{r'} \left[L_{BA}(r-r') \frac{\partial F}{\partial P_A(r',t)} + \right. \\ \left. L_{BB}(r-r') \frac{\partial F}{\partial P_B(r',t)} \right] \end{cases} \quad (1)$$

For ternary systems, $P_C(r, t) = 1 - P_A(r, t) - P_B(r, t)$, where $P_\alpha(r, t)$ ($\alpha = A, B$ or C) represent the probabilities of finding atom α at a given lattice site r at a given time t , t is the reduced time, $L_{\alpha\beta}(r-r')$ (α and $\beta = A, B$ or C) is the kinetic coefficient which is proportional to the probability of elementary diffusional jumps from site r to r' per unit time, and F is the total Helmholtz free energy of the system based on the mean-field approximation, which can be written as a function of single site occupation probability:

$$\begin{aligned} F = & -\frac{1}{2} \sum_r \sum_{r'} [V_{AB}(r-r') P_A(r) P_B(r') + \\ & V_{BC}(r-r') P_B(r) P_C(r') + V_{AC}(r-r') P_A(r) P_C(r')] + \\ & k_B T \sum_r [P_A(r) \ln(P_A(r)) + P_B(r) \ln(P_B(r)) + \\ & P_C(r) \ln(P_C(r))] \end{aligned} \quad (2)$$

where the effective pair interaction $V_{\alpha\beta}$ is deduced from pair interaction $\omega_{\alpha\beta}$ and $V_{\alpha\beta} = \omega_{\alpha\alpha} + \omega_{\beta\beta} - 2\omega_{\alpha\beta}$.

Equation (1) is solved in the reciprocal space using the Modified Euler's method with the time increment equal to 0.0002. The real-space atomic site occupation

probability of alloying elements is obtained by the Back-Fourier transformation of the solution of Eq. (1). The effective pair interactions (meV/atom), which have been used by PODURI and CHEN [14] and ZAPOLSY et al [21] in previous works and proved to fit for the real Ni–Al–V alloy system at a high temperature, are used as our simulation inputs. The applications of microscopic phase-field model on microstructure evolution of Ni-based alloys had shown an excellent agreement both with experiment results [21] and other simulation results [13].

3 Results and discussion

Ni₇₅Al_{7.5}V_{17.5} aged at 1185 K was simulated using microscopic phase-field model, and microstructure evolution during phase transformation is shown in Fig. 1. In Fig. 1, black sites represent Ni, gray sites represent V and white sites represent Al. L₁₂-Ni₃Al phases precipitate from the disordered phase first. And then, accompanying the formation and growth of L₁₂ ordered domains, V atoms start to segregate to the interfaces of L₁₂ ordered phase while the Al atoms deplete from the interfaces. As the degree of V segregation at the interfaces increases, the DO₂₂-Ni₃V ordered domains start to nucleate and grow at the interfaces of the L₁₂ ordered phase. At last, a two-phase mixture is formed.

Figure 2 gives the volume fraction variation of L₁₂ and DO₂₂ phases during aging process. The volume of L₁₂ phase decreases accompanied with the volume of DO₂₂ phase increasing. This verifies that DO₂₂ phases grow up at the expense of L₁₂ phases after DO₂₂ phases precipitate at the interfaces. As the volume of L₁₂ phase decreases, Ni and Al will be spared from the decreasing L₁₂ phase, whereas the growth of DO₂₂ phase needs Ni and V. It has been reported that the content of Ni in L₁₂ phase is slightly higher than that in DO₂₂ phase, and the concentration of ternary addition V is about 10% (mole fraction) in L₁₂ phase [21]. Thus, the Ni spared by the decreasing L₁₂ phase can satisfy the need of Ni for DO₂₂ growth, and part of V for DO₂₂ growth can be supplied from the decreasing L₁₂ phase. However, where does the other V come from to satisfy the growth of DO₂₂, and where does the Al go away when the volume of L₁₂ phase decreases? To answer this question, content evolution of alloying elements in L₁₂ phase was studied.

Considering the L₁₂ phase in the vicinity of interface will transform into DO₂₂ phase, only the content evolution of alloying elements in the centre part of L₁₂ phase (as the square denoted by arrow A in Fig. 1(f)) was investigated. Figure 3 shows that contents of Ni and Al in L₁₂ phase increase and content of V decreases during the phase transformation. The content of

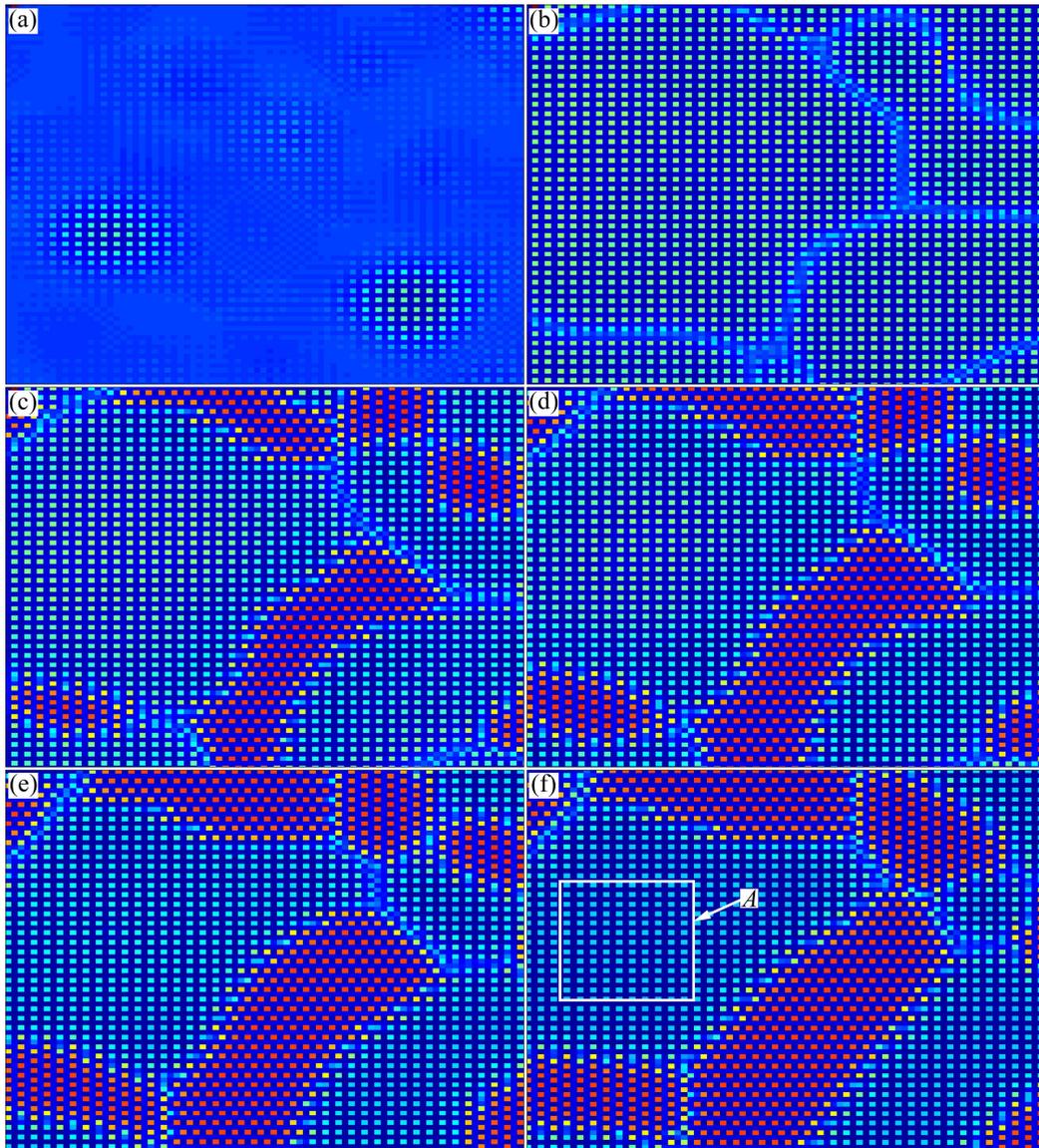


Fig. 1 Microstructure evolution during phase transformation from disordered (FCC-A1) phase to ordered (L1₂ and DO₂₂) phase of Ni₇₅Al_{7.5}V_{17.5} aged at 1185 K: (a) $t=8000$; (b) $t=20000$; (c) $t=70000$; (d) $t=100000$; (e) $t=200000$; (f) $t=400000$

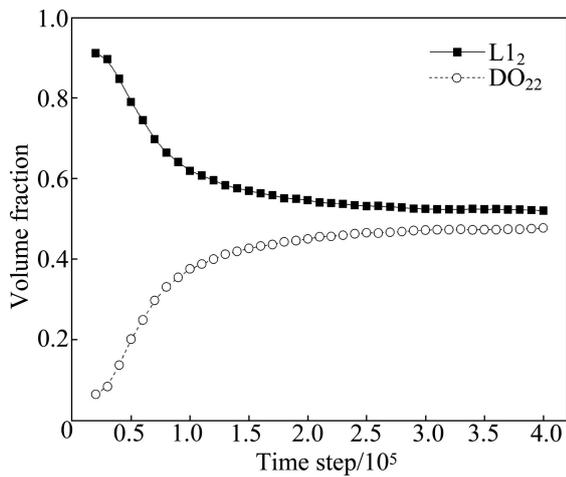


Fig. 2 Volume fraction variation of L1₂ and DO₂₂ phases of Ni₇₅Al_{7.5}V_{17.5} aged at 1185 K

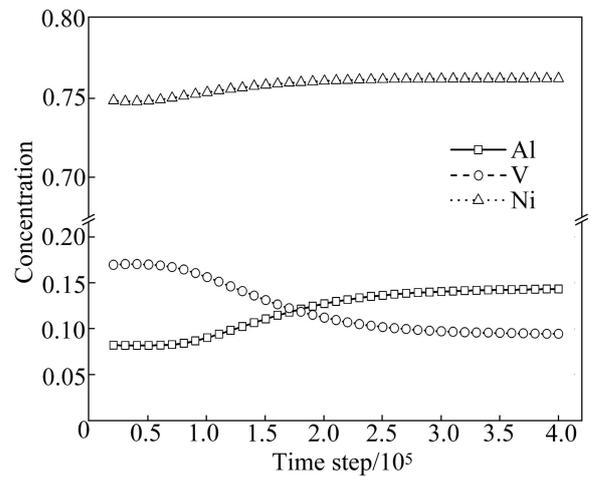


Fig. 3 Composition evolution of centre part of L1₂ phase in Ni₇₅Al_{7.5}V_{17.5} aged at 1185 K

V is higher than that of Al in the centre of $L1_2$ phase first, and it is reversed at later. This illustrates that part of V for growth of DO_{22} phase can be supplied from the centre of $L1_2$ phase, and the Al and Ni spared from decreasing $L1_2$ phase migrate from the interface to the centre of $L1_2$ phase.

Figure 4 illustrates the relationship between volume fraction of DO_{22} phase and composition of $L1_2$ phase. From Fig. 4, the growth of DO_{22} phase can be divided into two stages. At the early stage, volume fraction of DO_{22} phase increases from about 0.05 to 0.35 quickly, and the composition of the centre part of $L1_2$ phase almost remains unchanged. As mentioned above, the decreasing of $L1_2$ phase cannot supply enough V for the growth of DO_{22} phase. However, V segregates at the interface of $L1_2$ phase, and the amount of interfaces between $L1_2$ phases decreases quickly with the nucleation and growth of DO_{22} phase. Thus, the V for growth of DO_{22} phase at the early stage is supplied from both the decreasing $L1_2$ phase and interfaces between $L1_2$ phases. At the late stage, volume fraction of DO_{22} phase grows up slowly from 0.35 to about 0.48, accompanied with the contents of Al and Ni increasing, and content of V decreasing in the centre part of $L1_2$ phase. This implies that the growth of DO_{22} phase at the late stage is controlled by the content evolution of alloying elements in the centre part of $L1_2$ phase.

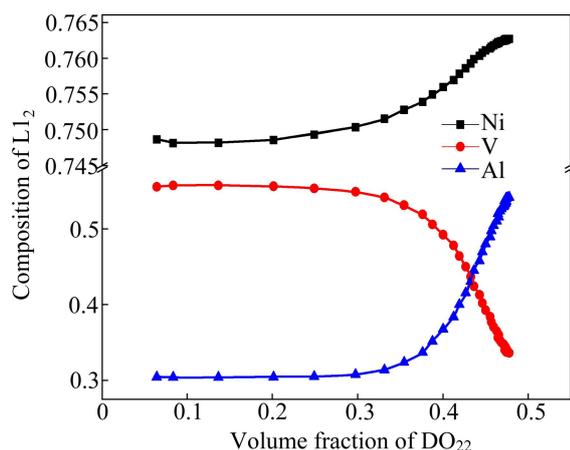


Fig. 4 Variation of composition of $L1_2$ phase with volume fraction of DO_{22} phase in $Ni_{75}Al_{7.5}V_{17.5}$ aged at 1185 K

As the $L1_2$ phase consists of two sublattices, content evolution of alloying elements at both Ni and Al sublattices in the centre of $L1_2$ phase was studied. Figure 5 shows that the ternary addition V prefers to occupy the Al sublattice, which is in consistent with the previous study [22]. As the DO_{22} phase grows up, the content of host atoms Al_{Al} (Al_{Al} denotes the Al atom at the Al sublattice) and Ni_{Ni} increase, the contents of ternary additions of V_{Ni} and V_{Al} decrease, and content of antisite atoms Ni_{Al} decreases but that of Al_{Ni} increases.

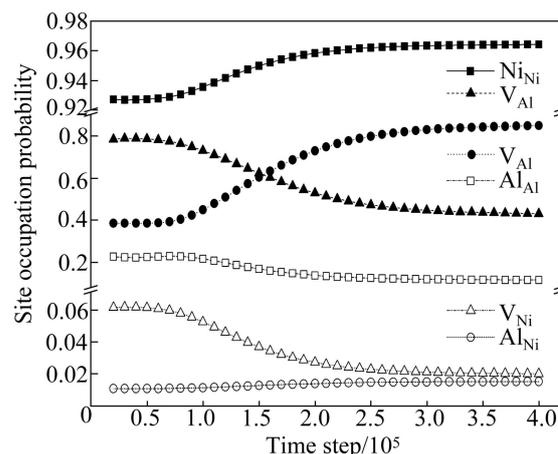


Fig. 5 Site occupation of alloying elements in $L1_2$ phase during phase transformation from $L1_2$ to DO_{22} in $Ni_{75}Al_{7.5}V_{17.5}$

The site occupation decrement of Ni_{Ni} is larger than the site occupation decrement of Ni_{Al} , thus content of Ni in the centre of $L1_2$ phase increases. This demonstrates that the excess Ni from decreasing $L1_2$ phase occupies the Ni sublattice. The site occupation decrement of V_{Ni} is less than that of V_{Al} , and the site occupation increment of Al_{Ni} is less than that of Al_{Al} . This demonstrates that part of V for growth of DO_{22} phase supplied from the centre of $L1_2$ phase mainly comes from Al sublattice, and Al from decreasing $L1_2$ phase mainly occupies the Al sublattice. Considering the discussion above, it can be concluded that the growth of DO_{22} phase is mainly controlled by the decrease of interface between $L1_2$ phases at the early stage, but at the late stage, it is mainly controlled by the evolution of antisite atoms and ternary additions in the centre part of $L1_2$ phase.

4 Conclusions

1) Correlation between site occupation evolution of alloying elements in $L1_2$ phase and volume of DO_{22} phase indicates that the process of growth of DO_{22} phase can be divided into two stages.

2) At the early stage, composition in the centre part of $L1_2$ phase almost remains unchanged, and the nucleation and growth of DO_{22} phase is controlled by decrease of interface between $L1_2$ phases. At the late stage, the growth of DO_{22} phase is controlled by site occupation evolution of alloying elements in the centre part of $L1_2$ phase.

3) At the late stage, Ni and Al spared from decreasing $L1_2$ phase migrate from the interfaces between $L1_2$ and DO_{22} phases to the centre of $L1_2$ phase, and the excess Ni exclusively occupies the Ni sublattice and Al mainly occupies the Al sublattice. Part of V for growth of DO_{22} phase is supplied from the centre part of $L1_2$ phase and mainly comes from Al sublattice.

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Ni₇₅Al_{7.5}V_{17.5} 相变过程中 L1₂ 相合金元素占位几率演化的微观相场模拟

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摘 要: 基于微观相场模型, 研究 Ni₇₅Al_{7.5}V_{17.5} 合金在相变过程中 L1₂ 相内合金元素演化与 DO₂₂ 相生长之间的关系。研究表明, 在 L1₂ 相向 DO₂₂ 相转变的过程中, DO₂₂ 相的长大可以分为两阶段。在早期, L1₂ 相内合金元素的成分基本不变, DO₂₂ 相的长大主要受 L1₂ 相间有序畴界的减少所控制。在后期, DO₂₂ 相长大所需的 V 一部分来自 L1₂ 相内部, 一部分来自 L1₂ 相体积的减少, 其中, 相内部为 DO₂₂ 相长大所提供的 V 则主要来自 Al 格点位置, 由于 L1₂ 相体积减少而富余的 Al 向 L1₂ 相内部扩散迁移并主要占据 Al 格点位置, 富余的 Ni 则同时向 L1₂ 相内部和 DO₂₂ 相内部扩散, 主要占据 L1₂ 相的 Ni 位置。DO₂₂ 相长大的后期主要受 L1₂ 相内反位缺陷和第三组元的演化所控制。

关键词: 镍基合金; Ni₇₅Al_{7.5}V_{17.5} 合金; 相变; 微观相场; 晶粒生长; 反位缺陷

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