

# EFFECT OF ELASTIC INTERACTION ENERGY ON THE SPINODAL DECOMPOSITION AND LATER COARSENING STAGE IN Fe-20%Mo ALLOYS

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**Abstract.** Effect of elastic interaction energy on the spinodal decomposition and subsequent coarsening stage in Fe-20%Mo alloys is systematically investigated by microscopic phase field kinetic model of considering elastic interaction energy. The results show that modulated wavelength and critical time (the time between spinodal decomposition and coarsening stage) decrease with increasing elastic interaction energy. During coarsening stage, macrolattice and basket-weave structures are formed by regular distribution of atom enrichment phases. Average size cubic of atom enrichment phases is not in accord with single linear relation, which is broken gradually with the increase of elastic interaction energy. Therefore, coarsening mechanism is not the single Ostwald ripening but interplay of Ostwald ripening and coalesce growth mechanism. With increasing elastic interaction energy, the size and number of atom enrichment phases along [01] or [10] direction increase. The simulation results are in accord with transmission electron microscopy (TEM) image aged for 5 h in Fe-20%Mo alloys.

## 1. INTRODUCTION

Spinodal decomposition is an effective phase transformation ways to obtain nanometer coherent microstructures, which has been found in nickel based high-temperature alloy, Al-Li alloy, Cu-Ti alloy, Fe-Mo alloy and maraging steel [1,2]. It is well known that an extensive atomic or lattice rearrangement between same type atoms towards a stable equilibrium state corresponding to a minimum free energy is induced by thermodynamic driving forces during spinodal decomposition. Several metastable or transient morphological structures are formed in this process. Therefore, investigations of microstructure evolution during spinodal decomposition have been a subject of wide interest in materials science in past years.

Different elaborate coherent phases were observed by experiment method in alloys [3]. How-

ever, the internal relations between different coherent phases and elastic interaction energy have been not explained. Theoretical investigations about effect of elastic interaction energy on a multi-phase morphology could be traced back to Cahn classical spinodal decomposition theory, and the theory was about initial stage of spinodal decomposition in a cubic alloy [4]. The linear diffusion equation which considered elastic interaction energy contribution was solved by Cahn, and the results showed that spinodal decomposition occurred by developing concentration waves along elastic soft direction firstly in elastic anisotropic alloys. The satellites near Bragg reflections along elastic soft direction in reciprocal space were formed by concentration waves. The Cahn spinodal decomposition theory showed that coherent elastic interaction energy resulted in the increase of total free energy. Therefore, spinodal

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decomposition was inhibited by increasing total free energy [5]. However, according to sphere-and-hole model of continuum elastic mechanics theory, Eshelby concluded that elastic interaction energy promoted spinodal decomposition [6]. Khachaturyan computed elastic interaction energy considering infinite radius interactions between atoms or phases, and a microscopic elasticity theory was founded. According to microscopic elasticity theory, elastic interaction energy was attributed to atom distribution and microstructure morphology in alloys, which was dynamic of spinodal decomposition [7].

Therefore, the objective of this paper is to investigate effect of elastic interaction energy on spinodal decomposition and subsequent coarsening stage in Fe-20%Mo alloys using a microscopic phase field kinetic model which considers long range elastic interaction energy. And the nonlinear dynamics of microstructure evolution during spinodal decomposition in Fe-20%Mo alloys is investigated systematically.

## 2. COMPUTER SIMULATION MODEL

### 2.1. Microscopic phase-field model

According to literatures [8-10], crystal lattice site diffusion of Fe-Mo binary alloys was determined by a diffusion relaxation of single-site occupation probability, which was represented by  $p(r,t)$ , the probability of finding an atom at a given time and given lattice site. The diffusion process during spinodal decomposition in Fe-20%Mo alloys was determined by Onsager equation:

$$\frac{dP(r,t)}{dt} = \frac{C_0(1-C_0)}{k_B T} \sum_{r'} L(r-r') \frac{\partial F}{\partial P(r',t)}, \quad (1)$$

where  $C_0$  was atomic fraction of solute atoms in Fe-20%Mo alloys,  $k_B$  was Boltzman constant,  $T$  was absolute temperature,  $L(r-r')$  was the kinetic coefficients which was related to probabilities of alloys atoms diffusion jumped from crystal lattice site  $r$  to  $r'$  during unit time, and  $F$  was total free energy including chemical interaction energy and elastic interaction energy. The summation over total lattice site was carried out. The conservation of atoms in the system presented a relation:

$$\sum_{r'} L(r-r') = 0. \quad (2)$$

### 2.2. Microscopic elasticity theory

According to microscopic elasticity theory, elastic interaction energy was related to spatial distribu-

tion of atoms and the volume of atom enrichment phases. The long range elastic interaction with an arbitrary atomic distribution  $p(r)$  was:

$$E_{el} = 1/2 \sum_r W(r-r') P(r) P(r'). \quad (3)$$

In the long wave approximation, the Fourier transform of  $W(r)_{el}$  was described as:

$$V(k)_{el} \approx B(\epsilon) = B(c_x^2 e_y^2 - 0.125), \quad (4)$$

$$B = -\frac{4(c_{11} + 2c_{12})^2}{c_{11}(c_{11} + c_{12} + 2c_{44})} \epsilon_0^2 \Delta. \quad (5)$$

In Eq. (5),  $\Delta = c_{11} - c_{12} - 2c_{44}$  was elastic anisotropy constant and  $c_{11}$ ,  $c_{12}$ ,  $c_{44}$  were elastic constants, which were  $c_{11} = 2274$  GPa,  $c_{12} = 1124$  GPa,  $c_{44} = 740$  GPa, respectively. The atomic size difference of Fe-Mo alloys was 0.089. The first, second and third nearest interatomic pair-potentials energies were, particularly, described by a set of values:

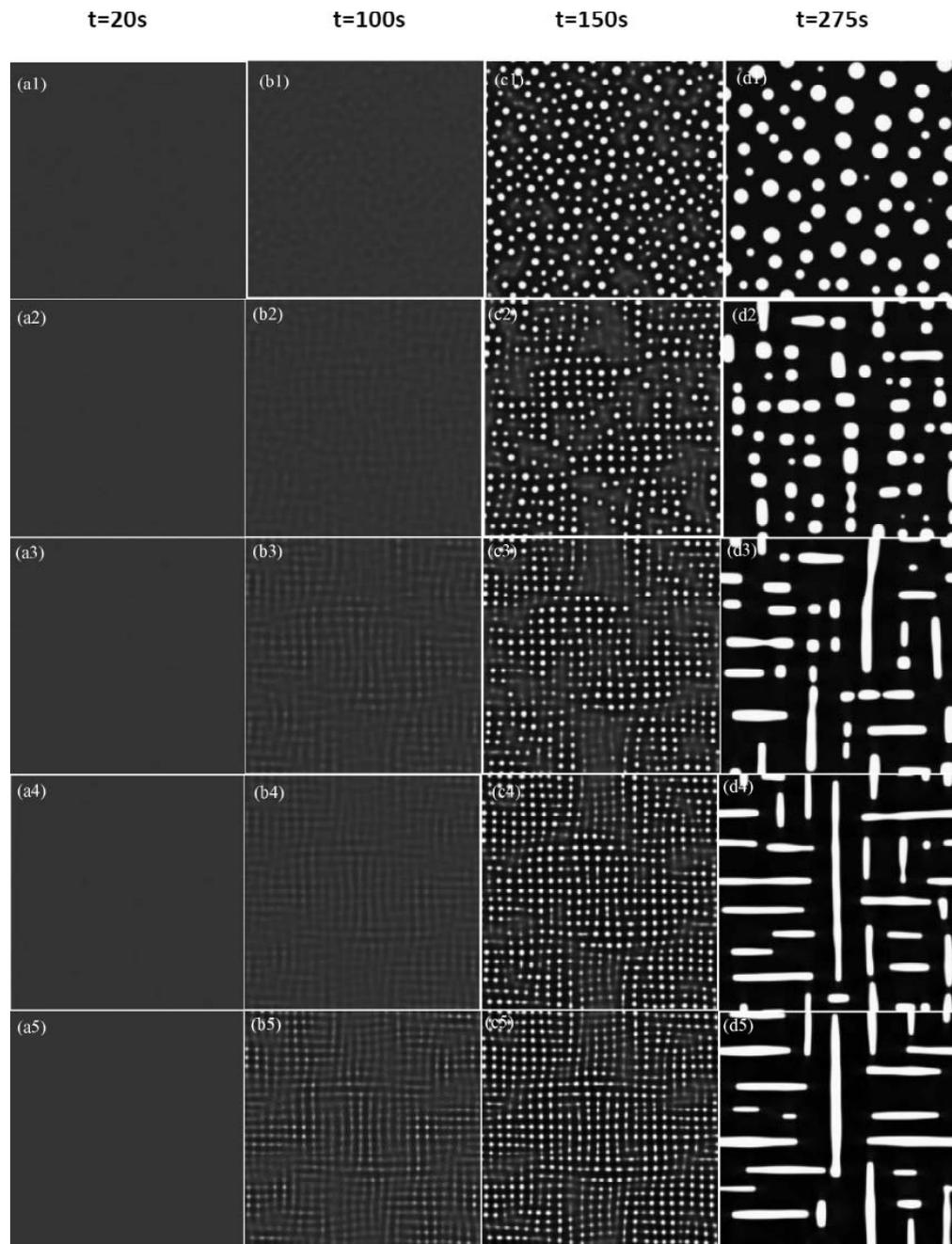
$$W_1 = -1.2 \text{ eV}, \quad W_2 = -0.9 \text{ eV}, \quad W_3 = -0.6 \text{ eV}.$$

The elastic constants were obtained by first-principle calculation, and Fe-Mo interatomic pair-potentials energy was computed by embedded atom method (EAM).

## 3. RESULTS

### 3.1. Microstructure evolution during spinodal decomposition and coarsening considering different elastic interaction energy in Fe-20%Mo alloys

Fig. 1 shows microstructure evolution during spinodal decomposition and coarsening in Fe-20%Mo alloys. The initial state atom images are presented in the first column of Fig. 1. As shown in Fig. 1 (a1) and (b1), concentration waves are observed in a random direction, and isotropic structures are formed during spinodal decomposition initial stage firstly. The concentration waves keep growing until atom occupation probabilities reach equilibrium concentrations, which leads to an obvious modulated structures, as shown in Fig. 1 (c1). At this stage, spinodal decomposition transformation has finished, and coarsening stage occurs. There are some considerable differences in concentration peak and modulated wavelength at this moment. Coarsening of the uniformly distributed atom enrichment phases follows Ostwald coarsening mechanism, larger atom enrichment phases grow and



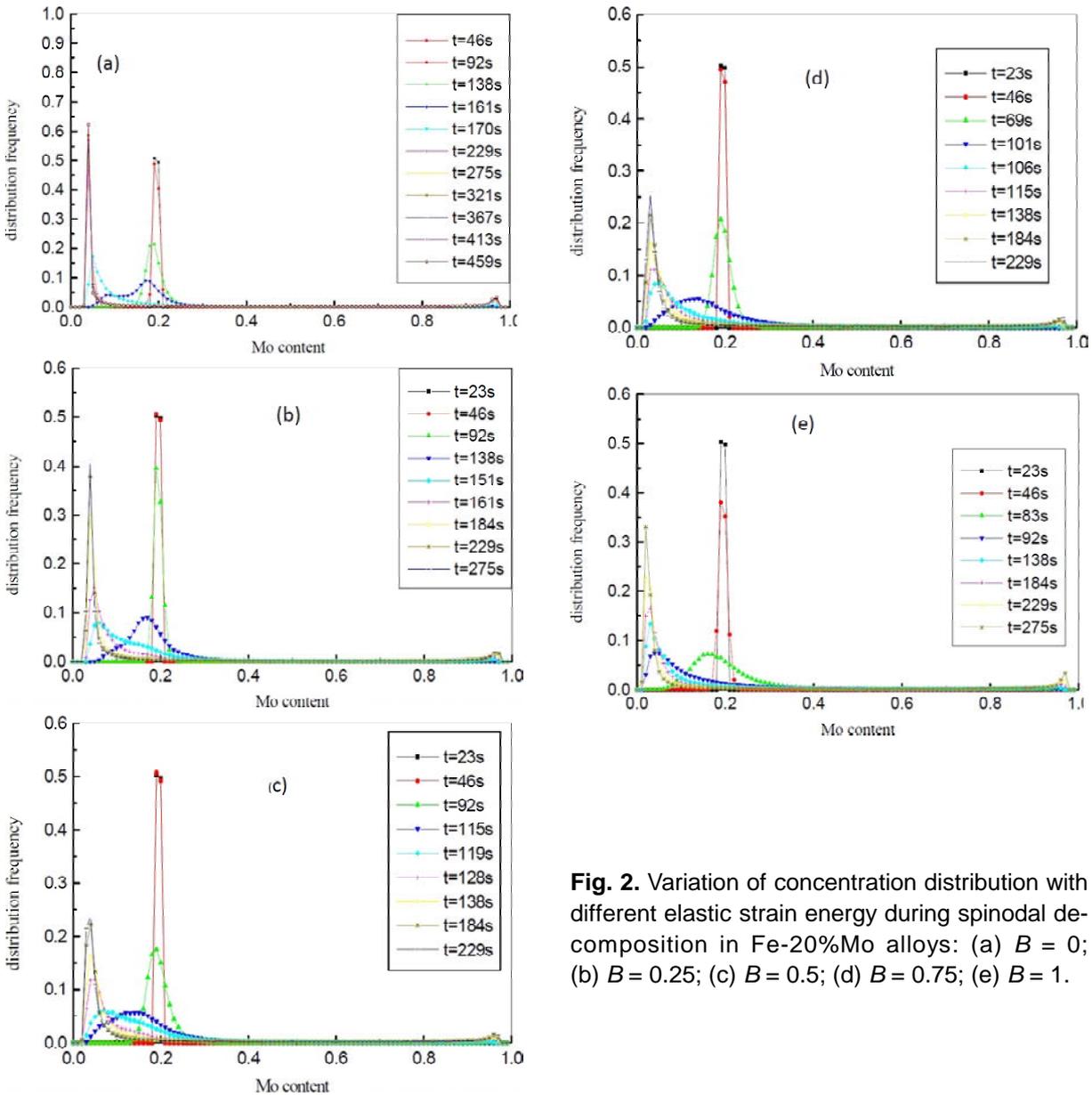
**Fig. 1.** Microstructure evolution of Fe-20%Mo alloy during different elastic strain energy: (a1) ~ (d1)  $B = 0$ ; (a2) ~ (d2)  $B = 0.25$ ; (a3) ~ (d3)  $B = 0.5$ ; (a4) ~ (d4)  $B = 0.75$ ; (a5) ~ (d5)  $B = 1$ .

smaller ones disappear. If we consider elastic interaction energy in model, different coherent atom enrichment phases are formed during spinodal decomposition and subsequent coarsening stage. One can see that concentration waves are formed along the [01] or [10] elastic soft direction firstly, not along random direction. At the coarsening initial stage, a noteworthy regular array of solute-rich white equixed phases within the solute-lean dark matrix are formed. The larger elastic interaction energy contribution is, the more obvious the modulation alignments are. As a result, the enrichment phases of square macrolattice alignment pattern are obtained during

coarsening stage of spinodal decomposition with moderate elastic interaction energy. The results are in accord with that obtained in the other cubic alloys [11].

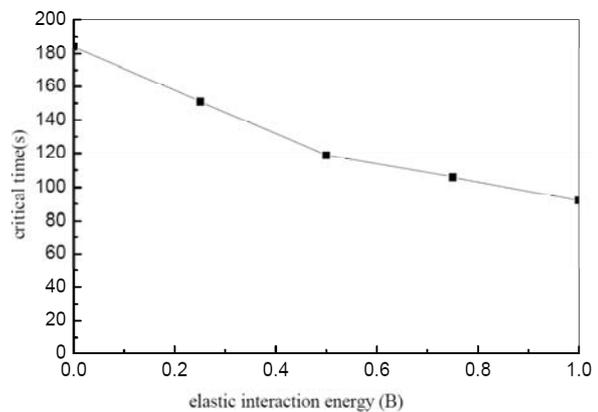
### 3.2. Variation of concentration distribution during spinodal decomposition and coarsening stage in Fe-20%Mo considering different elastic interaction energy

Fig. 2 shows concentration distribution during spinodal decomposition and coarsening stage with



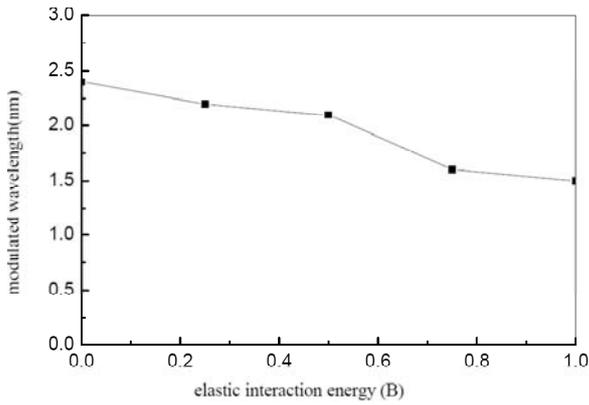
**Fig. 2.** Variation of concentration distribution with different elastic strain energy during spinodal decomposition in Fe-20%Mo alloys: (a)  $B = 0$ ; (b)  $B = 0.25$ ; (c)  $B = 0.5$ ; (d)  $B = 0.75$ ; (e)  $B = 1$ .

different elastic interaction energy in Fe-20%Mo alloys. It is shown that Mo atom concentration are distributed around  $c = 0.2$  at aging initial stage of Fe-20% alloys. At this stage, the alloy is homogeneous solid solution, which is in accord with feature of spinodal decomposition initial stage. With increasing aging time, amplitude of concentration distribution frequency decreases, indicating that homogeneous solid solution of Fe-Mo alloys is broken gradually. When concentration of two peak place is near to the concentration value of two equilibrium atom enrichment phases, single peak state of concentration distribution is replaced by a new two peak state during aging final stage. The concentration distribution frequencies of two peaks increase subsequently, but the frequency in the middle of con-



**Fig. 3.** Variation of critical time with different elastic strain energy in Fe-20%Mo alloys

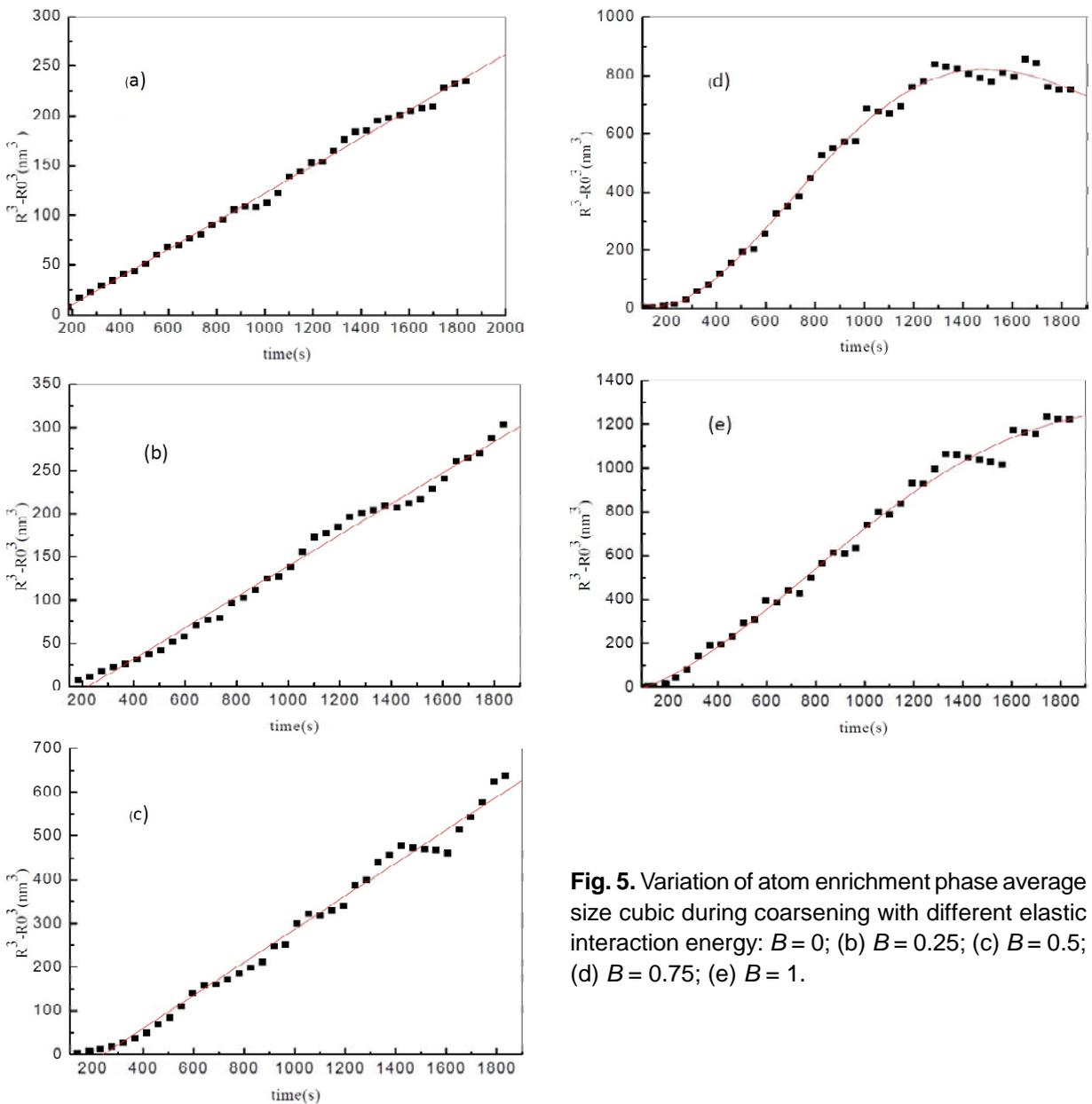
centration distribution curve decreases to around 0. At this time, spinodal decomposition has finished,



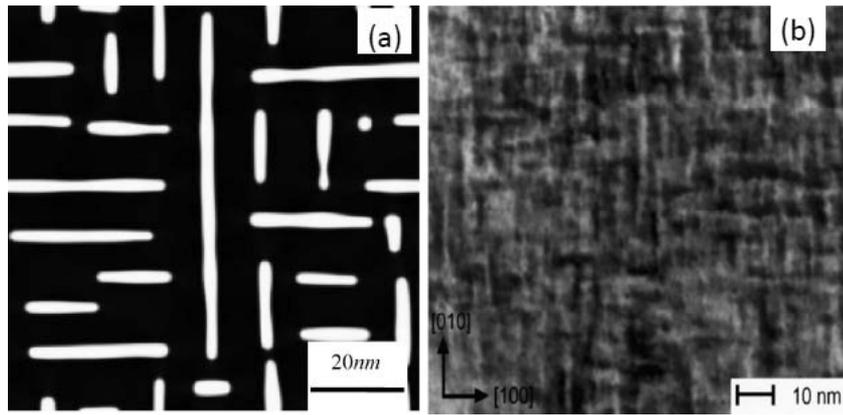
**Fig. 4.** Variation of modulation wavelength with different elastic interaction energy in Fe-20%Mo alloys.

and coarsening stage occurs.

Fig. 3 shows variation of critical time between spinodal decomposition and coarsening stage with different elastic interaction energy in Fe-20%Mo alloys. The elastic interaction energy not only has an effect on morphology and distribution of atom enrichment phases, but also influences transformation rates of spinodal decomposition. When elastic interaction energy ( $B$ ) is not considered, and the critical time is  $t = 170$  s; when  $B$  value is 0.25, and the time decreases to  $t = 151$  s; when  $B$  value is 1, and the critical time is about  $t = 92$  s. According to above results, we can find that the critical time decreases with increasing elastic interaction energy, so spinodal decomposition transformation is accelerated.



**Fig. 5.** Variation of atom enrichment phase average size cubic during coarsening with different elastic interaction energy: (a)  $B = 0$ ; (b)  $B = 0.25$ ; (c)  $B = 0.5$ ; (d)  $B = 0.75$ ; (e)  $B = 1$ .



**Fig. 6.** Comparing atom enrichment phases morphology from the simulation with TEM image and the simulation result: (a) Computer simulation result; (b) Experiment result [12].

Fig. 4 shows variation of modulated wavelength during spinodal decomposition considering different elastic interaction energy in Fe-20%Mo alloys. According to results in Fig. 4, we can find that modulated wavelength decreases with increasing elastic interaction energy. When the value of elastic interaction energy ( $B$ ) is zero, modulated wavelength is 2.4 nm. However, when elastic interaction energy is  $B=1$ , modulated wavelength is 1.5 nm. As well known, uphill diffusion occurs during spinodal decomposition, the reduction of modulated wavelength means that spinodal decomposition is accelerated.

### 3.3. Variation of atom enrichment phases average size during coarsening stage of spinodal decomposition in Fe-20%Mo with different elastic interaction energy

Fig. 5 shows variation of atom enrichment phase average size cubic during coarsening with different elastic interaction energy in Fe-20%Mo alloys. As shown in Fig. 5, if elastic interaction energy is zero or smaller, the average size cubic of atom enrichment phases follows Ostwald ripening mechanism. With increasing elastic interaction energy, the linear relationship is broken. When elastic interaction energy is considered, the coarsening mechanism is different from Ostwald ripening. Examining the microstructures development in Fig. 1 of aging later stage, one may see that atom enrichment phases coarsening are determined by relative position of the phase and its size. The atom enrichment phases grow along the elastic soft direction. Therefore, coarsening mechanism during aging follows the interplay of Ostwald ripening and coalesce growth in Fe-20%Mo alloys.

### 3.4. Comparison of simulation and experimental results

The simulation results with elastic interaction energy is shown in Fig. 6a. A transmission electron microscopic image of Fe-20%Mo alloys aged 5 h is presented in Fig. 6b, where  $\langle 100 \rangle$  modulated structure is clearly recognized. The wavelength of modulated structures is 6.2 nm, while simulation result is about 6 nm with the same calculation method. Comparing simulation results with experimental ones, the agreement in morphology and modulated wavelength proves simulation results correctly.

## 4. DISCUSSION

When elastic interaction energy is taken into account, different coherent microstructures are formed during spinodal decomposition in Fe-20%Mo alloys with a miscibility gap. The formation of special intermediate morphology is attributed to elastic interaction between the elastic strain fields generated by different concentration waves during spinodal decomposition and coarsening stage in Fe-20%Mo alloys. The long range elastic interactions result in arrangement or rearrangement of atom enrichment phases in the elastic soft direction. Therefore, the macrolattice structures are formed to reach minimum free energy at initial coarsening stage of Fe-20%Mo alloys.

When chemical interaction and long range elastic interaction energies are all considered, the macrolattices and basket weave structures are formed. If a new phase precipitates as equiaxed phases which are embedded coherently in matrix phases, a minimum energy stage will be obtained when the phases are arranged by one of the 14 Brava's lattices [11]. With increasing elastic inter-

action energy, macrolattice and basket weave structures become more obvious. It should be noted that in order to form a macrolattice structure, elastic interaction energy should be proper since shapes of the discrete phases forming the lattice are determined by competition between chemical interaction and elastic interaction energy. Therefore, in order to form macrolattice structure, elastic interaction energy should be small enough to preserve equiaxed phases shape minimizing the isotropic chemical interaction energy, but it should be sufficient to provide a regular spatial distribution of atom enrichment phases. This is a general condition applied irrespective of decomposition mechanisms, although the kinetic evolution ways may be different in different cases. For the spinodal decomposition in our simulation, the macrolattice is formed by a superposition of the  $\langle 01 \rangle$  concentration waves at initial stage of spinodal decomposition. The position of atom enrichment phases is predetermined by intersections of maximum amplitudes of two kinds of concentration waves.

## 5. CONCLUSIONS

The microstructure evolution during spinodal decomposition and later coarsening stage in Fe-20%Mo alloys are studied by microscopic phase field model with different elastic interaction energy. The results show that different microstructures are formed during spinodal decomposition and later coarsening stage with increasing elastic interaction energy. When chemical interaction energy and elastic interaction energy is properly selected, the macrolattices and basket weave structures are formed in Fe-20%Mo alloys. With the increase of

elastic interaction energy, the linear relation of average size cubic is broken gradually. The interplay of Oswald ripening and coalesce growth are found during coarsening stage of spinodal decomposition. The simulation results with moderate elastic interaction energy is in accord with experimental results in Fe-20%Mo alloys.

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