Interface Energy of Semicoherent Metal-Ceramic Interfaces

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An *ab initio* based approach to determine energies and structures for semicoherent interfaces is developed and applied to the Fe(001)/VN(001) system. To account for elastic displacements resulting from the lattice misfit, we compare an atomistic approach using a model potential (embedded-atom method) with a continuum approach using the Peierls-Nabarro model. The total interface energy of the atomistic modeling is found to be well reproduced by the Peierls-Nabarro model, demonstrating that accurate interface energies of semicoherent interfaces can be obtained by combining first principles for the chemical part of the energy and a Peierls-Nabarro model to account for the elasticity of the media.

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Understanding the stability and adhesion properties of interfaces between dissimilar materials is one of the most significant issues of contemporary materials research [1]. Such interfaces are prevalent in numerous industrial applications including, e.g., heterostructure devices, corrosion protection, and thermal barriers, where their functions and properties are of vital importance. A complication is that the energetics of interfaces is prohibitively difficult to determine experimentally. Theoretical tools such as density-functional theory (DFT) have, during the past years, been used extensively to calculate interface energies of various metal-ceramic interfaces [2]. Almost exclusively in these studies, only the chemical part of the interface energy in the coherent interface approximation is assessed; i.e., lattice misfit and the corresponding elastic contributions are neglected.

However, the effect of misfit on heterophase interface energies [3] is important and should be included in theoretical modeling. DFT has been used in a few cases to model interfaces with misfit [4–6], but normally, the required system size is beyond available first-principles computational capacity. Instead, such large scale modeling of defect structures has mostly been performed using semiempirical many-body model potentials, e.g., of the embedded-atom method (EAM) form [7]. An alternative theoretical framework for multiscale simulations of misfit dislocation properties is provided by the Peierls-Nabarro (PN) model [8,9].

In this work, we use both an atomistic model (AM) and a continuum model (CM) to demonstrate that a small deviation from coherency may have a very large influence on the interface energy. This is done by a systematic study of the energetics of semicoherent defect structures where DFT, used to map out the γ surface (chemical interaction energy across the interface) in one, two, and three dimensions, is combined with AM (EAM [10]) and CM [one-dimensional (1D) PN] methods to also account for elastic contributions. Comparing predictions from atomistic and continuum levels of modeling shows how to assess the energy of semicoherent heterophase interfaces in the simplest way from a few DFT calculations.

This methodology is applied to calculate the energy of the semicoherent Fe(bcc)/VN(nacl) metal-ceramic interface. This choice is motivated by the technological importance of VN particle strengthening in ferritic steels (α-Fe). In addition, the Fe/VN interface orientational relationship is well established. VN precipitates as platelets in α-Fe due to a small (2%) relative misfit parallel to the platelet and an appreciable (44%) misfit perpendicular to the platelet [11]. The small misfit results in a well-defined semicoherent interface structure with an orientation relationship given by the Baker-Nutting relation, $(001)_{\mathrm{nacl}} \parallel (001)_{\mathrm{bcc}}$, $[100]_{\mathrm{nacl}} \parallel [110]_{\mathrm{bcc}}$. The defect structure consists of a square dislocation network with Burgers vectors $\mathbf{b} \parallel [100]_{\mathrm{bcc}}$ and $[010]_{\mathrm{bcc}}$.

The calculated interface energy is defined as the energy cost of forming the interface from the respective bulk crystal phases. The basic assumption underlying both the CM and the AM approaches is that the total interface energy may be separated into elastic energy due to distortions and chemical interaction energy, making $E_{\mathrm{tot}} = E_{\mathrm{el}} + E_{\mathrm{chem}}$. The AM we use describes only the interatomic interactions between Fe atoms [10]. When comparing results from the atomistic and continuum modeling, we therefore treat the VN phase as fixed in both cases. In the AM simulations, atomic positions in the metal phase are relaxed to minimize E_{tot} using the interatomic potential in a slab geometry with *ab initio* interactions affecting the first Fe surface layer. The CM expresses the total interface energy E_{tot} as a functional of the continuous disregistry $\delta(x)$ between interface Fe atoms and their N neighbors in the VN phase. Upon taking the functional derivative of E_{tot} with respect to $\delta(x)$, a PN integrodifferential equation is obtained, which is solved following the procedure in Ref. [12].

The Fe/VN system has previously been studied using DFT, in the coherent interface approximation neglecting the small misfit [13]. It was found that the Fe/VN interface energy is very low, even slightly negative. The preferred interfacial site for Fe is on top of N. Such a geometrical configuration allows for an exceptionally strong metal-modified covalent bonding of the same nature as the

Co-W(Ti)(C,N) bonding in hard metals [14]. We use spin-polarized DFT to quantify the chemical interaction energies. The CM is one-dimensional, so a comparison between this model and the AM simulations requires the study of also one-dimensional geometries. In this respect, the most suitable cut of the γ surface is over coherent (N) sites, as illustrated in Fig. 1. Integrating γ along the chosen cut gives the lowest mean chemical energy which motivates this choice of cut. The 2D and 3D cases we consider both describe a square dislocation network but with different γ surfaces. The 2D γ surface is derived from a set of high-symmetry interface geometries including optimization of the Fe-VN intergrain distance; see Fig. 1. An extension to the 3D γ surface is obtained by interpolation to points with different intergrain distances for the various high-symmetry interface geometries. The minimum of the γ surface ($E_{\mathrm{coh}} = -0.061\ \mathrm{J/m^2}$) defines the coherent limit, which is a lower bound of the interface energy for any interface. A measure of the energy of an incoherent structure is given by an average value of the γ surface ($E_{\mathrm{incoh}} = 1.74\ \mathrm{J/m^2}$). Chemical interfacial interactions as given by the γ surface are used in both the AM and the CM.

In our AM, the electron density in the EAM description [10] of the first few layers of the slab is adjusted to minimize the artificial initial surface force field originating from the free Fe model surface. This ensures a chemical environment of the interfacial atoms in the model system as close to the situation at a real interface as possible. Periodic boundary conditions are applied in the [100] and [010] directions. For the 2% misfit, the computational cell consists of 140 layers of Fe atoms in the [001] direction. The last four layers are kept at bulk positions, and the location of their center of mass is also included in the relaxation procedure to optimize the relative position of the Fe layers and the VN crystal.

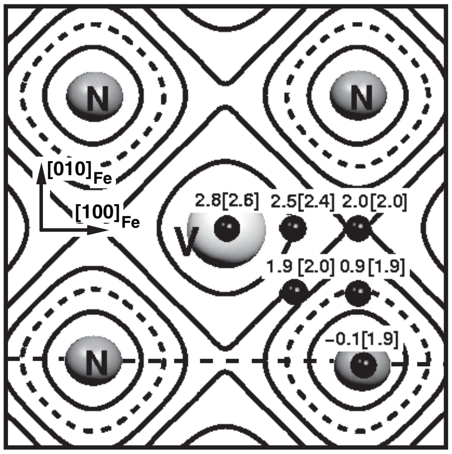

FIG. 1. Fe(001)/VN(001) 2D-γ surface. The dashed contour indicates a reference value of 1 $\mathrm{J/m^2}$ and consecutive contours differ by 0.5 $\mathrm{J/m^2}$. Black points show positions for interfacial Fe atoms with resulting energy values [intergrain distances (Å) in parentheses]. The horizontal dashed line delineates the cut used in the 1D calculations.

The PN model equates the elastic response from the medium due to displacements $\delta^{e}(x)$ with the interface forces $\frac{\partial \gamma}{\partial \delta}$ arising from misfit. We use a sinusoidal interface force, in which case analytical expressions [12,15,16] for the elastic and chemical energies exist, as well as for the dislocation half width ζ [17]. The magnitude of the elastic force is given by the so called energy coefficient K [18], which depends on the elastic constants of both materials. The isotropic (iso) and anisotropic (aniso) cases differ in the calculation of K [19]. The anisotropic case is treated using the energy coefficient of an interfacial dislocation in an anisotropic bicrystal as given in Ref. [20], which is calculated using the Stroh formalism as outlined in Ref. [21]. In the isotropic limit, K reduces to the expression derived by Dundurs and Sendeckyj [22], which we use for the isotropic calculation. In both cases, the VN phase is treated as fixed corresponding to an infinite shear modulus. We obtain the values $K_{\mathrm{iso}} = 266$ GPa and $K_{\mathrm{aniso}} = 225$ GPa using the elastic constants for Fe as given in Ref. [18].

An important result from our calculations is that the effect of misfit on the interface energy is very large. This conclusion has general validity, independent of dimensionality and computational method. Energies obtained from the CM and the AM are presented in Table I. There is good agreement in total energies ($\sim 0.5\ \mathrm{J/m^2}$) between all computational models. The total energies are quite far from the coherent limit, demonstrating that the coherent interface approximation is insufficient even for such small misfits as 2%. The elastic energy contribution is about two-thirds of the total energy. The most direct comparison between CM and AM is between 1D-CM(sine,aniso) and 1D-AM(sine), where the same sine function has been used for the 1D γ surface. Both models agree in total energy, but the CM gives a somewhat higher elastic energy and lower chemical energy. Dislocation widths ζ are also included in Table I, where it can be seen that CM predicts a more narrow dislocation core than AM. We see in the 1D AM simulations that the effect of going from a simple sine force to a more accurate force using an interpolation between all

TABLE I. Comparison of elastic, chemical, and total interface energies (in $\mathrm{J/m^2}$) calculated using Peierls-Nabarro continuum modeling (CM) and EAM atomistic modeling (AM). The one-dimensional (1D) results of the total interface energy have been scaled according to $E_{\mathrm{tot,1D}} = 2E_{\mathrm{el}} + 2(E_{\mathrm{chem}} - E_{\mathrm{coh}}) + E_{\mathrm{coh}}$, for a direct comparison with the 2D and 3D cases. Calculated values of the dislocation width ζ(Å) are also given.

Method	E_{el}	E_{chem}	E_{tot}	ζ
1D-CM(sine,iso)	0.192	0.057	0.559	5.62
1D-CM(sine,aniso)	0.178	0.040	0.498	4.78
1D-AM(sine)	0.164	0.057	0.502	6.52
1D-AM	0.158	0.056	0.487	6.58
2D-AM	0.318	0.175	0.492	6.74
3D-AM	0.322	0.167	0.489	6.54

calculation points of Fig. 1 is minor, since the γ surface between the preferable N sites is almost sinusoidal. Anisotropy is included in the CM, since it provides a more realistic estimate of the elastic response. Neglecting anisotropy results in higher elastic and chemical energies as well as larger ζ.

It must be taken into account that 1D results describe the energy of parallel dislocations, while the energy for a square dislocation network is included in the 2D and 3D results. Assuming that dislocations perpendicular to each other do not interact, we correct the 1D results according to $E_{\mathrm{tot,1D}} = 2E_{\mathrm{el}} + 2(E_{\mathrm{chem}} - E_{\mathrm{coh}}) + E_{\mathrm{coh}}$. The rationale for substracting E_{chem} with E_{coh} is that only the deviation of E_{chem} from E_{coh} is additive when going from 1D to 2D. We note that multiplying the 1D elastic energy of the AM simulation by 2 gives very good agreement with the 2D result, which indicates that the elastic energies due to distortion in the [100] and [010] directions are to a large extent additive. Examining the 2D and 3D elastic energies, we see that the variation of the γ surface in the [001] direction gives a negligible contribution to the elastic energy.

The atomic structure in the vicinity of a misfit dislocation obtained from the 3D-AM simulation is visualized in Fig. 2. The cut is made along a (010) plane midway between two $\mathbf{b} \parallel [010]$ dislocations. As seen, the Fe atoms have relaxed to gain coherency with the N atoms. One may also notice that the Fe lattice is slightly distorted in the [001] direction, due mainly to the compression of the lattice in the [100] direction near the dislocation.

To examine the width of the dislocation, the disregistry $\delta(x)$ in the interface plane as obtained from the 3D-AM simulations is shown in Fig. 3(a) together with the resulting distribution of elastic energy. We note that the disregistry is steplike and that most of the disregistry is taken up by the five atoms closest to the dislocation. The elastic energy is given as the energy stored in a vertical column of Fe atoms (corresponding to a connected line of atoms as plotted in Fig. 2) as a function of distance from the dislocation line. The elastic energy is rather constant positive outside the width of the dislocation and has a well-defined peak at the dislocation.

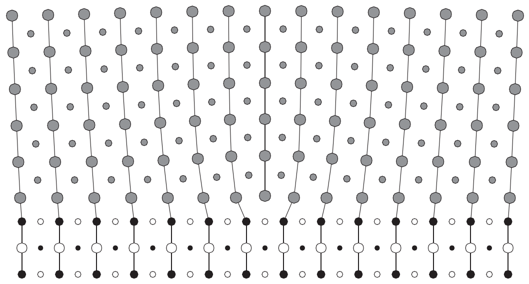

FIG. 2. (010) cut of the Fe(001)/VN(001) interface from the 3D atomistic simulation showing optimized atomic positions in a misfit dislocation. Black, white, and gray circles denote N, V, and Fe atoms, respectively. Smaller circles specify atoms in the layer below.

To get an estimate of the extent of the distortion into the Fe phase, the (001) layer averaged displacement $\bar{u}$ (rms displacements from bulk positions) and elastic energy as a function of distance from the interface are given in Fig. 3(b). The elastic energy drops sharply from the interface layer to the second layer and decreases rapidly into the Fe bulk. The rms displacements extend further into the Fe phase but have converged totally within the limits of the supercell.

So far, the misfit ϵ has been restricted to the 2% characteristic of the Fe/VN interface. To investigate the energy variation with misfit, further simulations are made with misfit ranging from ~ 0.01 to 0.25. It is assumed that the chemical interactions across these interfaces are the same as for Fe/VN, in the sense that max and min values on the γ surface are the same as for Fe/VN. Only the lattice spacing of the fictitious VN phase is scaled to the appropriate misfit.

In Fig. 4 the elastic, chemical, and total energies of the interface as predicted by the 3D-AM and 1D-CM anisotropic models are given. Both models follow the same trends and converge in the low misfit limit. The models agree very well on the chemical energy. The CM gives a somewhat higher elastic energy than the AM, which in turn yields a higher total energy. However, the discrepancy in total energy is smaller than 10% even in the large misfit limit. Both models predict a maximum in the elastic energy for misfits of ~6%. For larger misfits, the chemical contribution to the total energy is larger than the elastic part. For the largest misfits, the interface is expected to be incoherent and the chemical energy is dominating, ap-

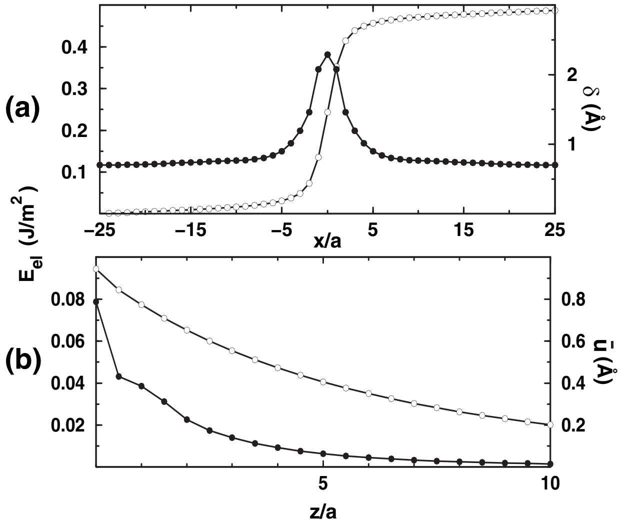

FIG. 3. (a) Elastic energy E_{el} (black) and displacement δ (white) as a function of distance from the dislocation line. (b) Layer averaged elastic energies E_{el} (black) and displacements $\bar{u}$ (white) in (001) planes as a function of distance from the interface.

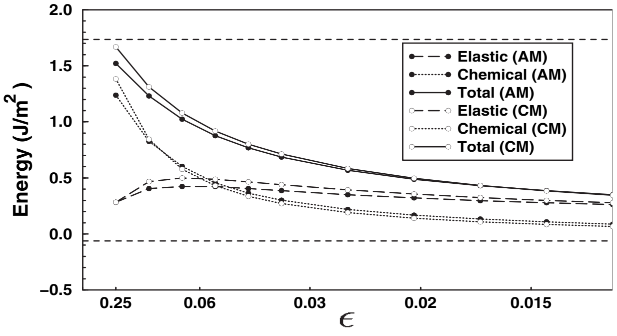

FIG. 4. Energies from the 3D atomistic modeling (AM) and the 1D anisotropic continuum modeling (CM) as a function of misfit ϵ. The dashed horizontal lines show the coherent ($E_{\mathrm{coh}} = -0.061$ J/m^2) and incoherent ($E_{\mathrm{incoh}} = 1.74$ J/m^2) limits. The values from the 1D CM have been scaled for direct comparison with the 3D AM results.

proaching the value calculated in the incoherent limit. This means that estimating the energy of an incoherent interface by an energetical average over high-symmetric local geometric configurations [23,24] is reasonable.

We conclude that there is a very good agreement between the AM and the CM predictions. This is a key result and it implies that the 1D Peierls-Nabarro CM is a very useful tool to describe the interface energy [12,25]. One may argue that, since the width of the dislocation ζ is small, the large strains near the dislocation make the predictions of the CM questionable. On the other hand, ζ/p is maximally ~0.05 in the Fe/VN interface, which limits the impact of the dislocation core energy to the total interface energy, explaining the good agreement between CM and AM for the total energies. However, discrepancies between the models grow as the misfit increases.

The comparison between the AM and the CM predictions has been based on the assumption that the VN phase is kept fixed. To obtain a correct interface energy, this phase also has to be relaxed. Treating both the Fe and the VN phases as anisotropic elastic semi-infinite media with appropriate elastic constants [26], we obtain the interface energy $E_{\mathrm{tot}} = 0.348$ J/m^2 and half width $\zeta = 2.90$ Å [19]. The effect of relaxing both phases is clearly important. Both the chemical and elastic energies are reduced, from $E_{\mathrm{chem}} = 0.040$ J/m^2 to $E_{\mathrm{chem}} = 0.004$ J/m^2 and from $E_{\mathrm{el}} = 0.178$ J/m^2 to $E_{\mathrm{el}} = 0.140$ J/m^2, respectively.

In summary, we have investigated the effect of misfit on the interface energy by calculating the interfacial interaction from an *ab initio* method and accounting for elastic displacements due to lattice misfit by both an atomistic modeling (EAM) approach and a continuum (PN) model. The results show that even a very small misfit has a large influence on the interface energetics. For a large misfit, corresponding to an incoherent interface, the interface energy may be taken as a mean of the γ surface. For a coherent interface, the interface energy is simply the minimum of the γ surface.

In the case of a semicoherent interface, we propose a method of determining the interface energy using a few points on the γ surface calculated from DFT to account for the chemical interactions combined with a one-dimensional anisotropic PN model whose result must be correctly scaled in the case of a 2D dislocation network. The validity of the method has been verified by comparison with atomistic modeling, showing very good agreement. The approach presented here provides an efficient and accurate way of assessing the energy of a semicoherent interface, even when the chemical interactions are complex.

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