A Model for Ferrite Nucleation Applied to Boron Hardenability

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A model for the nucleation of ferrite on austenite grain boundaries proposed by Sharma and Purdy is reexamined using the Cahn-Hoffman construction. The construction, which offers a rigorous method of predicting the shape of heterogeneous nuclei, indicates that the original proposal of a disk shaped nucleus should be modified to that of a spherical segment. Based on currently available thermodynamic and physical data, it is shown that the spherical segment model is very sensitive to the austenite grain boundary interfacial tension. Even small changes in interfacial tension of several mN/m, which could result from the equilibrium absorption of boron into austenite boundaries, is sufficient to delay the austenite transformation by a significant time.

In 1973 Sharma and Purdy[1] proposed that the ferrite nucleus in austenite be modeled as having a disk shape. The justification for this model was the coherent interface that can form between the α and γ phases when they satisfy the Kurdjumov-Sachs relationship. It was reasoned that the resulting low interfacial tension, $\sigma_{coh}^{\alpha-\gamma}$, would give rise to the large, flat faces of the disk. The edge of the disk was presumably semicoherent, like the tip of a Widmanstätten plate with tension $\sigma_{semi-coh}^{\alpha-\gamma}$. It was proposed that the disk would nucleate heterogeneously on incoherent grain boundaries, with the α-γ interface on the grain boundary being incoherent as well and having tension $\sigma^{\alpha-\gamma}$.

One outcome of this model was the prediction that small changes in interfacial tension would have little influence on the ferrite nucleation rate. For this reason Sharma and Purdy concluded that the effect of boron on hardenability could not be caused by equilibrium absorption of boron into the austenite grain boundaries. Instead they argued, following a suggestion by Zener,[2] that the formation of grain boundary borocarbides was responsible in boron containing steels for retarding ferrite nucleation. Recently Maitrepierre, Thivellier and Tricot[3] tried to prove this claim with a diversified study of boron and nonboron steels. However, as mentioned by these investigators, their results could not conclusively prove what mechanism was responsible for the boron hardenability.

At the time of the Sharma and Purdy study, inadequate methods were available for treating heterogeneous nucleation of anisotropic nuclei. Since their proposal, Cahn and Hoffman[4] have presented a construction for dealing with heterogeneous nucleation. With this construction and with a somewhat simplified assumption, we will show, in the following work, that the Sharma and Purdy model should be modified. The modified model has a different shaped nucleus and leads to different conclusions regarding boron hardenability.

The Cahn-Hoffman construction is a rigorous way of predicting the shape of grain boundary precipitates which are in equilibrium with their surroundings. It is in effect a construction for balancing the surface tensions and torques at the three-grain junctions where precipitates and adjacent grains meet. Although it can be applied only to cases in which the precipitate does not distort the grain boundary, it is adequate for this problem. (The difficulties encountered when dealing with puckered grain boundaries have been discussed and treated to some extent by Lee and Aaronson.[5])

In applying the Cahn-Hoffman construction we assume that the ferrite nucleus satisfies the K-S relationship with respect to one austenite grain, but not the other. From this we assume that the equilibrium form of the nucleus with respect to one grain is a disk while with respect to the other it is a sphere. Figures 1 and 2 show the equilibrium shape of the heterogeneous nucleus for two extreme orientations of the disk nucleus. In Fig. 1 it is a spherical segment while in Fig. 2 it is a disk segment. Although the shape given in Fig. 2, the one proposed by Sharma and Purdy, requires some distortion of the grain boundary, it is so small for this case, which can be seen on a scale drawing of the graphical construction, that we will assume that the effect is negligible. Orientations different from these extreme ones require more distortion of the grain boundary and are omitted from consideration as being less energetically favored. However, it should be noted that minimizing the grain boundary distortion in other systems does not always minimize the work to form a critical nucleus as has been shown by Lee and Aaronson.[5]

Whether the sphere or disk segment is more likely to occur can be estimated by comparing the work, $\Delta\Omega^*$, required to form a nucleus of each shape.† The work is related to the nucleus volume, V^*, according to

$$\Delta\Omega^* = -\frac{1}{2} V^* \Delta\Omega_v \qquad [1]$$

in which $\Delta\Omega_v$ is the Ω energy change per unit volume of γ transformed to α. Therefore, determining which shape is more likely to occur can be obtained by comparing their volumes.

In Fig. 3 this comparison is made by plotting the ratio of the heterogeneous nucleus volume to the

†We assume here that all orientations of grains are available so that there are no geometric restrictions on which shape can form.

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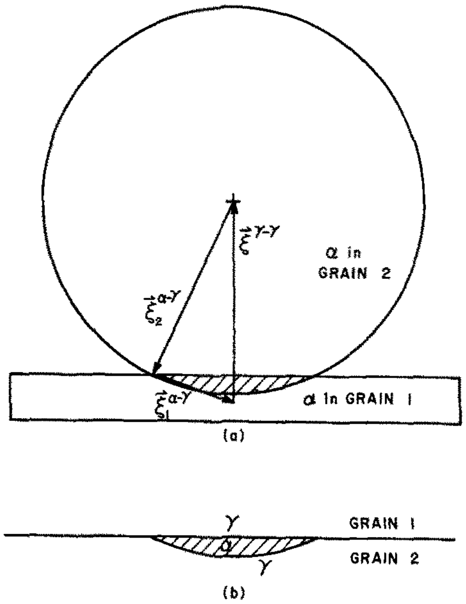

Fig. 1—(*a*) Cahn-Hoffman construction for determining the heterogeneous nucleus shape. The α nucleus in Grain 1 is a disk, shown here on edge. The α nucleus in Grain 2 is a sphere. All dimensions of the disk and sphere are related to their α-γ surface tensions, while the distance between the disk and sphere centers is related to the γ-γ surface tension. None of the dimensions on this figure are to scale in order to clarify the construction. The intersection of the two figures, the shaded region, is the nucleus. It has the shape of a spherical segment. (*b*) The α nucleus as it appears on the grain boundary. No distortion of the austenite grain boundary is required.

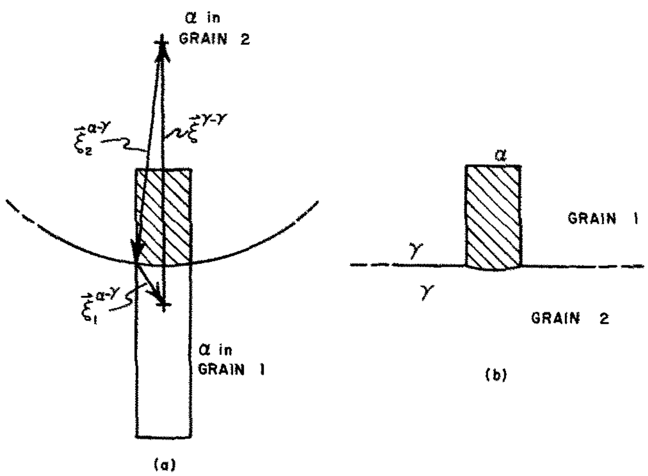

Fig. 2—(*a*) The same as Fig. 1(*a*) except with a different orientation of the disk with respect to the grain boundary. Again this figure is not to scale for clarity. The nucleus in this case is a disk segment. (*b*) The α nucleus as it appears on the grain boundary. Some distortion of the grain boundary is required, but it is neglected for the problem considered here.

homogeneous nucleus volume *vs* the grain boundary energy (note that this is equivalent to plotting the ratio $\Delta\Omega^*_{hetero}/\Delta\Omega^*_{homo}$, the ratio of work to nucleate heterogeneously over that to nucleate homogeneously). This is done for both the disk and spherical segment models. The equations used for the comparison are the standard mensuration formulae for the indicated shapes.

For the case of the disk segment the equation is

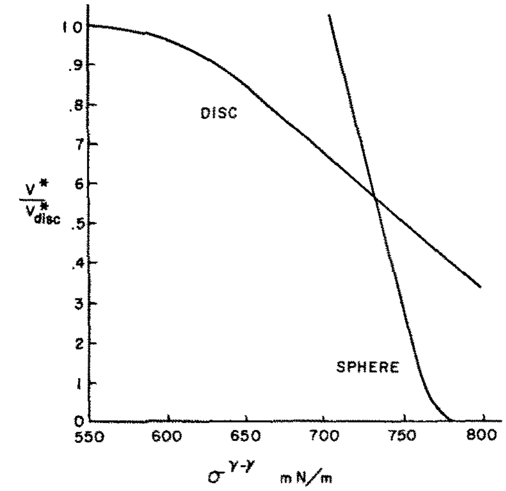

Fig. 3—A comparison of the critical nucleus volumes for a homogeneous nucleus in the shape of a disk, V^*_{disk}, and that of the spherical and disk shaped segments as a function of the austenite grain boundary surface tension. The spherical segment has a smaller volume, and hence is energetically favored for $\sigma^{\gamma-\gamma}/\sigma^{\alpha-\gamma} < 1.025$. Note that if this ratio is less than 0.962, spontaneous nucleation is predicted for grain boundary precipitates.

$$V^*_{ds} = (\pi r_d^2 - [x\sqrt{r_d^2 - x^2} + r_d^2 \operatorname{Sin}^{-1}\frac{x}{r_d}])y \qquad [2]$$

in which

$$r_d = \frac{-2}{\Delta\Omega_v}(\sigma^{\alpha-\gamma}_{semi\text{-}coh}) = \text{disk radius} \qquad [3]$$

$$y = \frac{-4}{\Delta\Omega_v}(\sigma^{\alpha-\gamma}_{coh}) = \text{disk thickness} \qquad [4]$$

$$x = \frac{-2}{\Delta\Omega_v}(\sigma^{\gamma-\gamma} - \sigma^{\alpha-\gamma}) = \text{distance from the disk center to the grain boundary intersection.} \qquad [5]$$

In obtaining Eq. [2] it was assumed that $\sigma^{\alpha-\gamma} \gg \sigma^{\alpha-\gamma}_{semi\text{-}coh}$ in order that the incoherent boundary could be treated to a good approximation as flat.

For the spherical segment the relevant equations are

$$V^*_{ss} = \frac{1}{3}\pi h^2(3r - h) \qquad [6]$$

in which

$$h = \frac{-2}{\Delta\Omega_v}(\sigma^{\alpha-\gamma}_{coh} - \sigma^{\gamma-\gamma} + \sigma^{\alpha-\gamma}) = \text{segment height} \qquad [7]$$

$$r = \frac{-2}{\Delta\Omega_v}\sigma^{\alpha-\gamma} = \text{sphere radius.} \qquad [8]$$

Eq. [6] is valid when the radius of the spherical segment base is less than the radius of the disk. Otherwise, the nucleus is a spherical segment atop a cylinder, the total having volume

$$V^*_{ss'} = \frac{1}{3}\pi h'^2(3r - h') + \pi r_d^2 h'' \qquad [9]$$

$$h' = r - \sqrt{r^2 - r_d^2} \qquad [10]$$

$$h'' = \frac{-2}{\Delta\Omega_v}(\sigma^{\alpha-\gamma} - \sigma^{\gamma-\gamma} + \sigma^{\alpha-\gamma}_{coh}) - h'. \qquad [11]$$

In making the calculations given in Fig. 3 the interfacial tension values used were those given by Sharma and Purdy: $\sigma^{\alpha-\gamma} = 750$ mN/m, $\sigma^{\alpha-\gamma}_{\text{semi-coh}} = 200$ mN/m and $\sigma^{\alpha-\gamma}_{\text{coh}} = 30$ mN/m. In addition they assumed that $\sigma^{\gamma-\gamma} \sim \sigma^{\alpha-\gamma}$.

It can be seen in Fig. 3 that when the austenite grain boundary tension and that of the incoherent austenite-ferrite boundary are similar, (*i.e.* $\sigma^{\gamma-\gamma} \sim 750$ mN/m) the spherical cap has a smaller critical size than the disk and, therefore, is energetically more favorable. Furthermore, in work by Gjostein *et al*[6] on the relative interfacial energies of γ-γ and α-γ boundaries, it was found, for alloys with a range of carbon concentrations, that $0.952 < (\sigma^{\alpha-\gamma}/\sigma^{\gamma-\gamma}) < 0.837$, a regime over which spontaneous nucleation is predicted (*i.e.* it is a regime of zero contact angle). Regardless of the accuracy of these values, they would seem to indicate that the spherical segment model is more likely than the disk segment one.

With regard to the influence of boron on hardenability, it is apparent in Fig. 3 that the work to form a sphericap nucleus could be quite sensitive to small changes in the austenite grain boundary tension, even changes of a few mN/m. The size of this effect is estimated in the following calculation.

Starting with a simple relationship between the time to form a fixed amount of microconstituent, t, the nucleation rate, $\dot{N}$, and growth rate, G,

$$t = \left(\frac{k'}{\dot{N}G^3}\right)^{1/4}, \qquad [12]$$

which can be obtained from dimensional analysis or from classical kinetic theory, one obtains

$$\log t = \frac{\Delta\Omega^*}{4(2.3)RT} + \frac{Q}{2.3RT} + \log k'' \qquad [13]$$

in which k' and k'' are constants, Q is the activation energy for diffusion, and RT has its usual meaning. For small changes in the grain boundary tension,

$$\Delta \log t = \frac{1}{9.2RT}\left(\frac{\partial\Delta\Omega^*}{\partial\sigma^{\gamma-\gamma}}\right)\Delta\sigma^{\gamma-\gamma} \qquad [14]$$

Eq. [14] assumes that the α-γ interfacial tensions are not changed.

In order to compute a value for $\Delta \log t$, T can be taken as 1000 K, a typical value for austenite decomposition, and $\Delta\sigma^{\gamma-\gamma}$ as several mN/m. This change in tension can be computed from the binding energy of boron to grain boundaries.[7] A value of $\partial\Delta\Omega^*/\partial\sigma^{\gamma-\gamma}$ can be obtained from the slope of Fig. 3 at a value of $\sigma^{\gamma-\gamma}$ = 750 mN/m.

$$\frac{\partial\Delta\Omega}{\partial\sigma^{\gamma-\gamma}} = \frac{1}{2}\,\Delta\Omega_v V_d^* \frac{(\partial(V^*/V_d^*)}{(\ \partial\sigma^{\gamma-\gamma}\ )} \simeq 20\ (\text{KJ/mole})/(\text{mN/m}). \qquad [15]$$

The value of $\Delta\Omega_v$ used in this calculation[8] was -4×10^7 J/m^3.

Substituting the above values into Eq. [14] one obtains a value for $\Delta \log t$ of about 0.4. This estimate is similar to the observed effects of small additions of boron on the transformation kinetics of low-carbon steels.

We conclude that the ferrite nucleus does not form in the shape of a disk, at least if energetic rather than geometric factors are governing the preferred shape. Instead, the shape of a spherical segment is favored. In addition, we conclude that the equilibrium absorption of boron into austenite grain boundaries is a plausible mechanism by which boron additions can increase the hardenability of steels. However, whether it or another mechanism prevails must still be considered a subject for debate and further investigation.

ACKNOWLEDGMENT

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