Effect of Mismatch of Atomic Configuration on Nucleation

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According to the Fe-C phase diagram, δ-Fe is transformed into γ-Fe through peritectic reaction with decreasing temperature. However, a recent investigations reported another type of transformation: When liquid phase Fe-C is cooled, whole system suddenly transformed into γ phase in a moment after it is solidified to δ phase[1]. This type of transformation is called the massive-like transformation and is observed at a cooling rate of as slow as 50 K/min, which is not rapid and slower than that at industrial steel casting. This observation indicates that the transformation does not always follow the phase diagram. It is argued that the massive-like transformation occurs due to difficulty of the nucleation of γ phase, but it is still unclear what kind of driving force causes the deviation from peritectic reaction or whether precipitated γ phase has a crystallographic relationship with the matrix δ phase. According to the classical homogeneous nucleation theory, the nucleation of another phase is assumed to occur by the formation of clusters of the new phase when energy penalty on the newly formed surface due to the formation is overcome by other energy components. The free energy of formation of a cluster ΔG of volumes V is given by

$$\Delta G = V(\Delta G_V + \Delta G_S) + A\sigma \tag{1}$$

where ΔG_V is the Gibbs free energy difference per volume between the new phase and the matrix phase, ΔG_S is the strain energy per volume of the new phase, A is the interface area of a cluster, and σ is the interface energy per unit area[2]. According to this equation the strain energy and the interface energy determine the nucleation. We examined the effect of the surface energy among these two factors at first. The interface energy is caused by mismatch of atomic configuration at either side of the interface. The degree of the atomic mismatch is supposed to have a relation with the interface energy. However, the interface energy between δ-Fe and γ-Fe is still unclear simply because it is almost impossible to measure it during the massive-like structural transformation in experiment. Moreover, the interface energy between solid phases is anisotropic because, as shown in Fig.1, the magnitude of the mismatch in atomic configuration changes depending on the misorientation angle θ. Thus, it is crucial to reveal the effect of mismatch of Fe configuration on the interface energy and the effect on the nucleation, which can be realized by calculating the interface energies by an atomistic simulation.

In order to calculate the anisotropic interface energy between solid phases, supercells containing the interface were constructed. We prepared models for δ/δ interface, γ/γ interface and δ/γ interface and calculated the free energy of each supercell by a lattice statics calculation. The interface energy γ_{ij} was given

$$\gamma_{ij} = \frac{E_{ij} - n \cdot E_{unit}}{2A} \tag{2}$$

where E_{ij} is the total energy of a supercell containing the i/j interface, E_{unit} is the free

energy of one Fe atom calculated from total energy of a unitcell, *n* is the number of atoms contained in the supercells and *A* is interface area. We tried to find out relationships between the interface energy and the atomic mismatch.

The calculated interface energy is shown in Fig. 2, in which δ and γ phases are denoted as bcc and fcc structure, respectively. From these figures, three facts were found for δ/γ interface. The first is that the interface energy is periodic similar to δ/δ and γ/γ interfaces, and the periodicity is originated from the interface structure. The second is that the δ/γ interface energy is larger than the other interface energies when the mismatch is large. This is because the mismatch of δ/γ interface is larger than that of γ/γ and δ/δ. The third is that the interface energy is small but exhibits non-zero value when mismatch is small. As shown in FIG.2, the δ/γ interface energy exhibit the smallest value when N-W relationship is satisfied where the mismatch between interfaces is rhe smallest[3]. These results indicate that the interface energy is strongly influenced by the atomic mismatch. Since δ/γ interface energy has non-zero minimal value, nucleation of γ phase in δ phase always experience difficulty according to Eq. (1). This may be one of the reasons why aforementioned massive-like structural transformation takes place with nucleation being blocked until driving force for the phase transition reaches high. For further research in the difficulty of the nucleation of γ phase, the strain energy needs to be evaluated. Besides, quantitative evaluation of interface energies for three interfaces enables to simulate an analyze microstructural evolution in this system using Phase-Field Modeling.

References

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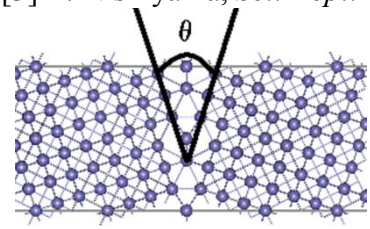

FIG. 1. A model to calculate interface energy between solid phases when misorientation angle is *θ*.

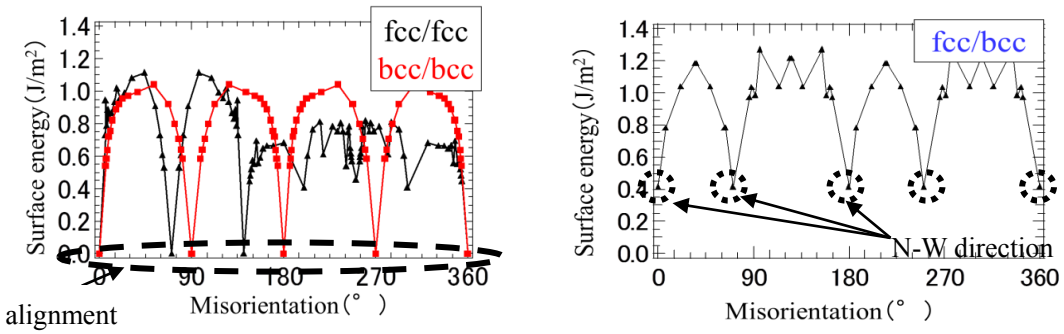

FIG. 2. Calculated interface energies for three interfaces: δ/δ and γ/γ interfaces on the left and δ/γ interface on the right. Note that crystal structures of γ and δ phases are fcc and bcc, respectively. For δ/γ interface misorientations that satisfy N-W relaton are specified.