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Ab initio study of the surface properties of austenitic stainless steel alloys

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ABSTRACT

Using *ab initio* calculations we investigated the surface energies of paramagnetic Fe$_{1-c-n}$Cr$_c$Ni$_n$ random alloys within the concentration range of $0.12 \leq c \leq 0.32$ and $0.04 \leq n \leq 0.32$. These alloys crystallize mainly in the face centred cubic (fcc) structure and constitute the main building blocks of austenitic stainless steels. It is shown that all alloys have the lowest surface energies along the most close packed crystal orientation, namely the fcc (111) surfaces. The amount of Ni seems to have little effect on the surface energy, while almost all composition-driven change may be attributed to the changes in the Cr content. Within the studied compositional range, the change of the surface energy with the composition is of the order of 10%. Trends of the surface energy can be related to the magnetic structure of surfaces. Using the total energy as a function of the concentration, we determine the effective chemical potentials in bulk and at the surface, which can be used to estimate the surface segregation energies.

1. Introduction

Stainless steels are the most widely used maintenance free and safe engineering materials. They have superior strength, stiffness, toughness and corrosion resistance in relation to their cost compared to other materials. Surface energy is one of the defining qualities of Fe alloys, because it determines many important phenomena, such as crystal growth, adhesion between metallic surfaces, growth of thin layers [1], and mechanical strength. Surface energies of solids cannot be directly measured; instead, the available "experimental" surface energies have been derived from liquid tension measurements. Therefore theoretical studies on the subject are of vital importance to the development of this field.

In this work, the surface energies of austenitic FeCrNi alloys (with varying Cr and Ni concentrations) were calculated. The crystal structure of these alloys was the face centered cubic (fcc) lattice. The two low index surfaces, fcc(100) and fcc(111) were studied, because they are the most closely packed ones, and thus the most likely candidates to have the lowest surface energy.

The minimum Cr amount in our study was chosen to be 12% (atomic % is used throughout the report), given by the stainless requirement [2], and the maximum 32%. Since almost all stainless steels contain at least some Ni, we chose the lower limit of Ni to be 4% corresponding to some metastable grades present e.g. in duplex steels. Since Ni also has a stabilizing effect on the austenitic phase, we mimic the effect of all austenite stabilizers by Ni. Therefore, we chose the upper limit for Ni to be as high as 32%, even though such an amount of Ni is not commonly used in any commercial steel grades.

The paper is organized as follows: In Section 2 the computational methods of calculating the surface energies are introduced and discussed. In Section 3 we display the results, and finally, in Section 4, the conclusions are presented.

2. Methods

2.1. Surface energy

Cutting a solid body into two disrupts its bonds, and therefore consumes energy. This additional energy fed into the system when the bonds are cut is called the surface energy, and it is expressed as energy per surface area. To acquire the surface energy via simulations, we considered two systems per each composition (varying c and n in Fe $_{1-c-n}$Cr$_c$Ni$_n$), namely a slab system and a bulk system. The slab system consisted of eight atomic layers, separated by a vacuum of 4 atomic layers thickness. Both the width of the slab and the width of the vacuum layer were chosen to be adequate for the material to attain bulk-like behavior in the middle of the slab, and for the surfaces

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to not be interfered by the repeated images (that is, they react as if exposed to infinite void, not to a small crack). The exact coordinates used for both the fcc(111) and fcc(100) cases can be found as supplementary material (online publication). The amount of "surplus energy" (surface energy) in the system is the total energy of the slab system minus the energy of the bulk system having the same amount of atoms as the slab system has. Mathematically, the surface energy is expressed as

$$\gamma = \frac{E_{slab} - n \cdot E_{bulk}}{2A}, \tag{1}$$

where E_{slab} is the total energy of the slab system, n is the number of atoms in the slab system, E_{bulk} is the energy per atom of the bulk system, and A is the area of an interface in the slab supercell. The "2" in the denominator stands for the two surfaces of the slab. It is worth mentioning here, that the surface of any alloy consisting of two or more different chemical elements assumes a certain surface chemical concentration profile which depends on the elements of the alloy and the surface considered. They might form a dilute alloy, or one of the elements might segregate to the surface, and the elements on the surface can form islands of varying shapes and sizes. Such phenomena are not considered here. Therefore, in the present study, the surfaces are in their bulk concentrations. We determined the equilibrium lattice parameter for each composition (that is, for each c and n in $\mathrm{Fe}_{1-c-n}Cr_cNi_n$) by performing a series of total energy calculations with a varying lattice parameter value, and then fitting a Morse equation of state to the *ab initio* total energies. The obtained theoretical volume (lattice parameter) was then adopted in the slab calculations. The variation in the lattice parameter was very small in the compositional range studied: the difference between smallest (3.6032 Å) and largest (3.6111 Å) value was 0.22%.

There are various ways one can use to define the bulk total energy, which is then used as a reference energy when calculating the surface energies (defined in Eq. ((1)). One possibility is to use as the bulk reference energy the total energy difference between two slabs consisting of $N+1$ and N atomic layers. Another solution is to use the same supercell (without vacuum layers) to compute the bulk energy as the one used for the slab calculation. Finally, one could limit the size of the slab to the minimum thickness and use the separate bulk total energy in the calculation. In this case the error due to the different sampling of the bulk and slab Brillouin zones can also be kept at minimum. We adopted the third approach for our simulations. Moreover, Fiorentini et al. [4] showed that the difference in the obtained surface energy between the described methods is in the range of 1–2%. That accuracy is enough for our purposes.

The convergence of the surface energies as a function of slab thickness was not tested as a part of this work, but previous surface energy studies [3] demonstrated that for the present close-packed surfaces 8 atomic layers give converged results. Also, Fiorentini et al. [4] showed that the obtained surface energy value between the various methods discussed in the last paragraph diverges with slab thickness, the methods being most consistent with each other when slab thickness is between 6 and 8 layers.

2.2. Computational details

For an adequate simulation of paramagnetic alloy steels both the chemical and magnetic disorder should be treated simultaneously [5]. In the present application, we modeled the bulk $\mathrm{Fe}_{1-c-n}Cr_cNi_n$ system by analloy with randomly distributed chemical species and local magnetic moments, *i.e.* by a four component random $\mathrm{Fe}^{\uparrow}_{(1-c-n)/2}Fe^{\downarrow}_{(1-c-n)/2}\,\mathrm{Cr}_cNi_n$ alloy. Here the arrows represent the two magnetic moments oriented up (↑) and down (↓). This disordered local moment (DLM) approach accurately describes the effect of loss of the net magnetic moment above the transition temperature [6]. Unlike in the bulk, the magnetic moments of Cr tend to split near the surface. Thus, for the slab system, instead of the four component alloy $\mathrm{Fe}^{\uparrow}_{(1-c-n)/2}Fe^{\downarrow}_{(1-c-n)/2}\,\mathrm{Cr}_cNi_n$ we have to use a six component alloy $\mathrm{Fe}^{\uparrow}_{(1-c-n)/2}Fe^{\downarrow}_{(1-c-n)/2}Cr^{\uparrow}_{c/2}Cr^{\downarrow}_{c/2}Ni^{\uparrow}_{n/2}Ni^{\downarrow}_{n/2}$. We should mention that in the paramagnetic state, the bulk and surface Ni atoms become polarized only if one takes into account the thermal (longitudinal) spin fluctuations. This is beyond the scope of the present work. On the other hand, Cr atoms show a much stronger surface moment enhancement (already in elementary Cr; [23]), which might explain why Cr has non-vanishing local magnetic moment at the surface.

Here we exclusively considered homogeneous substitutionally disordered FeCrNi alloys, without interstitials and precipitates. Also the effects of short range order and relaxation effects were omitted. It is well known that interstitial C and N have a strong effect on stabilizing the austenitic phase. However, modeling the effect of interstitials from the first principles theory is very cumbersome especially in the chemically and magnetically disordered matrix. For this reason, we mimic the effect of all austenite stabilizers with Ni, as mentioned earlier.

The most straightforward way to compute the total energy of a disordered alloy system would be to construct a large supercell with randomly distributed solute atoms. However, in the case of an alloy with four or even six components, the supercell would have to be huge, and thus calculations based on that would cause noticeable computational cost. It is worth pointing out that one would have to perform several such calculations for each composition in order to average over different configurations. There is, however, a more novel way to calculate the total energies of random substitutional alloys, with far smaller computational cost. In this study, we employed the Coherent Potential Approximation (CPA) [7], in which the alloy components are embedded in an effective medium, which is constructed in such a way that it represents, on the average, the scattering properties of the alloy. In the present application, we adopted the CPA implemented within the framework of the Exact Muffin-Tin Orbitals (EMTO) method [8,5].

The EMTO method is an improved screened Korringa-Kohn-Rostoker method [9], where the one-electron potential is represented by large overlapping muffin-tin potential spheres. By using overlapping spheres, the crystal potential can be described more accurately, when compared with the conventional non overlapping muffin-tin approach [10–12].

The FeCrNi alloys form the basis of the austenitic stainless steels. These alloys are paramagnetic at room temperature having sizable (disordered) local magnetic moments. The local moments depend sensitively on the volume, which becomes an important question especially in theoretical studies. Soft-core calculations yield equilibrium volumes which are substantially smaller than those observed in experiment. The obvious reason for this discrepancy is the thermal expansion, which has been neglected in the present theoretical study. The unusually large thermal expansion originates from the fact that the paramagnetic fcc Fe (and also the present alloys) shows a magnetic transition near the equilibrium volume [13]. As a consequence, a straightforward soft-core calculation cannot capture the proper magnetic state of the present alloys. (We should also mention that both the local- and the gradient-level density functional approximations underestimate the equilibrium volume of magnetic 3d metals and thus further increase the above error.) One (technical) possibility to overcome this difficulty is to perform frozen-core calculations, which yield larger equilibrium volumes and thus better account for the paramagnetic state. This is why all our calculations have been performed within the frozen-core scheme.

All calculations in the present work were carried out using the generalized-gradient approximation [14] for the exchange-correlation density functional. The EMTO basis set included *s*, *p*, *d*, and *f* orbitals. The one-electron equations were solved within the scalar-relativistic approximation. For each composition and crystal lattice, the EMTO Green's function was calculated self-consistently for 16 complex