The atomic site occupancies in the Fe-Cr σ-phase

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Abstract. The atomic site distribution of the complex σ-phase structure ($P4_2/mnm$) has been studied using density functional theory (within the EMTO and WIEN2k codes) applying the cluster expansion method in a mean field approximation at finite temperatures. We found that at low temperatures Fe atoms predominantly occupy the icosahedrally coordinated (A,D) sites, Cr atoms prefer the (B,E) sites with the high coordination numbers, while the C site remains mixed. However, at higher temperature close to 1000 K all occupations become more and more mixed and reproduce well the available experimental data.

Introduction

The Fe-Cr based alloys compose around 90% as the stainless steels and are widely used as structural materials in chemical and power industry as well in other branches due to their main property - the high-temperature corrosion resistance. However, being used at elevated temperatures, these steels are thermodynamically unstable, for which two processes are possible at high temperatures: (1) a phase decomposition into the Fe-rich α-phase and the Cr-rich α'-phase and (2) the α-σ phase transformation [1]. The $Fe_{1-x}Cr_x$ σ-phase usually exists in a very narrow concentration ($0.46 < x < 0.50$) and temperature ($800 < T < 1000$ K) range [2,3], but the limits can still vary depending on the conditions of the alloy preparation [1]. The σ-phase has a brittle and stable structure and usually occurs at grains boundaries. Precipitation of the σ-phase strongly decreases ductility and corrosion resistance of steels and increases brittleness as well as cracks formation. Usually this phase is paramagnetic at all temperatures, but for the Fe-Cr and Fe-V alloys weak magnetism appears at low temperatures. The latter was first found in the end of 1960s [4,5] and verified during the last 15 years in a broad experimental study of the Fe-Cr and Fe-V systems [6,7]. The Fe-Cr σ-phase has a small average magnetic moment of 0.20 μ_B at temperatures below the Curie temperature of about 50 K which depends on the alloy composition [6,7].

The σ-phase has a complex structure with a tetragonal unit cell (sp. gr. $P4_2/mnm$) of 30 atoms distributed in 5 nonequivalent sites (A,B,C,D,E) [2]. This structure belongs to the Frank-Kasper class of phases with high coordination numbers and can be written in a general form as $A^2_{12}B^4_{15}C^8_{14}D^8_{12}E^8_{14}$, where the top and bottom indices denote the site multiplicities and coordination numbers, respectively (see Fig. 1). The distribution of the alloy components in the nonequivalent sites is disordered, however some preferences in the occupation of these sites has been found [3]. The A and D sites are predominately occupied by Fe atoms (~90 to ~97%), the

(C,B,E) sites preferentially by Cr atoms (~55 to ~95%). These occupation numbers depend not only on temperature and alloy composition, but also on the conditions how the alloy was prepared [3].
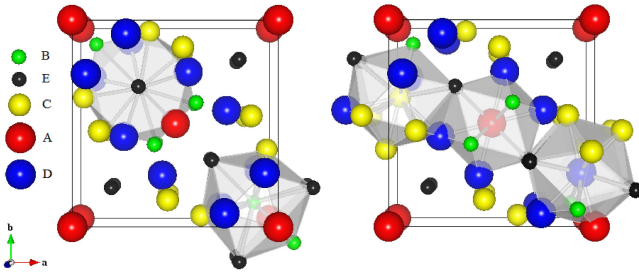

Figure 1. The σ-phase structure with 30 atoms distributed over 5 crystallographically inequivalent sites (A,B,C,D,E) in the unit cell.

The atomic site distribution in the σ-phase remains one of the main interests for theory as well as for experiment in understanding the formation process of the phase with such a brittle structure.

In the present work we calculate the Fe and Cr site occupancies in the $Fe_{1-x}Cr_x$ σ-phase for an equiatomic composition using density functional theory calculations at 0 K with the cluster expansion method in a mean field approximation at finite temperatures.

Method

In order to find the equilibrium state and the corresponding atomic distribution in the $Fe_{1-x}Cr_x$ σ-phase, we minimize the Helmholtz free energy F with respect to the Cr site occupation numbers c_i (i=A,B,C,D,E) for a given alloy composition x and temperature T:

$$F(\{c_i\}) = E_{tot}(\{c_i\}) - T(S_{conf} + S_{magn}). \tag{1}$$

$E_{tot}(\{c_i\})$ is the total energy of the $Fe_{1-x}Cr_x$ alloy with the corresponding Cr concentrations c_i, while S_{conf} and S_{magn} are the configurational and magnetic entropies corresponding to:

$$S_{conf} = k_B \sum_i n_i [c_i \ln c_i + (1-c_i)\ln(1-c_i)], \tag{2}$$
$$S_{magn} = k_B \sum_i n_i [c_i \ln(1+\mu_i(Cr)) + (1-c_i)\ln(1+\mu_i(Fe)))]. \tag{3}$$

In order to calculate the site occupation numbers c_i of the σ-phase with a random atomic distribution at finite temperatures, we expand the total energy near an equiatomic alloy composition as $E_{tot}(\{c_i\}) = \sum_i V_i^{(1)} c_i$, where $V_i^{(1)}$ are effective on-site interactions (i=A,B,C,D,E). In present work they are determined as $V_i^{(1)} = [\partial E_{tot}/\partial c_i - \partial E_{tot}/\partial c_E]|_{x=const}$ and are actually the relative effective chemical potentials at a fixed alloy composition and describe the preference of Cr atoms to occupy site i relative to the E site. In order to calculate the electronic structure of such a random alloy, we apply the coherent potential approximation (CPA) [8], which is formulated in terms of the multiple - scattering KKR (Korringa - Kohn - Rostocker) theory. It provides the same scattering properties of the one - component effective medium as the average of the alloy components, embedded in this effective medium [9]. Since the σ-phase is paramagnetic at ambient temperatures, the calculations were performed in the disordered local moment (DLM) state. We also took into account possible high temperature fluctuations of the magnitude of the local magnetic moments of Fe and Cr atoms (longitudinal spin fluctuations (LSF)) [10], which are specific for weakly itinerant magnets as Fe-Cr. LSF induce modified spin magnetic moments on Fe and Cr atoms and the corresponding magnetic entropy is given by Eq. 3. The local magnetic moments are obtained by minimization of the corresponding magnetic free energy in the first-principles calculations at a given T and the DLM is used for the paramagnetic state. The total energies were then calculated by the exact muffin-tin orbital (EMTO) method within the full charge density (FCD) formalism [11].

Although the EMTO-CPA-FCD method is one of the most efficient methods to simulate alloys with a random atomic distribution, lattice relaxations are not included. In order to estimate these effects and to perform structure optimizations ($V,c/a$), we applied the full-potential linearized augmented plane wave + local orbitals (LAPW+lo) method [12], as implemented in the WIEN2k code [13]. The exchange-correlation functional was evaluated using the generalized gradient approximation [14]. A k-mesh up to 7x7x13 was used for the 30 atoms unit cell in both WIEN2k

and EMTO simulations. In order to include magnetism of the Fe-Cr σ-phase at very low temperatures, we carried out the calculations in the ferromagnetic state.

Results and discussion

At very low temperatures we can neglect contributions from the configurational and magnetic entropy to the Helmholtz free energy F (see Eq. 1), and therefore the minimization of F is a minimization of the total energy of the ground state. Starting from some initial atomic arrangement guided by experiment [2,3] (see Table 1), we exchanged Fe and Cr atoms between the (B,C,D,E) sites in order to find the minimum of the total energy calculated by WIEN2k and EMTO. Both methods obtain the same final atomic arrangement with the lowest total energy (see Table 1), where only Fe atoms occupy the icosahedrally coordinated (A,D) sites, while Cr prefers the (B,E) sites with the high coordination numbers and only the C site remain mixed.

Table 1. The experimental and calculated site occupancies of Cr atoms of a $Fe_{50}Cr_{50}$ alloy. T_a is the temperature of annealing.

Site	n_{mult}	n_{coord}	n_i (exp.) [2] T_a=923 K	n_i (exp.) [3] T_a=973 K	n_i (calc.) T=0 K	n_i (calc.) T=500 K	n_i (calc.) T=1000 K
A	2	12	0.125	0.113	0.0	0.001	0.049
B	4	15	0.750	0.751	1.0	0.833	0.760
C	8	14	0.625	0.638	0.375	0.682	0.673
D	8	12	0.163	0.100	0.0	0.004	0.084
E	8	14	0.663	0.715	1.0	0.772	0.726

The enthalpy of formation for the σ-phase structure with the optimized atomic arrangement was calculated by the WIEN2k code including lattice relaxations. The calculated structure has a positive value 5 kJ/mol of the formation enthalpy, which agrees well with the calorimetrically determined enthalpy of formation of 6.5 kJ/mol [15]. The local lattice relaxations are small and the effect on the formation enthalpy is not greater than 0.1 kJ/mol. The latter is due to the similar atomic sizes of Fe and Cr. The corresponding equilibrium lattice parameters of the $Fe_{0.5}Cr_{0.5}$ σ-phase are a = 0.86433 nm and c/a = 0.518, while the value of the average magnetic moment per atom is μ = 0.53μ_B. These calculated data agree well with the experimental room temperature lattice parameters a = 0.87968(5) nm and c/a = 0.518 [2] and reasonably with the experimental magnetic moments μ = 0.20μ_B measured for an alloy composition x =0.49 at 4 K [4].

At finite temperatures the configurational and magnetic energy contributes to the Helmholtz free energy F (see Eq. 1) and were calculated by Eq. 2 and Eq. 3 respectively, while the total energy was expanded in terms of the effective on-site interactions $V_i^{(1)}$. The corresponding total energies (in definition of $V_i^{(1)}$) of the $Fe_{0.5}Cr_{0.5}$ σ-phase with a random atomic distribution were calculated for the lattice parameters a = 0.88484 nm and c/a = 0.5232 (the theoretical value for a homogeneous random $Fe_{0.5}Cr_{0.5}$ alloy calculated by the EMTO-CPA-FCD method). The a-parameter has been taken slightly larger than the experimental room temperature value in order to include the thermal lattice expansion effect. The obtained effective interactions are $V_i^{(1)}$ = {12.937; -0.656; 0.656; 10.969; 0.0}, while the Fe and Cr local magnetic moments (including LSF at 1000 K) have values μ_i(Fe) = {1.046; 1.773; 1.626; 1.236; 1.478} and μ_i(Cr) = {0.306; 0.481; 0.380; 0.350; 0.358}, respectively. A positive sign of the on-site effective interactions $V_i^{(1)}$ means a stronger preference of Fe atoms to occupy the particular site i relative to the E site.

The corresponding Cr site occupancies calculated for the obtained values of $V_i^{(1)}$ and μ_i at 500 K and 1000 K are given in Table 1. As can be seen at 500 K only the (A,D) sites remain predominantly occupied by Fe atoms, while the (B,C,E) sites show a significant atomic redistribution compared to 0 K. The Cr occupation of the (B,E) sites decreases, and therefore the C site has a significantly increased Cr content. At higher temperatures (close to 1000 K), where the Fe-Cr σ-phase actually forms, only the B site still significantly decreases the Cr content, while the (C,E) sites have much a smaller change. The excess of Cr is then distributed over the icosahedrally

coordinated (A,D) sites. As can be seen the obtained results are in a quite reasonable agreement with the experimental data [2,3] (see Table 1). The distribution of Cr(Fe) atoms in the Fe-Cr σ-phase has a different behavior for the 5 nonequivalent sites with some preferences in occupation depending on temperature. This may play a role in the structure formation.

Summary

In the present work we optimized the $Fe_{0.5}Cr_{0.5}$ σ-phase structure and found the low temperature distribution of Fe and Cr atoms using the full potential LAPW+lo method as implemented in the WIEN2k code. For finite temperatures we proposed a simple but powerful approach to calculate the atomic site occupations in the σ-phase based on the single-site mean-field approach which expands the total energy in terms of effective on-site interactions. The total energies of random alloys were calculated by the EMTO-CPA-FCD method in the DLM state including LSF. The results obtained for some alloy composition and temperatures are in very good agreement with the experimental data and are important for further investigation of the binary σ-phases.

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Solid Compounds of Transition Elements

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