

Impacts of Interface Energies and Transformation Strain from BCC to FCC on Massive-like δ - γ Transformation in Steel

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Abstract. Interface energies of δ/γ , γ/γ , δ/δ , L/δ , and L/γ interfaces, at first, as a function of misorientation were evaluated with an aid of atomistic simulations with embedded atom method. Then, under geometric constraints where grains or interfaces compete each other to minimize overall free energy, effective interface energies for those interfaces were quantified. It is found that neither the minimum nor effective δ/γ interface energies, 0.41 or 0.56 J/m², respectively, is significantly higher than those of other interfaces including liquid/solid interfaces, but the δ/γ interface energy is significantly high for the small entropy change upon δ - γ massive-like transformation, resulting in significantly higher undercooling required for γ nucleation in the δ phase matrix than in solidification. Detachment of δ -phase dendrite tips away from γ -phase dendrite trunks can be explained only from a viewpoint of interface energy if small misorientation is introduced at the δ/γ interface from the perfect lattice matching between BCC and FCC crystal structures. Examining the BCC-to-FCC transformation strain on the γ nucleation in the massive-like transformation, the γ nucleation is prohibited 170 K or more undercooling is achieved unless any relaxation mechanism for the transformation strain is taken into account.

1. Introduction

Recent *in situ* observations of solidifications to BCC-structured δ phase of carbon steel and following phase transformation to FCC-structured γ phase reported that, when the sample was furnace-cooled at a cooling rate of 0.33 K/s or more, the solid-state phase transformation was instantly completed, within 1 s in a millimetre-dimension window, instead of the peritectic reaction of $\delta + L \rightarrow \gamma$ suggested by the Fe-C phase diagram even if carbon content is more than peritectic composition [1-3]. The δ - γ massive-like transformation required much higher undercooling than it is expected for the peritectic reaction. This led to the idea that the difficulty in nucleation of γ phase in the solidified δ matrix is, at least in part, responsible for the high undercooling. The difficulty of the nucleation can be easily expected since lattice matching between BCC and FCC is poor, which can be quantified by δ/γ



interface energy. Since the massive-like phase transformation may lead to fracture upon continuous casting or may allow solute elements to diffuse through less dense BCC lattice than in FCC lattice at high temperature, it is crucial to understand the underlying mechanism of the massive-like phase transformation.

Experimental studies have reported δ/γ interface energy and α/γ interface both of which are identical to each other if magnetic energy contribution and temperature effects are put aside since α phase also has a BCC crystal lattice. However, the number of reports are much fewer than those for homo-phase interfaces, i.e., grain boundaries such as δ/δ and γ/γ ones. Furthermore, the reported values of δ/γ [4] and α/γ [5] interfaces are different from each other and experimental conditions methods for measuring grain boundary energies and the hetero-interface energies are also different from those for liquid/solid interface energies. Thus, it is not straightforward to examine interface energy dependence on nucleation in general on the same ground. Besides, it is not clear what kind of representative values of those interface energies should be compared in order to discuss the difficulty of the nucleation.

In order to quantify the difficulty of nucleation of γ phase in the solidified δ matrix in comparison with other sorts of nucleation of iron, at first we attempt in this paper to quantify the difficulty of δ -nucleation on the same ground based on interface energies evaluated in our previous studies [6,7]. Then, fragmentation of dendrite tip by re-melting at δ/γ interface [2] is discussed based on the interface energies. Finally, influence of the BCC-to-FCC transformation strain, an alternative factor, on the nucleation of γ phase [8], is also quantitatively examined using a simple geometric model of a γ nucleus and a δ matrix.

2. Methodology

Atomistic simulation for hetero-phase interfaces in addition to homo-phase interfaces were performed to obtain interface energies as a function of misorientation between neighbouring grains [6]. The static energy minimization technique using GULP code [9] was employed to optimize atomic coordinations near the interfaces using embedded atom method (EAM) [10-12] to describe interatomic bonding. In other words, temperature effects were excluded from the interface energies for simplicity so that they can be quantitatively compared on the same ground upon examining their influence on nucleation. Nishiyama-Wassermann (NW) orientation relationship [13,14] was assumed for the best lattice matching at δ/γ interface and further modifications proposed by Rigsbee and Aaronson [15] to improve the lattice matching were employed.

Although the minimum δ/γ interface energy is 0.41 J/m^2 [6], it is still unclear what misorientation should be given to δ/δ or γ/γ interface to compare either one with δ/γ interface energy since both of their minimum interface energies at the best lattice matching are, needless to say, zero. On the other hand, upon discussing grain growth, non-zero substantial values of δ/δ or γ/γ interface energies are used in many cases. Thus, in order to enable us to compare the hetero-phase interface energies including those for δ/γ , L/δ , and L/γ interfaces with the homo-phase interface energies including δ/δ and γ/γ on the same ground, representative values of the interface energies were evaluated under the same geometric constrains which mimic the one present in multi-phase multi-grain system in reality [7]. Phase-field modelling (PFM) [16-18] was employed to quantify a representative value for each interface and a converged value is determined for each interface as an effective interface energy, since morphologies of grains are determined only by free energy defined after influence of artificial initial morphologies vanished in the course of grain growth-like simulations by PFM [7]. For L/δ and L/γ interface energies, it makes little sense to define misorientation in this context, and thus interface between a crystal slab oriented as in the aforementioned δ/γ interface wetted with liquid region is defined as L/δ or L/γ interface and the effective interface energies of L/δ and L/γ interfaces were determined by statistical averaging over up to results obtained using six initial configurations solely from atomistic simulations.

To examine the influence of BCC-to-FCC lattice strain on the nucleation, a simple model is assumed so that it can be quantitatively compared with the results in preceding sections on the influence of interface energy. A homogeneous nucleation is assumed and it is assumed that a nucleus is strained without any strain in the matrix side. Bulk modulus was calculated using the same EAM potential and the strain energy term is added to the free energy change of nucleation.

3. Results and Discussion

3.1. Interface Energy

In NW orientation relationship, (111) plane of δ phase is parallel to (011) plane of γ plane. Introducing periodic lattice ledges and misfit dislocations introduced at the δ/γ interface following prescription proposed by Rigsbee and Aaronson resulted in inclination of the interface while it significantly reduce bond distortion as shown in Fig. 1(a). Bond distortion near the interface is confined to a several atomic layer at most even for the boundary of those dissimilar lattices. In spite of the good lattice matching at the δ/γ interface, its interface energies are found to be as high as 0.41 J/m^2 even when misorientation between two crystal slabs is absent. Table 1 summarizes the minimum interface energies for hetero-phase boundaries and homo-phase boundaries [6,7]. Needless to say, the minimum interface energies for homo interfaces are zero since there is actually no lattice discontinuity at the interfaces. It should be emphasized that the δ/γ interface energies is not significantly greater than those of liquid/solid interfaces, L/δ and L/γ . Thus, care must be taken upon discussing the difficulty of γ nucleation compared with those in solidification.

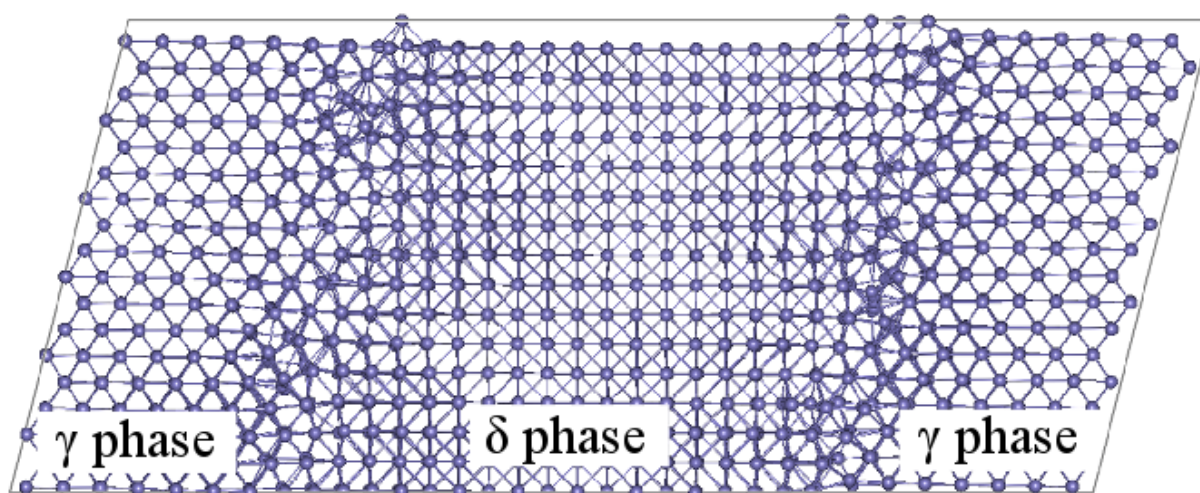


Figure 1. Optimized atomic configuration in a supercell containing two δ/γ interfaces projected to a two-dimensional plane. Ledges are on the projected plane and misfit dislocations are introduced parallel to the projected plane in the figure.

Effective interface energies computed with an aid of phase-field modelling taking into account the geometric constraints that grains or interfaces experience in practice during grain growth are shown together in the table. For the competition among grains or interfaces, volume free energy change is excluded from the total free energy used in the phase-field modelling and the competition is driven only by interface energies. To our surprise, the effective δ/γ interface energy does not increase as much as those of homo-phase interfaces, δ/δ and γ/γ , do. Close monitoring of temporal evolution of the interface energies under competition among grains or interface, it is found that the increase of the δ/γ interface energy is suppressed at the sacrifice of δ/δ and γ/γ interfaces which have much lower

interface energies thereby capable of decreasing overall total free energy of a system. Slightly higher effective δ/δ interface energy than those for γ/γ interface can be attributed to less symmetrical crystal structure of BCC than FCC.

Table 1. Minimum and effective interface energies for various interfaces [6,7]. (*) Note that L/δ and L/γ interface energies were obtained solely by atomistic simulations with several initial configurations.

Interface	Hetero-Phase			Homo-Phase	
	δ/γ	L/δ	L/γ	δ/δ	γ/γ
Minimum [J/m ²]	0.41	0.29 ± 0.03	0.34 ± 0.03	0.0	0.0
Effective [J/m ²]	0.56 ± 0.03	$0.29 \pm 0.03^{(*)}$	$0.34 \pm 0.03^{(*)}$	0.44 ± 0.01	0.37 ± 0.01
Difference [J/m ²]	0.15	-	-	0.44	0.37

3.2. Impact of Interface Energy on Nucleation and Dendrite Tip Detachment

Based on the effective energies, the difficulties of γ nucleation from δ matrix is quantitatively examined using a classical nucleation theory with a simplified geometric model shown in Fig. 2. In the model, nucleation of any phase takes place on an interface between phase-A and phase-B, and when phase-A and phase-B are identical to each other and there is no misorientation between the two phases, the model is reduced to a homogeneous nucleation model with a nucleus of a perfect sphere. It is assumed that contact angles of a nucleus on either side of the interface is determined only by interface energies between two phases in the matrix and a nucleating phase as if they were in equilibrium. To account for driving force of nucleation, it is assumed that entropy change upon phase transformation is independent of temperature, using values at the peritectic temperature obtained directly from a thermodynamic databook or interpolation or extrapolation of values from the databook [19,7].

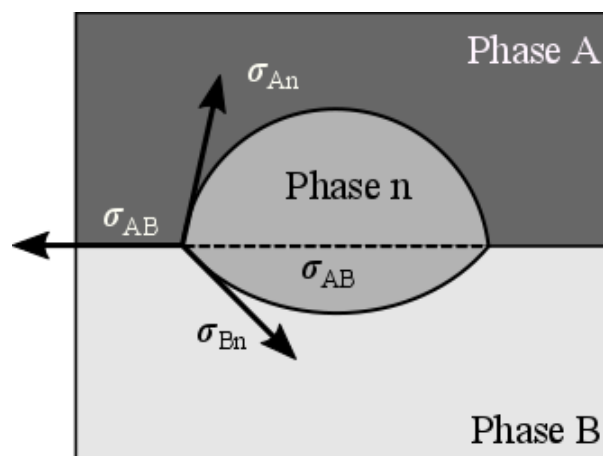


Figure 2. Nucleation model used. Dihedral angle of a nucleus and contact angle with matrix phases are determined by interface energies between phase i and j , σ_{ij} .

Through numerical analysis [6,7], it is found, in the case of homogeneous nucleation, that critical radius of γ nucleation in δ matrix at a given undercooling is more than one orders of magnitude larger than that for solidification to δ or γ phase. At a given critical radius, more than one orders of magnitude greater undercooling is needed for the γ nucleation than in the δ or γ solidification.

Furthermore, the energy barrier at respective critical radius differs by about three orders of magnitude, suggesting that δ - γ transformation is prohibitive. As shown in Table 1, effective δ/γ interface energy is not significantly higher than L/δ or L/γ interface energy, with about 0.2 J/m² difference. This can be attributed to the significant difference in entropy change upon phase transition: From liquid phase to δ phase or γ phase, it is -7.165 or -7.668 J/mol K at 1665 K, respectively, which is by more than one orders of magnitude greater than that for phase transformation from δ phase to γ phase at the same temperature, -0.503 J/mol K. According to a classical nucleation theory [20,21], critical radius r^* and energy barrier for nucleation ΔG^* are given by

$$r^*(\Delta T) = -2\sigma_{ij}/\Delta T \Delta S_{i \rightarrow j} \text{ and } \Delta G^*(\Delta T) = -16\pi\sigma_{ij}^3/3\Delta T^2 \Delta S_{i \rightarrow j}^2,$$

respectively, where ΔT is undercooling, σ_{ij} is interface energy between phases i and j , $\Delta S_{i \rightarrow j}$ is entropy change upon phase transformation from i to j . As evident in these equations, not only interface energy but also entropy change upon phase transformation determines critical radius, energy barrier for nucleation, and undercooling required for the nucleation. Thus, it is concluded that the difficulty of γ nucleation in δ matrix upon the δ - γ massive-like phase transformation is arisen from the relatively higher interface energy for the entropy change for the solid state phase transformation.

When γ nucleation takes place on a δ/δ grain boundary, a part of γ/γ grain boundary within a nucleus vanishes upon nucleation and thus it would be advantageous for the γ nucleation upon the massive-like phase transformation. Using the effective δ/δ interface energy in Table 1, energy barrier for the γ nucleation is reduced by a factor of 0.44. Furthermore, it is found that the γ nucleation on δ/γ interface, i.e. the γ nucleation on an existing γ nucleus, is more energetically advantageous. This indicates concurrent γ nucleation after high undercooling is achieved to trigger initial γ nucleation [7]. Microstructure of the solidified δ phase can be changed by controlling experimental conditions for solidification such as cooling rate. Besides, taking full advantage of grain boundary segregation or micro-segregation between dendrite trunks or arms, δ/δ grain boundary energy can be modified, although it is almost impossible to modify entropy change upon phase transition unless crystal structure or chemical composition is drastically changed. Therefore, it is suggested that controlling δ/δ interface energy through modifying solidified microstructure, thereby changing nucleation rate, is one of the principal ways to control the δ - γ massive-like phase transformation.

According to careful *in situ* observation [22], when δ/γ interface climbs up dendrite trunks and temperature is held, dendrite tips are simultaneously detached at the δ/γ interface away from the bottom of dendrites. Liquid is present between the detached δ -phase dendrite tips and remaining γ -phase dendrite trunks. It is as if the reverse peritectic reaction, $\gamma \rightarrow \delta + L$, takes place. If the δ/γ interface is at its best lattice matching, this phenomenon cannot be explained in terms of interface energy since δ/γ interface energy is 0.41 J/m² at its best lattice matching while the sum of interface energies of L/δ and L/γ interfaces is 0.63 J/m². Even when effective δ/γ interface energy, 0.56 J/m², is used, it cannot be explained solely from interface energies. However, close look at misorientation dependence of the δ/γ interface energy, if linear dependence of the interface energy on misorientation is assumed, only small misorientation by 4.19 deg. enables the dendrite tip detachment even if other factors are neglected [6]. The misorientation of 4.19 deg. is actually smaller than rotational orientation difference between NW orientation relationship and that of yet another well-known orientation relationship, Kurdjumov-Sachs (KS) orientation relationship, 5.26 deg. Therefore, unless δ/γ interface climbs up the dendrite trunks with nearly the best lattice matching, the detachment of dendrite tip can be explained solely in terms of interface energy. The detachment may promote refinement of solidified microstructure which, in turn, drastically changes resultant mechanical properties of the casted steel. Since it is likely that the misorientation between δ -phase dendrite tip and γ -phase dendrite trunks depends again on the solidification to δ phase, controlling solidification process may enable to further tailor the solidified microstructure.

3.3. Impact of Transformation Strain on Nucleation

In addition to interface energies and entropy change upon phase transformation, one more factor may govern the δ - γ massive-like phase transformation. That is the transformation strain from BCC to FCC lattices built up by the same number of the same atoms. Although exact value of the inevitable transformation strain changes with temperature due to thermal expansion, the temperature effect is excluded to enable direct comparison with other results in preceding subsections on the same ground. When the strain effect is taken into account, free energy change upon nucleation in the case of homogeneous nucleation is given by

$$\Delta G(\Delta T, C, r) = -\frac{4\pi r^3}{3} \Delta T \Delta S_{i \rightarrow j} + 4\pi r^2 \cdot \sigma_{ij} + \frac{4\pi r^3}{3} \cdot \frac{1}{2} C \varepsilon^2$$

where C is an elastic constant and ε is a strain. Third term on the right hand side of the equation is the strain term. Bulk moduli of both BCC δ phase and FCC γ phase were calculated using the same EAM interatomic interaction. It is assumed that the nucleating γ phase is uniformly strained without straining the δ matrix phase for simplicity. No further phenomena such as relaxation of strained γ nucleus by dislocations or creep deformation was taken into account for clarity and simplicity, which is plausible based on the experimental fact that relaxation of the strained γ nuclei follows the δ - γ massive-like phase transformation spending longer elapsed time than the δ - γ massive-like transformation itself according to *in situ* X-ray diffraction measurements [22]

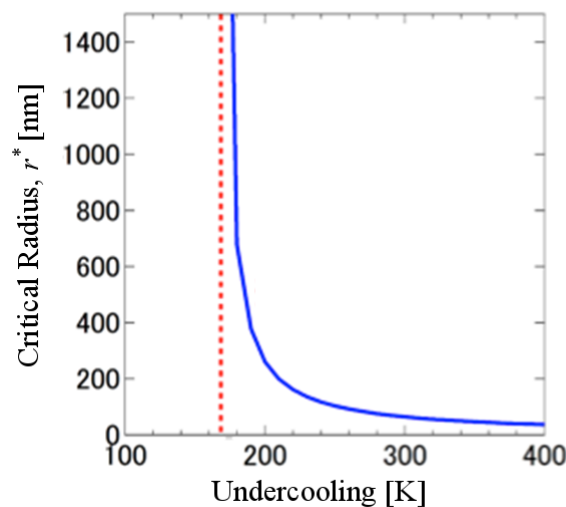


Figure 3. Critical Radius as a function of undercooling when the strain term is taken into account using bulk modulus as an elastic constant.

Figure 3 shows critical radius for homogeneous γ nucleation as in δ matrix a function of undercooling. One of the major differences from previous subsection where only effects of interface energy are taken into account is not that high undercooling is required for the nucleation but that the nucleation is prohibited due to the strain term up to about 170 K of undercooling. This can be easily understood from the equation of the free energy change: the strain term is also proportional to volume of a nucleus in addition to volume free energy change, the first term on the right hand side of the equation. Thus, simply increasing size of a nucleus does not lead to the negative ΔG unlike the interface term, but larger undercooling more than $C\varepsilon^2/2\Delta S_{i \rightarrow j}$ is required to realize the nucleation.

Although in reality an elastic constant such as Young's modulus decreases with increasing temperature, overall picture would not change. Thus, any means including aforementioned relaxation to decrease the strain is essential to give energetical advantage for the nucleation. In other words, if any microprocess that lowers the energy barrier for the nucleation due to the strain term is prescribed, then it would realize or promote the γ nucleation of the δ - γ massive-like phase transformation. Moreover, here lattice strain is assumed to be independent of the interface energy, which is not true in reality. For more quantitative assessment, strain energy needs to be determined in correlation with interface energy. Further details on the strain effect is addressed elsewhere [8].

4. Summary

By the combinational use of atomistic simulations and phase-field modelling, δ/γ interface energy was evaluated in comparison with those of other interfaces including homo-phase grain boundaries and hetero-phase interfaces including liquid/solid interfaces. It turned out that the minimum δ/γ interface energy, 0.41 J/m^2 is not significantly higher than those of L/δ and L/γ interfaces when two phases having dissimilar crystal structures are at the best lattice matching on the atomic level. Even under geometric constraints where grains or interfaces compete to minimize total free energy of a system, the δ/γ effective interface energy is, 0.56 J/m^2 , not significantly higher than those of other interfaces. However, the δ/γ interface energy is very high for the very small entropy change upon the phase transition compared with those for solidification. This results that very high undercooling is needed for the δ/γ massive-like phase transformation. However, results indicate that once initial γ nucleation is succeeded at high undercooling, then concurrent γ nucleation on existing γ nuclei is promoted by its reduced energy barrier. Neither minimum nor effective δ/γ interface energy justifies detachment of dendrite tips leading to fragmentation and, in turn, promoted heterogeneous nucleation in liquid, but if very small magnitude of misorientation, smaller than orientation difference between KS- and NW-orientation relationships, is allowed, then the detachment by re-melting at the δ/γ interface can be explained from an energetical viewpoint. Finally, γ nucleation in δ -phase matrix without involving liquid phase is prohibited until more than 170 K of undercooling is achieved. Thus, any mechanism to relieve the transformation needs to be introduced to enable nucleation in realistic undercooling range.

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