***Ab initio* investigation of the surface properties of austenitic Fe-Ni-Cr alloys in aqueous environments**

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Abstract

The surface energetics of two austenitic stainless steel alloys (Type 304 and 316) and three Ni-based alloys (Alloy 600, 690, and 800) are investigated using theoretical methods within the density functional theory. The relative stability of the low index surfaces display the same trend for all alloys; the most closely packed orientation and the most stable is the (111), followed by the (100) and the (110) surfaces. Calculations on the (111) surfaces using various surface chemical and magnetic configurations reveal that Ni has the tendency to segregate toward the surface and Cr has the tendency to segregate toward the bulk. The magnetic frustration present on the (111) surfaces plays an important role in the observed segregation tendencies of Ni and Cr. The stability of the (111) surfaces in contact with aqueous solution are evaluated as a function of temperature, *pH*, and concentration of aqueous species. The results indicate that the surface stability of the alloys decrease with temperature and *pH*, and increase slightly with concentration. Under conditions characteristic to an operating pressurized water reactor, the Ni-based alloy series appears to be of better quality than the stainless steel series with respect to corrosion resistance and release of aqueous species when in contact with aqueous solutions.

1. Introduction

Austenitic, γ -Fe-based stainless steels (SS) and Ni-based alloys exhibit key characteristics that make them suitable for service under conditions of extreme temperature and pressure. Excellent mechanical strength, good surface stability, and resistance to oxidation and corrosion are among the properties that make these alloys the most widely used materials in the nuclear energy industry. In particular, in pressurized water reactors (PWRs) the primary piping system and reactor vessel cladding are made of austenitic SS of types 304 and 316 (in SAE steel grades system), while the main materials used for steam generator (SG) tubing are Ni-based Alloys 600, 690, and 800. During reactor operation these materials are subjected to neutron irradiation, thermal and mechanical stresses, elevated temperatures (275-315 °C) and pressure (15.5 MPa), and a corrosive environment. The internal structures of the reactor, therefore, experience complex corrosion processes accompanied by release of corrosion products into the primary coolant [1]. In water-cooled reactors the presence of corrosion products, in either soluble or particulate form, represents a major operational problem. Dissolved species and particulates, cumulatively known as CRUD, deposit on the hot surfaces of the fuel rods and, consequently, reduce heat transfer in the core and accelerate corrosion of the fuel cladding [2].

In a PWR the vast majority of the corrosion products released into the coolant originates from the SG tubing that represents 65-75% of the surface area of the reactor coolant system.

Generally, the free surfaces of the alloys exposed to the primary coolant become passivated with an oxide layer (Cr_2O_3 , Cr-rich and Fe-rich spinel) that is thermodynamically more stable [3]. Therefore, the process of cation release could take place by diffusion through the oxide layer followed by dissolution of transition metal ions into the primary coolant. Recent modeling based on diffusivity calculations of Cr, Fe, Ni, and O through Cr_2O_3 suggests that the amount of corrosion products that could be released by cation diffusion through oxides is not enough to explain the observed quantities of CRUD on the fuel rods [4]. Therefore, it is possible that during reactor operation parts of the alloy surfaces are unpassivated and contribute with an increased release rate to the concentration of soluble species present in the coolant. In this case the release rate is determined by the coolant properties (temperature, pH , metal concentration, local flow velocity of the coolant) as well as the alloy composition. The latter is important because it determines the surface free energy, a fundamental quantity that plays a central role in the thermodynamic stability of the alloy in contact with the coolant.

Experimentally the “average” surface free energies of solid metals, for temperatures ranging from 0 K to melting temperature, are estimated from measurements of liquid surface tension above the melting point [5, 6]. This method, however, does not provide information about the energetics of particular surface orientations and it is inadequate to account for the influence of surface defects or adsorbing species on surface stability. In this context, first-principles calculations within the Density Functional Theory (DFT) can be extremely helpful to the advancement of this area, due to the relatively straightforward way the surfaces are modeled and surface energies are calculated. Using first-principles DFT calculations with the supercell method to capture the surface properties of fcc austenitic Fe-Ni-Cr alloys, however, is not trivial. Difficulties arise mainly because of the extremely diverse magnetic properties displayed by these materials. This is illustrated by the numerous first-principles calculations carried out on single component γ -Fe that found many, energetically almost degenerate magnetic ground state configurations [7-13]. Modeling multicomponent Fe-Ni-Cr alloys is further complicated by the multitude of magnetic phases that can develop as a function of composition [14-16]. Also local magnetic properties are affected in an intricate way by impurities or vacancies present in the structure [17-19]. Despite all the complexities, first-principles calculations play a key role in establishing and predicting fundamental electronic, magnetic and structural properties in austenitic Fe-Ni-Cr alloys.

There are relatively few DFT studies focusing on surface properties of these materials [20, 21]. Yu *et al.* investigated the surface relaxation and energies of low index surfaces of fcc- Fe and SS 304 ($\text{Fe}_{23}\text{Cr}_6\text{Ni}_3$) using supercell methods, excluding magnetic effects [20]. A more recent study reported by Pitkänen *et al.* investigated the energetics of (100) and (111) surfaces of paramagnetic Fe-Ni-Cr alloys for a wide range of compositions, using the coherent potential approximation (CPA) [21].

In this paper we report the results of an investigation of the energies of low index surfaces of five austenitic Fe-Ni-Cr alloys (SS 304 and 316 and Alloy 600, 690, and 800) using DFT calculations in combination with supercell models. The concentrations of the three major components (Fe, Cr, and Ni) in these alloys, along with the composition used in the DFT

modeling, are listed in Table I. We also combine results of the first-principles calculations with thermodynamic data to evaluate the surface stability of these alloys in contact with aqueous solution for temperatures, pH values, and concentrations of dissolved species that are characteristic of operating PWRs.

2. Details of calculations

The results presented in this paper were obtained using the projector augmented wave (PAW) method [22] within the DFT as implemented in the VASP code [23-26]. The exchange-correlation potential was approximated by the generalized gradient approximation, as parameterized by Perdew, Burke, and Ernzerhof (PBE) [27]. The standard PAW potentials, supplied with the VASP code, with eight, six and ten valence electrons for Fe, Cr, and Ni, were employed in the calculations. The convergence of the self-consistent cycles was assumed when the energy difference between them was less than 10^{-4} eV and the atomic positions were relaxed until the forces on the Hellmann-Feynman forces on the nuclei were less than 0.02 eV/Å. After a series of convergence tests on different bulk Fe-Cr-Ni compositions, to ensure a precision better than 1 meV/atom the cut-off energy for the plane wave basis was set to 400 eV. The bulk alloys were modeled by $2 \times 2 \times 2$ supercells (32-atoms) while the surfaces were represented by periodic slab geometries containing 32 atoms arranged in 8 atomic layers and separated by a vacuum region of 12 Å. These values were found to be sufficient to ensure a convergence of 0.01 J/m² for the unrelaxed surface energies of γ -Fe [20]. The Brillouin zones of bulk and slab systems were sampled by Γ -centered $12 \times 12 \times 12$ and $16 \times 16 \times 1$ Monkhorst-Pack [28] k-point meshes, respectively. The equilibrium bulk lattice constants were determined for all of the compositions by performing a series of calculations with varying lattice parameters and then fitting the Birch-Murnaghan equation of state to the calculated total energies. We found small variations in the lattice parameters (Table I) as a function of composition; the values are in the range from 3.54 to 3.58 Å, relatively close to ~ 3.6 Å reported in Ref. [21]. The calculated lattice constants are used in the slab calculations.

The surface energy is defined as the energy required to separate the bulk material into two semi-infinite slabs. In principle, using this definition, it is straightforward to calculate the surface energy by taking the difference between the slab and bulk total energies:

$$\gamma = \lim_{N \rightarrow \infty} \frac{1}{2A} (E_{slab}^N - N \cdot E_{bulk}) \quad (1)$$

where E_{slab}^N is the total energy of the slab containing N atoms, E_{bulk} is the total energy per atom of the bulk reference system, and A is the surface area of the slab. The factor of 1/2 appears in Eq. (1) to account for the two equivalent surfaces of the slab model.

3. Surface energies

In this work two sets of surface energy calculations were carried out: one in which the chemical disorder in the bulk and slab models are represented by special quasirandom structures (SQS) [29, 30] and one where the surface atomic configurations were deliberately modified to study the correlation between surface magnetism, segregation of elements, and surface stability.

For consistency between the bulk and slab calculations, and to be able to compare surface energies across compositions, the collinear spin-polarized calculations were performed with the initial moments on Fe, Cr, and Ni set to 3, -3, and 1 μ_B . This setup is consistent with results of previous studies that established that Cr moments tend to couple antiferromagnetically to neighboring Fe moments, while Ni moments are ferromagnetic with respect to Fe neighbors [18, 31].

The surface energies of austenitic SS 304, 316 and Alloys 600, 690, and 800 calculated using SQS models are listed in Table II. It is apparent that the (111) surfaces have the lowest energy. This is reasonable because the (111) surface is the most closely packed orientation in an fcc lattice. A similar trend was obtained by Pitkänen *et al.* [21], who analyzed the energetics of the (111) and (100) surfaces in a wide composition range. The surface energies calculated by Pitkänen *et al.* for the (111) and (100) surfaces are in the range of 2.7-3.0 J/m² and 3.0-3.3 J/m², respectively, somewhat higher than the ones reported here. The difference between our results and those of Pitkänen *et al.*, could probably be related to their use of the CPA approach, which excludes ionic relaxations. Yu *et al.* [20] also calculated the surface energies of SS 304 using the DFT-PBE method with the supercell approach and obtained energies of 2.07, 2.28, and 2.10 J/m² for the (100), (110), and (111) surfaces. Although on average the values of Yu *et al.* are closer to ours than those of Pitkänen, the trend is different: Yu *et al.* found the (100) surface to be the most stable. This is somewhat unexpected considering that the surface energy quantifies the disruption in the interatomic bonds when the surface is created. The differences between the Yu *et al.* results and ours might be that Jun Yu *et al.* neglected magnetic effects.

In the case of alloys, elements can segregate to the surface creating surface concentration profiles that are different from the chemical concentration in the bulk. Surface energies depend sensitively on the surface chemical composition. To obtain consistent surface energies for all five Fe-Cr-Ni alloys and all surface orientations, calculations were carried out on slabs with similar surface compositions. More precisely, the surface chemical profiles were set up such that the four surface sites of the slabs were occupied by one Fe, one Cr and two Ni cations. The surface energies calculated using these slabs are listed in Table III. As expected, the lowest-energy orientations are (111), but now the trend is evident for the other two low index facets as well. The second most stable surface for all compositions, except for Alloy 690, belongs the (100) orientation followed by (110). In the case of Alloy 690 it appears that the energy of the (110) surface (2.30 J/m²) is slightly lower than that of the (100) surface (2.31 J/m²), however the difference between these energies is within the calculational uncertainty. Besides the surface composition, the calculated surface energies are also influenced by local atomic arrangements inside the slabs. This effect is not taken into account in our calculations.

Establishing a trend in the surface energies across the alloy series is difficult because the concentrations of at least two components change from one alloy to another. However, by comparing the energies of the (111) surfaces of SS 304, 316 and Alloy 600, where the concentration (at. %) of Cr is the same, we notice an increase in surface energy with the increase/decrease in Ni/Fe concentration. Because Pitkänen *et al.* [21] established that the amount of Ni has little effect on surface energies, it is likely that the increase in energy of the

(111) surfaces observed here is due to the decrease in Fe concentration. Ignoring the small changes in the amount of Cr, the same trend is apparent in going from Alloy 800 to 690 to 600.

4. Surface magnetism and surface segregation

Because the lowest energy orientation is (111), we focus our attention on the influence of surface magnetism on segregation tendencies of elements on these surfaces. The local magnetic moments of Fe and Cr are larger at the surface than inside the bulk. The values for Fe and Cr decrease rapidly from ~ 2.5 to $\sim 1.6\mu_B$ and 3.0 to $\sim 1.9\mu_B$ as a function layer depth. On average, the magnetic moment of Fe appears to be larger by $\sim 0.15\mu_B$ in Alloy 600 and 690 than in SS 304 and 316, whereas the Cr moments seem to be smaller in the bulk region of the alloys by approximately $0.1\mu_B$ compared with the SS series. The magnetic moments of Ni display similar behavior as a function of layer depth, although their values are considerably lower (0.2 to $0\mu_B$) than those of Fe and Cr.

To study the segregation tendencies of the alloy components, we performed extensive calculations with various surface chemical and magnetic configurations. The hypothesis is that because the local magnetic moments of Fe and Cr are the largest in the surface layers, the magnetic coupling (ferromagnetic or antiferromagnetic) between them plays an important role in the surface energetics. Test calculations indicate that the surface energies are minimized when the surface spins are aligned antiferromagnetically. However, because the (111) surface of an fcc structure forms a triangular lattice the spin magnetic moments that reside on the surface and tend to arrange antiferromagnetically, give rise to magnetic frustration. This magnetic frustration, and therefore the surface energy, are minimized when one corner of the triangle is occupied by a nonmagnetic atom or by an atom with a small magnetic moment such as Ni. On the other hand, if the surface is populated by atoms with large magnetic moments (such as Cr) the frustration will be higher and consequently the surface will be less stable. This assumption implies that Ni has the preference to segregate toward the surface while Cr tends to move deeper in the bulk.

To test the hypothesis we calculated the (111) surface energies of an fcc Fe system, with one Cr and one Ni atom located in various atomic layers relative to the surface. First we kept the Cr atom in the surface layer and shifted the Ni deeper into the bulk, then we swapped Cr and Ni, keeping the Ni in the top and moving Cr toward the bulk. The results are illustrated in Fig. 1. When Cr is located in the top layer, there is an increase of 0.4 eV in the slab energy as Ni moves from the surface to the subsurface layer. As Ni is shifted deeper into the bulk, the system appears to become slightly more stable, however, the energy gain between the configurations with Ni in the second and fourth layer is smaller than the uncertainty in the calculation. It is energetically favorable for Ni to occupy surface sites, but as it moves deeper into the bulk it has little effect on stability. The location of Cr relative to the surface has a more prominent effect on surface energetics, as illustrated in the lower panel of Fig.1. If Ni is held in the top layer and Cr is shifted successively to deeper layers the system becomes more and more stable. There is a gain of 0.4 eV as Cr moves from the top to the fourth deepest layer. This suggests that in the dilute limit Cr has the tendency to segregate toward the bulk, while Ni prefers to segregate toward the surface.

To further test the idea of surface segregation, we carried out a series of calculations where the surface chemical compositions were altered so that all possible configurations of three elements occupying four surface sites were explored. The calculations were carried out for SS 316, Alloys 600, and 800 where the double sided 32-atom slabs models contain enough Ni atoms to occupy at least two surface sites. The results are illustrated in Fig. 2, where the relative energies of the slabs are represented as a function of surface chemical profiles. Based on these calculations, and keeping in mind that the energies are also influenced by local atomic arrangements within the slabs, the trend is evident: the most stable surfaces are the ones that are enriched in Ni, while the presence of Cr on the surface tends to increase the surface energies. This trend is notably apparent in the Ni-rich Alloys 600 and 800. Pitknen et al. [21] estimated Ni and Cr segregation energies based on effective chemical potential calculations and reached similar conclusions to ours. The tendency of Ni to segregate toward the surface was also observed in annealing experiments performed by Jusilla et al. [32]. When exposed to an oxygen containing environment, however, due to its higher oxygen affinity, Cr migrates to the surface and forms a protective oxide layer that makes the stainless steel corrosion resistant.

5. Stability of Fe-Ni-Cr alloys in aqueous environments

To estimate the thermodynamic stability of Fe-Ni-Cr surfaces in contact with aqueous solution under conditions of an operating PWR, we calculated the energies associated with vacancy formation in the surface layers of the alloys. Using the methodology described in Ref. [33], we set up the equilibrium between the surface of the solid and the surrounding aqueous solution by setting the chemical potentials of the ionic species in the solid ($\mu_{i^{z+}}$, $i = \text{Fe, Ni, Cr}$) to be equal to the aqueous chemical potentials of the dissolved cations ($\mu_{i^{z+},aq}$). Under these conditions, the formation energy of a surface vacancy can be written as:

$$\Delta H(V_i) = E_{slab}(V_i) - E_{slab}^0 + \sum_i n_i \mu_{i^{z+},aq} - \sum_i n_i z E_F \quad (2)$$

The first two terms on the right side of eq. (2) are the DFT total energies of the vacancy containing and the defect free slabs. The third term represents the energy necessary to exchange a number of n_i ions between the surface and the aqueous reservoir. The last term represents the energy required to exchange electrons between the electron reservoir with energy E_F , and the bulk system to create an ion with a $z+$ oxidation state. The aqueous chemical potential ($\mu_{i^{z+},aq}$) can be expressed by combining results of the DFT calculations and data from thermodynamic databases [33-35]:

$$\mu_{i^{z+},aq} = \Delta G_f^0(i^{z+},aq) + \mu_{i,solid}^0 + z \left(\mu_{H^+,aq}^0 - \frac{1}{2} \mu_{H_2,gas}^0 \right) + RT \ln a_{i^{z+}} \quad (3)$$

In eq. (3) ΔG_f^0 represents the Gibbs free energies of formation of the aqueous species and are obtained from the SUPCRT database [36, 37]. The chemical potentials of the solid phases

$(\mu_{i,solid}^0)$ are approximated by the total energy per atom of the elemental solids as calculated from DFT. The elemental phases considered here are bcc Fe, bcc Cr and fcc Ni. The chemical potential of an aqueous proton is related to pH through the relation $\mu_{H^+} = RT \ln(10^{-pH})$ and the chemical potential of H_2 gas is expressed as a function of temperature [38]. The last term in eq. (3) depends on temperature and the activities of ionic species in solution. Because the Fe-Cr-Ni alloys are weakly soluble in water, the activities are approximated by concentrations.

Using the method briefly described above we calculated the energies associated with the creation of an Fe, Cr, or Ni vacancy on the surfaces of the SS 304, 316 and Alloys 600, 690 and 800 as a function of temperature, pH and concentrations. The vacancy formation energies as a function of temperature are plotted in Fig. 3. The concentration of aqueous cations was assumed to be $[Fe^{2+}] = [Fe^{3+}] = 1.4$ ppb, $[Ni^{2+}] = 0.22$ ppb, and $[Cr^{2+}] = 1$ ppb, concentrations characteristic to operating PWR [39]. As a general trend, Fig. 3 illustrates that formation energies decrease with temperature. This suggest that at high temperatures the rate of vacancy formation is higher and the alloy surfaces become less stable. For all alloys the lowest vacancy formation energies belong to Fe^{3+} and Ni^{2+} . However, because of the reducing conditions in the primary loop of PWRs, most of Fe^{3+} released from the alloy surfaces is probably reduced to Fe^{2+} . The high energy associated with the formation of Cr vacancies is in line with the observed low Cr^{2+} concentration in the PWR coolant. An important feature revealed in Fig. 3 is that the formation energies of vacancies on the Ni-based alloy surfaces are higher than those on the SS surfaces. This indicates that the Ni-based alloys (Alloy 600, 690, 800) are more stable than the 300-series SS and therefore represent a better choice of materials with regard to corrosion resistance and release of corrosion products into the PWR coolant.

The formation energies of vacancies as a function of pH is illustrated in Fig. 4. All vacancies display similar behavior, namely, their formation energies decrease with increasing pH . This suggests that the release of corrosion products (aqueous cations) in a PWR could be reduced by decreasing the pH of the coolant. The concentration dependence of the formation energies is illustrated in Fig. 5 for the SS 304 alloy. We observe a minor increase in formation energies when the concentration of aqueous species increase three orders of magnitude. The other alloys (not illustrated here) display similar behavior, in line with the very low solubility of these materials in aqueous environments.

6. Summary

The energetics of the low-index surfaces of SS 304, 316 and Ni-based Alloys 600, 690, and 800 were investigated using first principles methods within the DFT. The surface energy trend for all alloys in this study is $(111) < (100) < (100)$. Based on the simple bond-cutting model, this trend is expected and it is in agreement with previous theoretical modeling [21]. The surface chemical composition and surface magnetic moments have a dramatic influence on the surface energetics. Due to the geometrical frustration on the (111) surfaces Ni has the tendency to segregate toward the surface while Cr is driven deeper into the bulk.

Combining results of DFT calculations with thermodynamics data, the formation energies of surface vacancies were evaluated as a function of temperature, pH, and concentrations. To evaluate the performance of these materials in nuclear reactors, the parameters chosen were typical to an operating PWR. The results indicate that the surface stability of the alloys decrease with temperature and pH , and increase slightly with concentration. The Ni-based Alloy series appears to be of better quality than the SS series with respect to corrosion resistance and release of aqueous species when in contact with aqueous solutions.

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Figure captions:

Fig. 1. Relative segregation energies of Cr and Ni.

Fig. 2. Relative DFT energies of the slab models as a function of surface chemical composition for (a) SS 316, (b) Alloy 600, and (c) Alloy 800.

Fig. 3. Formation energies of surface vacancies as a function of temperature.

Fig. 4. Formation energies of surface vacancies as a function of pH .

Fig. 5. Formation energies of surface vacancies in SS 304 as a function of concentration of aqueous species.

Table I. Calculated lattice parameters and the chemical composition of the Fe-Cr-Ni alloys.

Alloy	Lattice constant (Å)	Alloy composition (wt. %)			DFT model (wt. %)		
		Fe	Cr	Ni	Fe	Cr	Ni
304	3.55	66-74	18-20	8-10.5	75.65	17.69	6.67
316	3.58	62-72	16-18	10-14	69.10	17.63	13.27
600	3.54	6-10	14-17	72-80	6.07	17.03	76.90
690	3.56	7-11	27-31	58-66	12.31	25.92	61.76
800	3.56	39.5-50.7	19-23	30-35	43.69	23.36	32.95

Table II. Surface energies of austenitic SS 304, 316 and Ni-based Alloys 600, 690 and 800 calculated using SQS models for the bulk and slab systems. Values are given in J/m².

Surface orientation	304	316	600	690	800
(100)	2.39	2.53	2.40	2.16	2.30
(110)	2.31	2.40	2.30	2.26	2.32
(111)	2.25	2.32	2.15	2.06	1.92

TABLE III. Surface energies of austenitic SS 304, 316 and Ni-based Alloys 600, 690 and 800 calculated with 1Fe-1Cr-2Ni surface chemical profiles. Values are given in J/m².

Surface orientation	304	316	600	690	800
(100)	2.29	2.35	2.41	2.31	2.31
(110)	2.53	2.37	2.53	2.30	2.33
(111)	1.65	2.04	2.38	2.03	1.58

Fig. 6. Relative segregation energies of Cr and Ni.

Fig. 7. Relative DFT energies of the slab models as a function of surface chemical composition for (a) SS 316, (b) Alloy 600, and (c) Alloy 800.

Fig. 8. Formation energies of surface vacancies as a function of temperature.

Fig. 9. Formation energies of surface vacancies as a function of pH .

Fig. 10. Formation energies of surface vacancies in SS 304 as a function of concentration of aqueous species.

References

- [1] B.M. Gordon, Corrosion and Corrosion Control in Light Water Reactors, JOM-US 65 (2013) 1043-1056.
- [2] Axial Offset Anomaly (AOA) Mechanism Verification in Simulated PWR Environments, EPRI Report 1013423, Palo Alto, CA, 2006.
- [3] T.M. Devine, Influence of Primary Water Chemistry on Oxides Formed on Alloy 600 and Alloy 690, 15th International Conference on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors (2011) 967-992.
- [4] Multiscale Modeling of the Crud Source Term in Pressurized Water Reactors, EPRI Report 3002008163, Palo Alto, CA, 2016.
- [5] W.R. Tyson, W.A. Miller, Surface Free-Energies of Solid Metals - Estimation from Liquid Surface-Tension Measurements, Surf. Sci. 62 (1977) 267-276.
- [6] U.M. Ahmad, L.E. Murr, Surface Free-Energy of Nickel and Stainless-Steel at Temperatures above Melting-Point, J. Mater. Sci. 11 (1976) 224-230.
- [7] H.C. Herper, E. Hoffmann, P. Entel, Ab initio full-potential study of the structural and magnetic phase stability of iron, Phys. Rev. B 60 (1999) 3839-3848.
- [8] C. Domain, C.S. Becquart, Ab initio calculations of defects in Fe and dilute Fe-Cu alloys, Phys. Rev. B 65 (2002) 024103.
- [9] D.E. Jiang, E.A. Carter, Carbon dissolution and diffusion in ferrite and austenite from first principles, Phys. Rev. B 67 (2003) 214103.
- [10] L.T. Kong, B.X. Liu, Distinct magnetic states of metastable fcc structured Fe and Fe-Cu alloys studied by ab initio calculations, J. Alloys Compd. 414 (2006) 36-41.
- [11] K. Knopfle, L.M. Sandratskii, J. Kubler, Spin spiral ground state of gamma-iron, Phys. Rev. B 62 (2000) 5564-5569.
- [12] E. Sjostedt, L. Nordstrom, Noncollinear full-potential studies of gamma-Fe, Phys. Rev. B 66 (2002) 014447.

- [13] I.A. Abrikosov, A.E. Kissavos, F. Liot, B. Alling, S.I. Simak, O. Peil, A.V. Ruban, Competition between magnetic structures in the Fe rich fcc FeNi alloys, *Phys. Rev. B* 76 (2007) 014434.
- [14] J.S. Wrobel, N.M. Duc, M.Y. Lavrentiev, M. Muzyk, S.L. Dudarev, Phase stability of ternary fcc and bcc Fe-Cr-Ni alloys, *Phys. Rev. B* 91 (2015) 024108.
- [15] H. Pitkanen, M. Alatalo, A. Puisto, M. Ropo, K. Kokko, M.P.J. Punkkinen, P. Olsson, B. Johansson, S. Hertzman, L. Vitos, Ab initio study of the phase stability in paramagnetic duplex steel alloys, *Phys. Rev. B* 79 (2009) 024108.
- [16] A.K. Majumdar, P. Vonblanckenhagen, Magnetic Phase-Diagram of Fe₈₀-X_nCr₂₀ (10-Less-Than-or-Equal-to-X-Less-Than-or-Equal-to-30) Alloys, *Phys. Rev. B* 29 (1984) 4079-4085.
- [17] L. Delczeg, B. Johansson, L. Vitos, Ab initio description of monovacancies in paramagnetic austenitic Fe-Cr-Ni alloys, *Phys. Rev. B* 85 (2012) 174101.
- [18] J.B. Piochaud, T.P.C. Klaver, G. Adjanor, P. Olsson, C. Domain, C.S. Becquart, First-principles study of point defects in an fcc Fe-10Ni-20Cr model alloy, *Phys. Rev. B* 89 (2014) 024101.
- [19] T.P.C. Klaver, D.J. Hepburn, G.J. Ackland, Defect and solute properties in dilute Fe-Cr-Ni austenitic alloys from first principles, *Phys. Rev. B* 85 (2012) 174111.
- [20] J. Yu, X. Lin, J.J. Wang, J. Chen, W.D. Huang, First-principles study of the relaxation and energy of bcc-Fe, fcc-Fe and AISI-304 stainless steel surfaces, *Appl. Surf. Sci.* 255 (2009) 9032-9039.
- [21] H. Pitkanen, M. Alatalo, A. Puisto, M. Ropo, K. Kokko, L. Vitos, Ab initio study of the surface properties of austenitic stainless steel alloys, *Surf. Sci.* 609 (2013) 190-194.
- [22] P.E. Blochl, Projector Augmented-Wave Method, *Phys. Rev. B* 50 (1994) 17953-17979.
- [23] G. Kresse, J. Hafner, Abinitio Molecular-Dynamics for Liquid-Metals, *Phys. Rev. B* 47 (1993) 558-561.
- [24] G. Kresse, J. Hafner, Ab-Initio Molecular-Dynamics Simulation of the Liquid-Metal Amorphous-Semiconductor Transition in Germanium, *Phys. Rev. B* 49 (1994) 14251-14269.
- [25] G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B* 54 (1996) 11169-11186.
- [26] G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comp. Mater. Sci.* 6 (1996) 15-50.
- [27] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865-3868.
- [28] H.J. Monkhorst, J.D. Pack, Special Points for Brillouin-Zone Integrations, *Phys. Rev. B* 13 (1976) 5188-5192.
- [29] A. Zunger, S.H. Wei, L.G. Ferreira, J.E. Bernard, Special Quasirandom Structures, *Phys. Rev. Lett.* 65 (1990) 353-356.
- [30] A. van de Walle, P. Tiwary, M. de Jong, D.L. Olmsted, M. Asta, A. Dick, D. Shin, Y. Wang, L.Q. Chen, Z.K. Liu, Efficient stochastic generation of special quasirandom structures, *Calphad* 42 (2013) 13-18.
- [31] C. Niu, A.J. Zaddach, A.A. Oni, X. Sang, J.W. Hurt, J.M. LeBeau, C.C. Koch, D.L. Irving, Spin-driven ordering of Cr in the equiatomic high entropy alloy NiFeCrCo, *Appl. Phys. Lett.* 106 (2015) 161906-161906.

- [32] P. Jussila, K. Lahtonen, M. Lampimäki, M. Hirsimäki, M. Valden, Influence of minor alloying elements on the initial stages of oxidation of austenitic stainless steel materials, *Surf. Interface Anal.* 40 (2008) 1149-1156.
- [33] Z. Rak, E.W. Bucholz, D.W. Brenner, Defect formation in aqueous environment: Theoretical assessment of boron incorporation in nickel ferrite under conditions of an operating pressurized-water nuclear reactor (PWR), *J. Nucl. Mater.* 461 (2015) 350-356.
- [34] C.J. O'Brien, Z. Rak, D.W. Brenner, Free energies of (Co, Fe, Ni, Zn)Fe₂O₄ spinels and oxides in water at high temperatures and pressure from density functional theory: results for stoichiometric NiO and NiFe₂O₄ surfaces, *J. Phys.: Condens. Matter* 25 (2013) 445008.
- [35] C.J. O'Brien, Z. Rak, D.W. Brenner, Calculated Stability and Structure of Nickel Ferrite Crystal Surfaces in Hydrothermal Environments, *J. Phys. Chem. C* 118 (2014) 5414-5423.
- [36] T. Windman, T. Windman, E. Shock, A web-based interactive version of SUPCRT92, *Geochim. Cosmochim. Acta* 72 (2008) A1027-A1027.
- [37] J.W. Johnson, E.H. Oelkers, H.C. Helgeson, Supcrt92 - a Software Package for Calculating the Standard Molal Thermodynamic Properties of Minerals, Gases, Aqueous Species, and Reactions from 1-Bar to 5000-Bar and 0-Degrees-C to 1000-Degrees-C, *Computers & Geosciences* 18 (1992) 899-947.
- [38] K. Matsunaga, Theoretical investigation of the defect formation mechanism relevant to nonstoichiometry in hydroxyapatite, *Phys. Rev. B* 77 (2008) 104106.
- [39] S. Dickinson, J. Henshaw, J. McGurk, H. Sims, Modeling PWR Fuel Corrosion Product Deposition and Growth Processes: Final Report, EPRI Report 1009734, Palo Alto, CA, 2005.