Phase field simulation of interatomic potentials for double phase competition during early stage precipitation

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Phase field model was employed to study the variations of interatomic potentials of Ni3Al (L12 phase) and Ni3V (DO22 phase) as a function of temperature and concentration. The long-range order (LRO) parameter related interatomic potentials equations formulated by Khachaturyan were utilized to establish the inversion equations for L12 and DO22 phases, with which interatomic potentials could be calculated. The interatomic potentials of Ni-Al and Ni-V exhibited approximately linear increases and decreases, individually, with enhanced Al concentration. Substituting the inverted interatomic potentials into the microscopic phase field equations led to three cases of precipitation sequence: the DO22 phase preceded L12 phase precipitating at the interatomic potentials of Ni-V > Ni-Al; the vice cases; and two phases precipitated simultaneously at interatomic potentials of Ni-V and Ni-Al were equal.

Phase field model, L12 and DO22 phases, interatomic potentials, double phase competition

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Phase transformation involves atomic diffusion and clustering, which occurs under potential energy produced external changes. During solid-state phase transformation, the product phase often nucleates and forms at the interface of the parent phase. Multiple-phase mixtures are likely coexisting in multiple component alloys, which precipitate sequentially and form first or second-phase precipitates during the early stages of precipitation [1]. Ni-Al-V alloy, which two ordered phases are produced at different temperatures and composition, is a typical alloy exhibiting this behavior. When Ni-Al-V alloy is quenched into a miscibility gap, a coherent mixture of disordered face-centered cubic (FCC) matrix, DO22 phase and L12 phase develop. Because of the differences in interatomic potentials and nucleation mechanism of these two phases, their precipitation sequences will differ accordingly. Lattice mismatch between L12 and DO22 is minimal, and their atomic arrangement is similar, thus they can coexist at lattice interfaces.

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lattice structure, the most straightforward approximated form of the interatomic potentials is to break the lattice structure into atomic pair potentials. The study concerning interatomic potentials-composition relation which is closely related with each other has been draw attention from both experimental and theoretical point of view. The concentration dependence properties of an intermetallic compound are predominantly demonstrated by concentration dependent interatomic potentials. Hu et al. [8] obtained phase transformation samples of TiAl alloy after continuous cooling by quenching and air cooling, and showed that the phase transformation microstructures were related to alloy composition. Li et al. [9] studied alloy phases using X-ray and electron microscopy methods, and demonstrated that the volume fractions of γ' and β phases depended on double phase competition which was explained by nucleation dynamics and dendritic growth. Liu et al. [10] performed a super-cooling conditions experiment, illuminating the existence of phase competition in growth processes and multiple phase nucleations by which the formation of a second-phase between equilibrium and metastable phases was explained. Kim et al. [11] investigated interface properties as well as interfacial-misfit energies using modified analytic embedded atom method (MEAM) potential energies, which were consistent with first principles prediction under the same conditions. Pasianot et al. [12] developed an interatomic potentials method for evolutional microstructure and point defects of the Fe-Cu system based on the embedded atom method (EAM) method. Liubich et al. [13] discussed the relationship between double phase competition and composition with the concentration wave (CW) method, and showed that interaction parameters of the disordered A2 and stable B2 phases depending on atomic concentration.

In this study, phase field theory and the CW method were combined to calculate the concentration-dependence of atomic interactions. The precipitation sequences of DO22 and L12 competitive system of Ni52Al, V25Al alloy were evaluated using these interatomic potentials.

1 Theoretical model

1.1 Microscopic phase field model

The phase field dynamic equation is based on the Onsager and Ginzburg-Landau theory, which is written as

$$\frac{\partial P(\bar{r}, t)}{\partial t} = \sum_{r'} L(\bar{r} - \bar{r}') \frac{\delta F}{\delta P(\bar{r}', t)}.$$

This describes the atomic configuration and precipitation sequence of ordered phases using the occupation probability $P(\bar{r}, t)$ at the crystal lattice site $\bar{r}$, and the time $t$, whose change rate is proportional to the variation in free energy. $L(\bar{r} - \bar{r}')$ is a constant related to exchange probabilities of a pair of atoms at lattice site $r$ and $r'$ per unit time. $F$ is the free energy. For the ternary system, which the author only considers the response of the integrated lattice to atomic diffusion, the occupation probabilities satisfy

$$P_A(\bar{r}, t) + P_B(\bar{r}, t) + P_C(\bar{r}, t) = 1,$$

where the subscripts $A$, $B$, and $C$ designate three kinds of atoms. According to eq. (2), the following equations can be obtained:

$$\frac{dP_A(\bar{r}, t)}{dt} = \frac{1}{k_B T} \sum_{r'} \left[ L_{AA}(\bar{r} - \bar{r}') \frac{\delta F}{\delta P_A(\bar{r}', t)} + \zeta_1(\bar{r}, t) \right],$$

$$\frac{dP_B(\bar{r}, t)}{dt} = \frac{1}{k_B T} \sum_{r'} \left[ L_{BB}(\bar{r} - \bar{r}') \frac{\delta F}{\delta P_B(\bar{r}', t)} + \zeta_2(\bar{r}, t) \right].$$

In the mean-field approximation, the free energy for the ternary system is given by

$$F = -\frac{1}{2} \sum_{r} \left[ (-V_{ab}(\bar{r} - \bar{r}') + V_{ac}(\bar{r} - \bar{r}') + V_{bc}(\bar{r} - \bar{r}') + V_{ac}(\bar{r} - \bar{r}') P_A(\bar{r}') + V_{ac}(\bar{r} - \bar{r}') P_B(\bar{r}') + V_{bc}(\bar{r} - \bar{r}') P_A(\bar{r}') P_B(\bar{r}') + k_B T \sum_P \left[ P_A(\bar{r}) \ln P_A(\bar{r}) + P_B(\bar{r}) \ln P_B(\bar{r}) + (1 - P_A(\bar{r}) - P_B(\bar{r})) \ln (1 - P_A(\bar{r}) - P_B(\bar{r})) \right] \right].$$

where the first sum represents the chemical energy, the second represents the thermal dynamic energy of the system, and $k_B$ is the Boltzmann constant, $T$ is temperature. The effective interaction energy $V_{ab}(\bar{r} - \bar{r}')$ is given as

$$V_{ab}(r - r') = W_{aa}(r - r') + W_{bb}(r - r') - 2W_{ab}(r - r'),$$

where $W_{aa}$, $W_{bb}$ and $W_{ab}$ are the pairwise potentials between $a-a$, $b-b$, and $a-b$, respectively, and $V_{ab}$ corresponds to the interaction energy. The four nearest neighbor interaction energies are adopted to maintain reliability of the simulation. The first-nearest ($V_{ab}^{1}$), second-nearest ($V_{ab}^{2}$), third-nearest ($V_{ab}^{3}$) and fourth-nearest ($V_{ab}^{4}$) interaction energies are substituted into the FCC reciprocal space:

$$V_{ab}(k) = 4V_{ab}^{1}\cos \pi k \cdot \cos \pi l + \cos \pi k \cdot \cos \pi l + 2V_{ab}^{2}\cos 2\pi k + \cos 2\pi l + 8V_{ab}^{3}\cos 2\pi k \cdot \cos 2\pi l + \cos \pi k \cdot \cos \pi l + 4V_{ab}^{4}\cos 2\pi k + \cos 2\pi k \cdot \cos 2\pi l + \cos 2\pi k \cdot \cos 2\pi l.$$
where \( k, h \) and \( l \) are reciprocal lattice sites obtained from

\[
\tilde{k} = (k_x, k_y, k_z) = h\tilde{a}_x^* + k\tilde{a}_y^* + l\tilde{a}_z^*,
\]

where \( \tilde{a}_x^*, \tilde{a}_y^*, \tilde{a}_z^* \) are the unit reciprocal lattice vectors of the FCC structure along three directions.

### 1.2 Interatomic potentials

Equations for interatomic potentials evaluation were first proposed by Khachaturyan [14]. Their relation to the occupation probability of solute atoms (B atoms) and free energy were determined based on CW equations as follows:

\[
c(1+\eta_i + \eta_j) = \left[\exp\left(-\mu + c \cdot V(0) - c \cdot V(k_i) \cdot \eta_i \cdot E_s(r)\right) + 1\right]^{-1},
\]

\[
(9)
\]

where \( c \) is the atomic concentration of solute \( B \), \( \eta_i \) is the LRO parameter, \( E_s(r) \) is a function associated with lattice symmetry, \( \mu \) is the chemical potential, \( t-1 \) indicates the number of non-zero vector \( k_i \) in the superlattice structure, and \( V(0) \) the potential energy of disordered atoms, \( V(k_i) \) is the potential energy of ordered atoms.

The occupation probability and energy of the L12 phase can be related according to eq. (8):

\[
c(1-\eta_i) = \left[\exp\left(-\mu + c \cdot V(0) - c \cdot V(k_i) \cdot \eta_i \cdot E_s(r)\right) + 1\right]^{-1},
\]

\[
(10)
\]

The combination of eqs. (9) and (10) and subsequent simplification leads to an equation relating \( V_{ab} \) and the LRO parameter:

\[
-4V_{ab} \cdot \eta_i = \ln \left(1-\eta_i\right) - \ln \left(1+c(1+3\cdot\eta_i)\right)
\]

\[
(11)
\]

This equation can be used to calculate \( V_{ab} \) of the L12 phase at different temperatures and atomic concentrations.

In a similar manner, the occupation probability and energy of the DO22 phase can be related based on eq. (8):

\[
c(1+\eta_i + 2\eta_j) = \left[\exp\left(-\mu + c \cdot V(0) + c \cdot V(k_i) \cdot \eta_i + 2V(k_j) \cdot \eta_j\right) + 1\right]^{-1},
\]

\[
(12)
\]

\[
c(1+\eta_i - 2\eta_j) = \left[\exp\left(-\mu + c \cdot V(0) + V(k_i) \cdot \eta_i - 2V(k_j) \cdot \eta_j\right) + 1\right]^{-1},
\]

\[
(13)
\]

An equation relating \( V_{ab} \) to the LRO parameters can be obtained by combining eqs. (12)–(14), followed by simplification:

\[
-2V_{ab} \cdot \eta_i = \ln \left(1-c(1+\eta_i + 2\eta_j)\right) - \ln \left(1-c(1-\eta_i)\right) \left(1+\eta_i + 2\eta_j\right).
\]

Similarly, the first nearest neighbor interatomic potentials \( V_{ab} \) of the DO22 phase under varying temperature and atomic concentration can be calculated using eq. (15).

These equations were applied to the Ni53Al, V25−x alloy study. Such equations overcome the deficiencies of conventional models which ignore the impact of temperatures and concentrations using only fixed interatomic potentials in a computation.

### 2 Computational results

#### 2.1 Interatomic potentials

\( V_{ab} \) values for the L12 phase (Ni-Al) with different temperatures and concentrations are obtained by solving eq. (11). Interatomic potentials are measured at a constant temperature of 1000 K with different Al (L12) or V (DO22) concentrations, and plot against the long-range order (LRO) parameter (Figure 1(a) is for L12, and Figure 1(b) for DO22). The curves increase gradually at comparatively low LRO parameter, but increase dramatically when the LRO parameter approaches one. One likely explanation for this phenomena is that the calculation of interatomic potentials is based on the integrated nucleated L12 phase from which the interatomic potentials are obtained by optimizing the mean interatomic potentials at the LRO parameter range of 0.95–0.99. The Ni-Al interatomic potentials increase with Al concentration ranging from 3–9 at.% (Figure 1(a)). For the DO22 phase, the Ni-V interatomic potentials increase with enhanced LRO parameter and enhanced V level (16–22 at.%). Similar to the L12 phase, the calculation of interatomic potentials for DO22 phase is based on the integrated nucleated DO22 phase from which the interatomic potentials are obtained by optimizing the mean interatomic potentials at the LRO parameter range of 0.95–0.99.

With the temperature holding as a constant at 1000 K, the interatomic potentials obtained at different atomic concentrations are listed by Table 1. \( V_{ab} \) for L12 phase increase from 112.89 to 128.60 meV as Al concentrations increase from 2 at.% to 14 at.%, While \( V_{ab} \) for DO22 phase decrease from 132.20 to 100.51 meV as the V concentrations decrease from 23 at.% to 11 at.%, which indicates that interatomic potentials of L12 will increase with enhanced Al level.
Figure 1  Interatomic potentials versus LRO parameter for (a) Ni-Al and (b) Ni-V, at different Al concentrations.

Table 1  Variation of interatomic potentials with concentration for L12 and DO22 phases

| c_Al (at.%) | c_V (at.%) | V_{L12}^{abV} (meV) | V_{DO22}^{abV} (meV) |
|------------|------------|----------------------|----------------------|
| 2          | 23         | 112.89               | 132.20               |
| 6          | 19         | 116.99               | 116.52               |
| 10         | 15         | 122.04               | 107.19               |
| 14         | 11         | 128.60               | 100.51               |

but decrease with enhanced V concentration in Ni_{75}Al_{25−x}V_{25−x} alloy. As a contrast, the interatomic potentials of DO_{22} phase will decrease with enhanced Al level but increase with enhanced V level. The computed values of this work approach to the results reported by Chen et al. [3, 4] which V_{abV}^{L12}=122.30 and 107.2 meV for respective L12 and DO_{22} phases for 10 at.% Al alloy, which inverses verified the credibility of the model we employed. We then substitute the computed interatomic potentials into the microscopic phase field for further simulation.

2.2 The microstructure morphology and volume fraction

The precipitation sequence is closely related to the interatomic potentials. In this study, we employ the evolutional microstructure morphology and volume fraction of the two competitive L12 and DO_{22} phases, at the early stage of precipitation for different Al concentrations, exploring precipitation sequence-interatomic potentials relation. At a constant temperature of 1000 K, the evolutional microstructure morphology of the L12 and DO_{22} phases of Ni_{75}Al_{25−x}V_{25−x} alloy with enhanced Al level is illustrated by Figure 2. The DO_{22} phase precipitates first at a 4 at.% Al alloy (Figure 2(a)), and L12 phase precipitates gradually at the boundary of DO_{22} phase with time proceeds. L12 and DO_{22} phases precipitate simultaneously at a 6 at.% Al alloy (Figure 2(b)), and the two phases grow competitively with time proceeds. L12 phase precipitates first and the DO_{22} phase precipitates later at the phase boundary of L12 at 8 at.% Al alloy, which is shown as Figure 2(c) and (f).

The evolutional curves of the volume fractions for L12 phase and DO_{22} phase in a Ni_{75}Al_{25−x}V_{25−x} alloy aging at 1000 K are presented in Figure 3. As to a 4 at.% Al alloy, the system at the beginning which is known as the gestation stage (incubation period) (Figure 3(a)) is disordered, and the volume fraction for both L12 phase and DO_{22} phase are almost zero. With time proceeds, the volume fraction of DO_{22} phase increases rapidly, and then a steadily decreasing decrease till the ordered stage, and attains equilibrium gradually. The volume fraction for L12 phase increases after the formation of the DO_{22} phase, which indicates that the L12 phase has a longer gestation stage than DO_{22}. This result is in good agreement to the first-phase precipitation of DO_{22} at a 4 at.% Al alloy(Figure 2(a)). The final equilibrium volume fraction of DO_{22} is larger than that of the L12 phase (Figure 3(a)), which suggests that DO_{22} is dominated the Ni_{75}Al_{21}V_{21} system. And this also is testified by microstructure morphology in Figure 2(d). With respect to a 6 at.% Al alloy (Figure 3(b)), the volume fractions of DO_{22} and L12 increase simultaneously and rapidly indicating the drastically growth and compotation of the two ordered phases, and the two approach equilibrium rapidly with time proceeds. This phenomenon is consistent with the microstructure morphology at the 6 at.% Al alloy (Figure 2(b) and 2(e)). When the Al concentration is enhanced till 8 at.%, the volume fraction of L12 increases quickly at the initial stage, and grows quickly into a stable ordered phase, then finally approaches equilibrium (Figure 3(c)), all of which is in line with microstructure morphology within the same concentration (Figure 2(c)). The final equilibrium values were approximately the same for the two phases, which is in agreement with the results in Figure 2(f).

3 Discussion

The interatomic potentials curves (Figure 4) are applied to investigate the variations of precipitation sequence with Al concentration ranging from 1 to 21 at.%. The Ni-Al interatomic potentials increase in an approximately linear manner with enhanced Al level, at constant 1000 K (solid line, Fig-
Figure 2 Variation of interatomic potentials with Al concentration ($c_{Al}$) and time step ($t'$). (a), (d) $c_{Al} = 4$ at.%, (b), (e) $c_{Al} = 6$ at.% and (c), (f) $c_{Al} = 8$ at.%. 

Figure 3 Volume fraction of Ni$_{75}$Al$_{25-x}$V$_x$ alloy as a function of Al concentrations (a) 4, (b) 6 and (c) 8 at.%. 

Figure 4 Variation of interatomic potentials with atomic concentrations at (a) 1000 and (b) 1100 K. 

ure 4). Similarly, the Ni-V interatomic potentials decrease linearly with enhanced Al level (dashed line, Figure 4). The two curves have an intersection at 6 at.% Al alloy, where the interatomic potentials of Ni-Al equal to those of Ni-V. On the left side of this intersection, the dashed line is greater than the solid line, which implied the interatomic potentials of Ni-Al were larger than those of Ni-V. On the right of the intersection, the solid line is greater than the dashed line, which indicates the interatomic potentials of Ni-V are larger than those of Ni-Al. Similar curves were obtained at concentrations range from 1 at.% to 21 at.%, at 1100 K (Figure 4(b)). The two curves intersect at a different concentration (5 at.% Al) with that of 1000 K, however. For this case, the interatomic potentials of Ni-Al and Ni-V are equal at the 5 at.% Al alloy. With the enhanced Al level, the Ni-Al interatomic potentials increase while Ni-V interatomic potentials decrease, individually.

Based on the above analysis, the following precipitation
patterns are evident: the first precipitated phase is DO$_{22}$ (Figure 2(a)) for a 4 at.% Al alloy, which is contributed to the higher interatomic potentials of Ni-V than those of Ni-Al (Figure 4(a)). L$_1$2 and DO$_{22}$ phases precipitate simultaneously for 6 at.% Al alloy (Figure 2(b)), which occur due to the equality of the interatomic potentials of the two phases (Figure 4(a)). The L$_1$2 phase precipitates first for the 8 at.% Al alloy (Figure 2(c)) attributing to the interatomic potentials of Ni-Al are higher than those of Ni-V (Figure 4(a)). In summary, the precipitation sequences for the two phases were closely associated with the interatomic potentials.

### 4 Conclusions

The equations for interatomic potentials for L$_1$2 and DO$_{22}$ phases are formulated according to the relationship equations proposed by Khachaturyan. These equations are then applied to computed the interatomic potentials of Ni-Al (L$_1$2 phase) and Ni-V (DO$_{22}$ phase) with varying temperature and concentration. The computed results are in good agreement with the experimental results, which verifies the reliability of the results.

Both interatomic potentials vary in an approximately linear manner with enhanced Al level, which the interatomic potentials for Ni-Al increase but those for Ni-V decrease. The microstructure morphology and temporal evolutionary volume fraction for the two phases are obtained by substituting the interatomic potentials into microscopic phase field theory, which shows that the competitive precipitation sequence of the phases relate to the interatomic potentials closely. The Ni-V interatomic potentials are larger than those of Ni-Al when the Al concentration is smaller than 6 at.%, and DO$_{22}$ phase precipitates first and incubates shorter than the L$_1$2 phase. The Ni-Al interatomic potentials are larger than those of Ni-Al when the Al concentration is greater than 6 at.%, and L$_1$2 phase precipitates first with a shorter gestation stage than DO$_{22}$. At 6 at.% Al concentration, the interatomic potentials are equal leading to the two phases simultaneous precipitation of L$_1$2 and DO$_{22}$ phases.

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1. Li L, Lu X Y, Cao C D, et al. Solidification microstructure and phase constitution of Fe-7.5%Mo-16.5%Si ternary quasiperitectic alloy (in Chinese). Chinese Sci Bull, 2009, 54: 2108–2112
2. Pareige C, Blavette D. Simulation of the FCC→FCC+L12→DO22 kinetic reaction. Scrip Mater, 2001, 44: 243–247
3. Poduri R, Chen L Q. Computer simulation of atomic ordering and copositional clustering in the Pseudobinary Ni$_3$Al-Ni$_3$V system. Acta Mater, 1998, 46: 1719–1729
4. Zapolsky H, Pareige C, Marteau L, et al. Atom probe analyses and numerical calculation of ternary phase diagram in Ni-Al-V system. Calphad, 2001, 25: 125–134
5. Li Y S, Chen Z, Lu Y L, et al. Microscopic Phase-Field simulation of coarsening behavior of precipitates in Ni$_3$Al$_{25-x}$V$_{25-x}$ alloy (in Chinese). Acta Metall Sin, 2006, 42: 239–244
6. Li Y S, Chen Z, Lu Y L, et al. Microscopic phase-field simulation for nucleation incubation time of Ni$_3$Al$_{25-x}$V$_{25-x}$ alloy. J Cent South Univ Technol, 2005, 12: 635–640
7. Hou H, Zhao Y H, Chen Z, et al. Prediction for the early precipitation progress of Ni$_3$Al$_{25-x}$V$_{25-x}$ system with lower Al concentration by the Phase-Field model (in Chinese). Acta Metall Sin, 2005, 41: 695–702
8. Hu D, Huang A J, Wu X. On the massive phase transformation regime in TiAl alloys: The alloying effect on massive/lamellar competition. Intermetallics, 2007, 15: 327–332
9. Li Q, Tang Y L, Shen N F, et al. Effects of solidification kinetics on phase selection of Ni-Al alloys. J Alloy Compd, 2001, 329: 157–161
10. Liu Y C, Yang G, Zhou Y H. Phase competition in the undercooled hypoperitectic Ti$_{17}$Al$_{53}$ alloy. Mater Lett, 2002, 57: 315–324
11. Kim H K, Jung W S, Lee B J. Modified embedded-atom method interatomic potentials for the Fe-Ti-C and Fe-Ti-N ternary systems. Acta Mater, 2009, 57: 3140–3147
12. Pasianot R C, Malerba L. Interatomic potentials consistent with thermodynamics: The Fe-Cu system. J Nucl Mater, 2007, 360: 118–127
13. Liubich V, Dorfman S, Fuks D. Non-empirical study of phase competition in A2-B2 mixture in Fe-Al alloy. Comput Mater Sci, 2002, 24: 268–272
14. Khachaturyan A G. Theory of Structural Transformation in Solids. New York: Wiley, 1983

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