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Effect of multicomponent alloying with Ni, Mn and Mo on phase stability of bcc Fe-Cr alloys

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ABSTRACT

Fe-Cr system attracts lot of attention in condensed matter physics due to its technological importance and extraordinary physics related to a non-trivial interplay between magnetic and chemical interactions. However, the effect of multicomponent alloying on the properties of Fe-Cr alloys are less studied. We have calculated the mixing enthalpy, magnetic moments, effective chemical, strain-induced and magnetic exchange interactions to investigate the alloying effect of Ni, Mn, Mo on the phase stability of the ferromagnetic bcc Fe−Cr system at zero K. We demonstrate that the alloying reduces the stability of Fe-Cr alloys and expands the region of spinodal decomposition. At the same time, the mixing enthalpy in ternary $Fe_{100-c-05}Cr_cNi_{05}$ alloys indicates a stability of solid solution phase up to 6 at. % Cr. In $Fe_{100-c-07}Cr_cNi_{05}Mn_{01}Mo_{01}$ alloys, we did not find any alloy composition that has negative enthalpy of formation. Analyzing magnetic and electronic properties of the alloys and investigating magnetic, chemical and strain-induced interactions in the studied systems, we provide physically transparent picture of the main factors leading to the destabilization of the Fe-Cr solid solutions by the multicomponent alloying with Ni, Mn, Mo.

1. Introduction

Fe-Cr alloys are widely used as important construction and industrial steels, e.g. as wall materials in fusion reactors because of the resistance to irradiation-induced swelling at high temperatures. Moreover, there is great practical interest in alloys with Cr content above 10 at. % due to their high corrosion resistance. Fe-Cr alloys with low Cr concentration show anomalous phase stability. On the other hand, in Fe-Cr system there is a miscibility gap within which alloys decompose into iron rich and chromium rich phases [1]. This decomposition could cause steel embrittlement due to Cr precipitation. The anomalous stability of the Fe-Cr was a subject of detailed theoretical calculations, which have substantially improved an understanding of the processes occurring in the binary Fe-Cr system [2–9].

An analysis of properties of Fe-Cr alloys intended for energy applications show that the improvement of an exploitation reliability and equipment efficacy might rely on multicomponent Fe-Cr steels that contain other elements such as Ni, Mn and Mo. Alloying with Ni improves impact strength, ductility and resistance to corrosion. Mo increases corrosion resistance in aggressive environments, for instance, in the salt and acid conditions. Moreover, addition of Mo improves the toughness of the stainless steels at the high temperatures. Manganese can improve the hardness of the steels. Interestingly, while Cr and Mo are α-phase stabilizers, Ni and Mn are γ-phase stabilizers. At the same time, alloying elements can reduce some mechanical properties of Fe-Cr steels. Unfortunately, there is a limited knowledge about the influence of multicomponent alloying on the phase stability of bcc Fe-Cr alloys. Some work has been devoted to studies of Fe-Cr-Ni ternary system, which appears as the base material for the most types of austenitic, ferritic and martensitic steels. In this system, a high temperature isothermal sections (above 900 °C) have the wide regions with bcc and fcc structures (1213K–1618K) with an inclusion of the so-called σ-phase, which forms at $T < 1213K$, and might be the source of brittleness [10–13]. Modeling of the phase equilibria and corresponding phase diagram calculations in Fe-Cr-Ni have

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predominantly been carried out at high temperatures [14–17]. Thermodynamic and kinetic properties of Fe-Cr-Ni system have been studied in Ref. [18] using an experimental (calorimetry, atom probe tomography) and the theoretical methods (CALPHAD, phase field simulation, and *ab initio* modeling). CALPHAD method has extended the description of the lattice stability down to T = 0K, followed by the study of spinodal decomposition by means of the phase field modeling [19]. Moreover, it has been noted that thermodynamic modeling of the Fe-Cr-Ni system can accurately describe the phase boundaries for bcc and fcc phases at the temperatures above than 1073 K [18]. At the same time, an understanding has emerged that to develop a new generation of stainless steels based on the ternary Fe-Cr-Ni system, it is necessary to obtain its thermodynamic and kinetic description at lower temperatures [18].

An extensive systematic study on bcc and fcc magnetic binary Fe-Cr, Fe-Ni, Cr-Ni alloys and ternary Fe-Cr-Ni alloys has been performed in Refs. [20–22]. Results for bcc alloys, obtained using a combination of DFT and Monte-Carlo calculations with a Hamiltonian based on chemical and magnetic cluster expansions, are in agreement with earlier studies showing full solubility of Cr in Fe in the 0–9% range of concentrations [20].

Using first-principles simulations, Souvatzis et al. [23] proposed Fe-Cr based alloys with Ni and Mn additions as a potentially interesting material for magneto-caloric cooling. Because of the phase transition from ferromagnetic bcc phase with full magnetic moment ~1.4 μ_B into paramagnetic fcc phase, the authors demonstrated that Fe-Cr-Ni-Mn alloys with ~15 at.% Cr could be considered as good candidates for the cooling systems working at the room temperature.

In our work, we have studied the influence of multicomponent alloying on the electron structure and phase stability of Fe-Cr based alloys with 5 at. % Ni, 1 at. % Mn and 1 at.% Mo. According to Massalski [24] at the low temperatures α-Fe dissolves less than 5 at. % Ni, but for alloys obtained by mechanical mixing the stability boundary of bcc-solution can be shifted to 10–20 at. % Ni depending on the ball milling intensity. It is also possible to obtain a wide range of single-phase bcc alloys by thermal evaporation [25] or sputtering produce [26]. We performed the calculations of the mixing energies, effective chemical and exchange interactions, magnetic moments and density of states in order to study the influence of alloying on the thermodynamic properties of Fe-Cr alloys.

2. Details of the calculations

The calculations of the electronic structure and thermodynamic properties of $Fe_{100-c}Cr_c$,$Fe_{100-c-05}Cr_cNi_{05}$ and $Fe_{100-c-07}Cr_cNi_{05}Mn_{01}Mo_{01}$ alloys were performed by the exact muffin-tin orbital (EMTO) method within the coherent potential approximation (CPA) [27,28], the locally self-consistent Green's function (LSGF) [29,30] method implemented within the exact muffin-tin orbital (EMTO) technique (ELSGF) [31] and the projector augmented-wave (PAW) method as implemented in the Vienna *ab initio* simulation package (VASP) [32–34].

For EMTO and ELSGF calculations, the full charge density (FCD) [FCD] [35] was represented by a single-center expansion of the electron wave functions in terms of spherical harmonics with orbital moments l_{FCD}^{max} up to 8. Self-consistent electron densities were obtained within the spherical cell approximation and the local density approximation (LDA) [36]. Then the total energies were calculated in the generalized gradient approximation (GGA) [37] using the FCD formalism. Integration in the reciprocal space was performed over a grid of 29 × 29 × 29 k-points; energy integration was carried out in the complex plane using a semielliptic contour comprising 24 energy points. Calculations were performed for a basis set including valence *spdf*- orbitals and by means of the frozen-core approximation, i.e. the core states were kept fixed. Ekholm and Abrikosov [38] demonstrated that the use of the latter leads to better, though probably fortuitous, cancellation of errors in a description of magnetic Fe-based alloys within the EMTO formalism. The total energy was converged within 10^{-7} Ry. In our calculations, we neglected electronic and vibrational thermal excitations.

The parameters of the intrasite screened Coulomb interactions, α and β [39,40], that describe electrostatic interactions in the single-site approximation, as well as the intersite screening constants, $\alpha_{scr}(R)$, for the intersite screened Coulomb interactions were evaluated in 1024-atom supercell calculations using ELSGF method [31]. The former parameters are used in calculations of the total energy of random alloys within CPA, while the latter contributes to the pair screened generalize perturbation method (SGPM) interactions. The ELSGF method has also been used explicitly for selected total energy calculations and study local environment effects in the electronic structure and effective interactions in Fe-base alloys.

A 128-atom (4 × 4 × 4(x2)) supercell has been used in the direct calculations the fully renormalized pair chemical and strain-induced interactions by the PAW method implemented in the VASP [29,30]. The generalized gradient approximation [37] has been used for the exchange-correlation energy. The energy cutoff was 500 eV. The integration over the Brillouin zone has been done using the Monkhorst–Pack grid [41] using 4 × 4 × 4 k-point mesh.

3. Thermodynamic analysis of effects of multicomponent alloying

3.1. Lattice parameters

In order to study the effect of multicomponent alloying we have calculated thermodynamic properties of ferromagnetic (FM) ternary $Fe_{95-c}Cr_cNi_{05}$ alloys and quinary $Fe_{93-c}Cr_cNi_{05}Mn_{01}Mo_{01}$ alloys as a function of Cr composition. Fig. 1 illustrates the dependence of lattice parameter on Cr concentration for these alloys in the FM state. In addition, Fig. 1 displays an experimental data for binary Fe-Cr alloys [42–44] for comparison. Our results for the lattice parameter for binary Fe-Cr alloys differ slightly from those

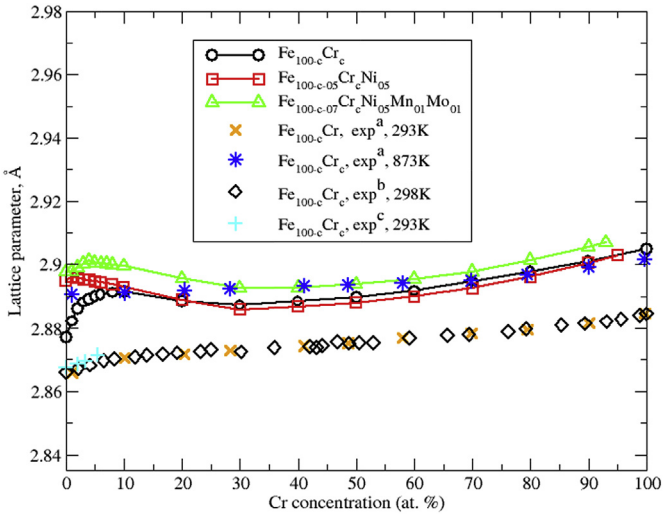

Fig. 1. Lattice constants of $Fe_{100-c}Cr_c$, $Fe_{100-c-05}Cr_cNi_{05}$ and $Fe_{100-c-07}Cr_cNi_{05}Mn_{01}Mo_{01}$ alloys. Experimental data are taken from [a]Ref. [42], [b]Ref. [43], [c]Ref. [44].