Calculation of the Equilibrium Shape of TiN Particles in Iron

M. ENOMOTO, Z.-G. YANG and T. NAGANO

Department of Materials Science, Ibaraki University, Hitachi 316-8511, Japan.
1) Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, P. R. China.

(Received on January 27, 2004; accepted in final form on May 13, 2004)

1. Introduction

A fine interweaving microstructure found in steel and steel welds, so-called acicular ferrite, is formed by multi-variant ferrite plates that are nucleated at, and grow radially from, austenite grain boundaries. For instance, inclusions of rectangular shape may be effective in suppressing grain growth in the heat-affected zone of welds. In addition to the absolute value of the chemical energy of coherent interfaces at liquid Fe. The chemical energy of coherent interfaces between an austenite (fcc) lattice and a rock salt-type carbide (or nitride) having an identical (cube-on-cube) orientation is expressed by the equation:

\[
\sigma = E'_{\gamma/B1} - \frac{E_{\gamma} + E_{B1}}{2} \quad \text{(1)}
\]

Here, \( E'_{\gamma/B1} \) is the sum of the bond energies across the interface, \( E_{\gamma} \) is the sum of the bond energies across a plane of the same orientation in the austenite lattice, and \( E_{B1} \) is the corresponding sum of the bond energies in the lattice of the carbide (or nitride).

Under the assumption that TiN has a stoichiometric composition \( E_{\gamma/B1} \) can be calculated from the following equation:

\[
E_{\gamma/B1} = n_e Z(e_{11}(1-y) + e_{22}y) + Z'(n_e e_{11}(1-y) + e_{22}(n_s y + n_i y')) + n_e' Z'e_{33}y' \quad \text{(2)}
\]

where \( e_{ij} \) is the bond energy between \( i \) and \( j \) atoms (\( i = 1, 2 \) and \( j = \{Fe, Ti\} \)). These bond energies were evaluated from the cohesive energy of Fe, Ti and TiN, \( n_s \) and \( n_i \) are the numbers of substitutional and interstitial sites per unit area of interface. Likewise, \( E_{\gamma} \) and \( E_{B1} \) are calculated from the equations:

\[
E_{\gamma} = n_e Z(e_{11}(1-y) + 2e_{12}(1-y) + e_{22}y) + (n_e + n_i) Z'(e_{11}(1-y) + e_{22}(n_s y + n_i y')) + n_e' Z'e_{33}y' \quad \text{(3)}
\]

and,

\[
E_{B1} = n_e Z'e_{22}(n_e + n_i) Z'(e_{33}(1-y) + e_{22}y) \quad \text{(4)}
\]

where \( y \) and \( y' \) are the sums of the M–M (or I–I) and M–I nearest neighbor bonds, respectively, summed over the planes from the interface in which nearest neighbor atoms are located (M and I stand for substitutional and interstitial atoms). They are written as:

\[
Z = \sum_{j=1}^{\bar{j}} jz_j \quad \text{and} \quad Z = \sum_{j=1}^{\bar{i}} jz_i' \quad \text{(5)}
\]

where \( j \) and \( j' \) are the numbers of nearest neighbor M and I atoms lying in the \( j \)-th plane from the interface and \( j' \) are the furthest layers in which atoms can form a nearest neighbor bond with an M atom of the other phase across the interface. These are calculated from the vector method and results are shown in Table 1, together with \( n_s \) values for lower index planes. \( n_s \) is in units of \( a^2 \), where \( a (=0.424 \text{ nm}) \) is the lattice parameter of TiN. The \( n_s \) value for a plane with all odd \( h \) and \( k \) indices is nearly double the value of a plane with similar, but mixed \( h \) and \( l \) indices. This is because for an interface characterized by all odd indices, substitutional and interstitial atoms occupy \( (2h 2k 2l) \) planes alternately; whereas, for an interface orientation with mixed \( h \), \( l \) and \( l \) indices, substitutional and interstitial atoms occupy \( (2h 2k 2l) \) planes in a mixed fashion with equal numbers.

2. Calculation Method

2.1. Interfacial Energy with Austenite

The NNBB model is outlined here because it is the basis of the calculation of interfacial energy in both austenite (\( \gamma \)) and liquid Fe. The chemical energy of coherent interfaces between an austenite (fcc) lattice and a rock salt-type carbide (or nitride) having an identical (cube-on-cube) orientation is expressed by the equation:

\[
\sigma = E'_{\gamma/B1} - \frac{E_{\gamma} + E_{B1}}{2} \quad \text{(1)}
\]

In an earlier model of solid/liquid interfaces, it was considered that the structure of the liquid is unaltered up to the interfacial plane. It was later proposed that the liquid phase is adjusted to some extent to accommodate the crystal structure in the layers immediately adjacent to the inter-
On the basis of a hard sphere model, it was also proposed that the number of atoms in the 1st layer is somewhat less than that in the crystal phase for an interface parallel to the close packed plane. Thus, one extreme assumption is that the atomic arrangement within the nearest neighbor distance in the 1st few layers has essentially a coherent structure with the crystal phase, but that the \( Z \) and \( Z' \) (or equivalently \( n_s \) and \( n_s' \)) values might be somewhat smaller. In this case, \( E_{L/B_1} \) can be calculated from Eq. (2) and thus, only \( E_L \) is independent of interface orientation.

It is seen in Table 1 that with varying interface orientation the values of \( n_s Z \) are between 6.9 and 8.9 (with a mean value of 7.8), and the range of scatter is \( \approx 30\% \) of the absolute value. On the other hand, the \( n_s' Z' \) values range from 2.4 to 3.5 (with a mean value of 3.1), with the exception of the (100)-type interfaces. (The \( n_s' Z' \) values of the interfaces with all odd indices are halved for the reasons mentioned above.) Thus, in view of the earlier conjecture that the liquid structure persists up to the interfacial plane, one could assume that \( E_{L/B_1} \) is independent of interface orientation, and then observe how the anisotropy of the interfacial energy varies with the assumed coordination numbers.

### 2.3. Three-dimensional Visualization

The interfacial energy was calculated for \( \approx 3 \times 600 \) orientations in which \( h, k \), and \( l \) did not exceed 10. The polar plot of calculated energies and the resultant Wulff construction were obtained following the procedures previously described. Both the energy surface and the surface of the equilibrium shape were rendered, dividing them into triangles that connect three neighboring orientations.

### 3. Results and Discussion

#### 3.1. Polar Plot of Interfacial Energy and Wulff Construction

Figure 1 shows the polar plot of the interfacial energy and the equilibrium shape of TiN particles in austenite. In a previous report, the equilibrium shape was deduced to be a cube, based on a two-dimensional section. The solubility of Ti and N is so small that the interfacial energy is not significantly affected by their presence in austenite. In contrast to a binary fcc/fcc interface \{100\}-type interfaces of TiN have the minimum energy, and \{111\}-type interfaces have the maximum energy. This is because the contribution from strong M–I interactions is greater than the contribution from M–M interactions. The energy of the \{100\}-type interface is \( \sigma_{(100)} = 1.1 \text{ J/m}^2 \).

#### 3.2. Three-dimensional Visualization

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shape become somewhat round, but the overall cube morphology is maintained.

Figures 3(a) and 3(b) show the (100) section and 3D visualization, respectively, of both the polar plot of the chemical interfacial energy, and the equilibrium shape. These were calculated under the assumption that $E_L/B_1$ is independent of orientation. $n_s Z$ and $n_s/Z$ values were assumed to be 7.0 and 2.5, respectively. The equilibrium shape is a cube surrounded by {100}-type facets that have a very low energy, as compared to other orientations.

3.2. Morphology of TiN Particles

Experimentally, TiN particles are observed to have a cuboidal or rectangular shape. 8,9) Liu and Jonas 9) observed in a series of Ti-bearing HSLA steels that TiN particles had a bimodal size distribution. This distribution included both large (mean size of a few $\mu m$) and small (0.1–0.2 $\mu m$) particles having a cuboidal shape. Whereas the smaller ones were precipitated from austenite after solidification, the large particles were likely formed prior to or during solidification. Thus, the result of the present calculation—that the equilibrium shape of TiN is a cube in both austenite and liquid Fe—agrees with these observations. The cuboid morphology has also been reported for NbC and Nb(CN) precipitates,13,14) which may have more irregular shapes when nucleated on dislocations, due to a larger misfit with the austenite. It should also be noted that the morphology of some rock salt-type carbides formed in highly alloyed austenite was observed to be that of an octahedron surrounded by {111} atom planes in the austenite matrix.15)

4. Summary

The interfacial energies of TiN/austenite and TiN/liquid Fe interfaces were calculated by applying the nearest neighbor broken bond formalism to a ternary system composed of metallic and non-metallic atoms. Three-dimensional visualization of the polar plot of interfacial energy and the Wulff construction for the equilibrium shape was performed by rendering the surfaces corresponding to a few thousand interface orientations. The equilibrium shape is nearly a cube in both austenite and liquid Fe, in spite of the uncertainty of the parameters characterizing the structure and the atom density of liquid in the layers adjacent to TiN. These findings agree well with experimental observations.

Acknowledgements

The authors express thanks to Mr. R. Kato (student) for assistance in image processing. One of the authors (Z.-G. Yang) is grateful to the National Natural Science Foundation of China (NSFC) for financial support under the contract No.50201007.

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