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Abstract

The properties of point defects in Fe-Cr-Ni alloys are investigated, using density functional theory (DFT), for two alloy compositions, Fe₅₀Cr₂₅Ni₂₅ and Fe₅₅Cr₁₅Ni₃₀, assuming various degrees of short-range order. DFT-based Monte Carlo simulations are applied to explore short-range order parameters and generate representative structures of alloys. Chemical potentials for the relevant structures are estimated from the minimum of the substitutional energy at representative atoms sites. Vacancies and <100> dumbbells are introduced in the Fe₂CrNi intermetallic phase as well as in two Fe₅₅Cr₁₅Ni₃₀ alloy structures: the disordered and short range-ordered structures, generated using Monte Carlo simulations at 2000 K and 300 K, respectively. Formation energies and relaxation volumes of defects as well as changes of magnetic moments caused by the presence of defects are investigated as functions of the local environment of a defect.

Keywords: density functional theory, Fe-Cr-Ni alloys, point defects, short-range order

1. Introduction

Austenitic stainless steels, based on Fe-Cr-Ni alloys, like the 316L steel, are materials used in a broad range of fusion and fission applications [1]. Their advantage, in comparison with ferritic-martensitic steels, is the absence of brittle-ductile transition. On the other hand, the high volumetric void swelling occurring at doses >20 dpa at temperatures 400-500°C resulted in that the 316L steel was initially rejected as a material for the first wall reactor applications. However, it has been shown experimentally that in austenitic Fe_{85-x}Cr₁₅Ni_x (x=15, 20, 25, 30) alloys irradiated to 6 dpa, voids do not form above 350 °C if the concentration of Ni equals 30% [2]. This observation shows that irradiation-induced phenomena are strongly correlated with the composition of alloy, also suggesting that other compositions may potentially exhibit better properties than alloy compositions currently used in steels.

To understand radiation damage effects in materials, it is necessary to compute energies of formation and migration of point defects. In a multicomponent alloy these energies depend not only on the average composition of the alloy but also on the local environment of a defect. The latter in turn depends on the local chemical order. Owing to difficulties of probing the local environment of defects, experimental information on point defects in austenitic Fe-Cr-Ni alloys is limited. This information can instead be derived from *ab initio* DFT simulations. To our knowledge, there have been

only a few DFT studies of point defects in austenitic Fe-Cr-Ni ternary alloys [3-6,15]. In all these studies, Fe-Cr-Ni alloys were assumed to be fully chemically disordered. This assumption is not realistic, since there is experimental evidence showing that many Fe-Cr-Ni alloys exhibit short-range order [7-9].

In this work, properties of point defects are investigated using representative structures of austenitic Fe-Cr-Ni alloys with chemical short-range order generated using DFT-based Monte Carlo (MC) simulations described in detail in Ref. [10].

2. Computational methods

DFT calculations were performed using the projector augmented wave (PAW) method implemented in VASP [11][12]. Exchange and correlation were treated in the generalized gradient approximation GGA-PBE [13]. To accelerate DFT calculations, we used PAW potentials without the semi-core *p* electron contribution. Total energies were calculated using the Monkhorst-Pack mesh [14] of *k* points in the Brillouin zone, with *k*-mesh spacing of 0.2 Å⁻¹. The value of the plane-wave cut-off energy used in the calculations was 400 eV. The total energy convergence criterion was set to 10⁻⁵ eV/cell, and force components were relaxed to 10⁻² eV/Å. Collinear spin-polarized DFT calculations of perfect and defect structures were performed assuming that the initial atomic magnetic moments of Fe, Cr, and Ni atoms were +3, -1, and +1 Bohr magnetons, respectively. Representative structures of Fe₅₅Cr₁₅Ni₃₀ alloy were

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generated using MC simulations with effective cluster interaction parameters derived from the Cluster Expansion (CE) method of Ref. [10]. Simulations were performed using a super-cell containing 108 atoms in the form of 3x3x3 conventional fcc cells at two different temperatures: 300 K and 2000 K. Structures without defects contained 58 Fe, 16 Cr and 34 Ni atoms. Vacancies were introduced by removing one Fe atom from the reference perfect structure. A-Fe dumbbells, where A=Cr or Ni or Fe, were introduced by replacing atom A by a pair of A and Fe atoms. Vacancy and dumbbell formation energies were calculated using chemical potentials of Fe, Cr and Ni estimated from the minimum of substitutional energy of representative atoms sites, following Ref. [6].

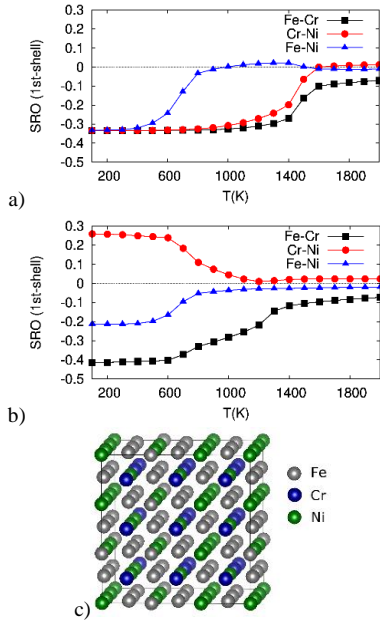


Figure 1. Short-range order parameters computed as functions of temperature for Fe-Cr, Cr-Ni and Fe-Ni pairs occupying first coordination shell in: (a) Fe₅₀Cr₂₅Ni₂₅ and (b) Fe₅₅Cr₁₅Ni₃₀ alloy. (c) The structure of Fe₅₅Cr₁₅Ni₃₀ alloy at 300 K.

3. Results and discussion

3.1. Chemical ordering in Fe-Cr-Ni alloys.

Properties of point defects in an alloy depend both on the nominal composition of the alloy as well as on the local atomic environment of a defect site. The latter depends on chemical ordering that varies as a function of temperature. Temperature effects can be investigated using the Cluster Expansion method combined with Monte Carlo simulations. Short-range order (SRO) can be described using the Warren-Cowley parameters as in Ref. [10]. SRO parameters of Fe₅₀Cr₂₅Ni₂₅ and Fe₅₅Cr₁₅Ni₃₀ alloys computed as functions of temperature are shown in Figs. 1(a,b). In both cases SRO

parameters of Fe-Cr and Fe-Ni pairs are negative, indicating that Fe atoms attract both Cr and Ni atoms. Chemical order characterising Fe-Cr and Fe-Ni pairs vanishes in both cases above approx. 1450 K and 650 K, respectively. A significant difference between the Fe₅₀Cr₂₅Ni₂₅ and Fe₅₅Cr₁₅Ni₃₀ alloys is observed for the Cr-Ni pairs. The Cr-Ni SRO parameter for the Fe₅₀Cr₂₅Ni₂₅ alloy is negative and vanishes above approx. 1450 K, whereas for the Fe₅₅Cr₁₅Ni₃₀ alloy it is positive and vanishes above approx. 1000 K. This means that atoms in Cr-Ni pairs repel or attract each other in Fe₅₀Cr₂₅Ni₂₅ and Fe₅₅Cr₁₅Ni₃₀ alloys, respectively. At low temperatures, Fe₂CrNi phase is formed in the first alloy and it is not observed in the second one.

3.2. Point defects in the Fe₂CrNi intermetallic phase.

Since Fe₂CrNi is an ordered intermetallic phase, it has only four non-equivalent atomic positions. Therefore, the values of formation energies of vacancies and dumbbells, as well as chemical potentials, are easy to compute without probing a large variety of local atomic configurations. Values of chemical potentials of Fe, Cr and Ni obtained for the Fe₂CrNi phase are more negative in comparison with pure crystals. For example, μ_{Fe} in that phase equals 0.095 eV, and is 0.109 eV smaller than its value for pure ferromagnetic bcc and fcc crystals, respectively. Properties of point defects in Fe₂CrNi phase at various atomic positions are given in Table 1. Formation energies of vacancies and dumbbells are significantly larger than those obtained for pure ferromagnetic fcc Ni and fcc Fe as well as vacancy formation energies in disordered fcc Fe₇₀Cr₁₀Ni₂₀ alloy, where they vary in the range from 1.76 to 2.19 eV [6]. The lowest vacancy formation energy of 2.783 eV is found for a vacancy at the Cr site whereas the lowest dumbbell formation energy is obtained for dumbbells at Fe1 and Ni sites. Relaxation volumes of vacancies and dumbbells are less negative and less positive, respectively, in comparison with the values obtained for pure fcc Ni and fcc Fe. Changes in magnetic moments caused by a vacancy and a dumbbell vary significantly depending on the choice of an atomic site. As a consequence, presumably due to magneto-volume effects, a vacancy replacing a Ni atom has a more negative relaxation volume than the one replacing a Fe atom.

3.3. Point defects in Fe₅₅Cr₁₅Ni₃₀ alloy.

Investigation of point defects in the Fe₅₅Cr₁₅Ni₃₀ alloy was restricted to vacancies and <100> Fe-Fe dumbbells, which were found to be the most stable defect configurations in the Fe₇₀Cr₂₀Ni₁₀ alloy [3][6]. Contrary to what was found in the Fe₂CrNi intermetallic phase, the chemical potentials of Fe in both Fe₅₅Cr₁₅Ni₃₀ structures

are similar to that of pure ferromagnetic fcc Fe crystal. Values obtained for the 300 K and 2000 K structures are only 0.010 and 0.007 eV/atom less negative than the latter one.

Vacancy formation energies and relaxation volumes calculated for the structures generated using MC simulations at 300 K and 2000 K are shown in Figs. 2(a-d). In the 300K structure with short-range order, shown in Fig. 1(c), it is observed that the vacancy formation energy increases as a function of the number of Ni atoms in the first coordination shell around a defect when the number of Cr atoms is constant, see Fig. 2(a). On the other hand, it increases when the number of Cr atoms in the first coordination shell around a vacancy decreases. As a consequence, the smallest vacancy formation energies of 1.845 eV and 1.935 eV are found for configurations without Ni atoms and without Cr atoms, respectively. Vacancy formation energies observed for disordered structures generated using MC simulations at 2000 K are significantly smaller than those obtained for the 300 K structure, see Fig. 2(b). This shows that vacancies are more difficult to form in a short-range ordered structure. The average value of vacancy formation energy for the latter one equals 2.006 eV, and is 0.240 eV larger than the value calculated for the 2000 K structure. Both of them are larger than the values characterising fcc Ni and fcc Fe but smaller than those found for the Fe₂CrNi phase. Average relaxation volumes of vacancies are -0.371 and -0.329 average atomic volume units for the 300 K and 2000 K structures, respectively, and are less negative than those calculated for fcc Ni and fcc Fe. Changes in magnetic moment caused by the presence of a vacancy are negative and the moment decreases as the number of Ni atoms increases. Like in the case of vacancies, the average formation energy of a dumbbell in the short-range ordered 300K structure, equal to 3.463 eV, is significantly higher than for the disordered 2000 K structure, where it is equal to 2.948 eV. The average relaxation volume of a dumbbell in the 2000K structure equals 1.374, and is 0.195 atomic volume units smaller than that one obtained for the 300 K structure, and is smaller than the value calculated for fcc Ni. For the 300K structure, the change in magnetic moment caused by a dumbbell is mainly positive. The only exception is the configuration with four Cr and no Ni atoms, which results in the reduction of magnetic moment of $-5.156 \mu_B$. In the 2000 K structure, there are more configurations where reduction of magnetic moment is found, however the average change in the magnetic moment caused by all the considered configurations is still positive. Values of formation energies, relaxation volumes, and changes of magnetic moments caused by both vacancies and dumbbells, are

more dispersed for the 2000 K structure in comparison with the 300 K structure.

4. Conclusions

We have investigated point defects in fcc Fe-Cr-Ni alloys using chemical potentials estimated from the minimum of substitutional energy at the representative atoms sites. The chemical potential of disordered and short range ordered Fe₅₅Cr₁₅Ni₃₀ structure is similar to the one of pure bcc Fe crystal whereas the chemical potential of the Fe₂CrNi phase is significantly more negative.

Analysis of formation energies, relaxation volumes and changes in magnetic moments caused by defects in various fcc Fe-Cr-Ni structures considered here highlights an important role played by the local environment of a defect, especially its first coordination shell. Moreover, properties of defects depend on short-range order. The formation energies of vacancies and dumbbells are the smallest in the disordered Fe₅₅Cr₁₅Ni₃₀ structure generated using MC simulations at 2000 K. Formation energies of point defects are higher in the short-range ordered 300 K structure and are the highest in the fully ordered Fe₂CrNi intermetallic phase. With increasing degree of chemical ordering, the magnitudes of relaxation volumes of point defects increase, too, bearing in mind that vacancies and dumbbells are characterised by negative and positive relaxation volumes, respectively.

Acknowledgements

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Table 1. Formation energies, E_f , relaxation volumes, Ω_r , and changes of magnetic moments, Δm , calculated for configurations with a vacancy (Vac) and a dumbbell (A – Fe), replacing atoms (A=Fe,Cr,Ni) in Fe_2CrNi compared with the values obtained for fcc Ni and Fe.

Wyckoff position	E_f^{Vac} (eV)	Ω_r^{Vac}	Δm^{Vac} (μ_B)	$E_f^{\text{A-Fe}}$ (eV)	$\Omega_r^{\text{A-Fe}}$	$\Delta m^{\text{A-Fe}}$ (μ_B)
$\text{Cr}_1 1f$	2.783	-0.325	5.908	4.826	1.622	1.870
$\text{Fe}_1 1d$	2.817	-0.310	-2.037	4.455	1.229	-0.275
$\text{Fe}_2 1g$	2.817	-0.310	-2.307	4.837	1.618	-3.623
$\text{Ni}_1 1a$	2.815	-0.334	-0.115	4.683	1.559	1.763
fcc Ni	1.427, 1.43 ^[15]	-0.400	-0.873	4.091, 4.07 ^[15]	1.867	0.547
fcc Fe	1.580	-0.447	-2.685			

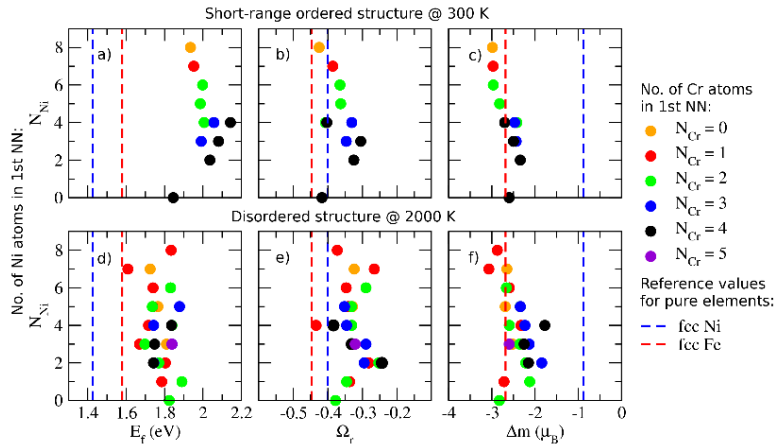


Figure 2. Formation energies, E_f , relaxation volumes, Ω_r , and changes of magnetic moment caused by a vacancy, Δm , calculated as a function of the local environment of a vacancy for the 300 K and 2000 K structures of $\text{Fe}_{55}\text{Cr}_{15}\text{Ni}_{30}$ alloy and compared with the values for fcc Ni and Fe.

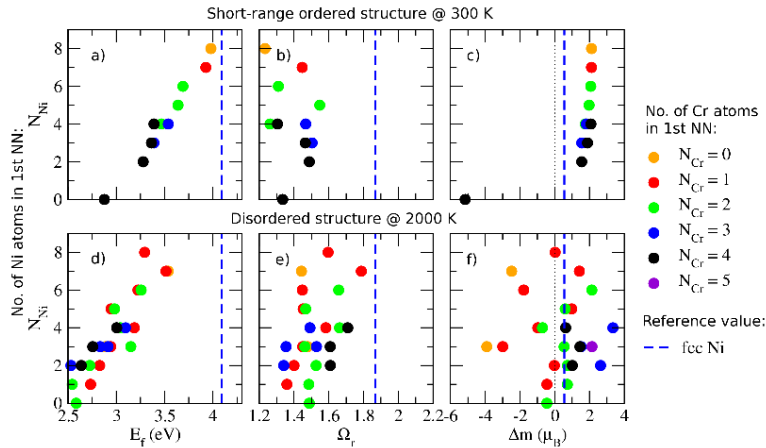


Figure 3. Formation energies, E_f , relaxation volumes, Ω_r , and changes of magnetic moment caused by a dumbbell, Δm , calculated as a function of the local environment of a dumbbell for the 300 K and 2000 K structures of $\text{Fe}_{55}\text{Cr}_{15}\text{Ni}_{30}$ alloy and compared with the values for fcc Ni.