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On the existence of additional miscibility gap in Ni_cCu_{1-c} *fcc* alloy

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Magnetic and interatomic interaction parameters for Ni_cCu_{1-c} alloys were calculated by *ab-initio* full potential linearized augmented plane wave method. Using these parameters solid state part of the phase diagram was constructed in mean-field approximation for Hamiltonian containing both chemical and magnetic interactions. Calculations revealed the presence of additional stable miscibility gap due to magnetic interactions between Ni atoms. Within this approach a general condition for existence of such a gap was derived.

Ab initio методом линеаризованных присоединенных плоских волн (FLAPW) вычислены параметры магнитного и межатомного взаимодействия в сплаве Ni_cCu_{1-c}. Используя эти параметры, построена часть фазовой диаграммы системы в приближении среднего поля с гамильтонианом, который содержит как химические так и магнитные взаимодействия. Вычисления показали существование дополнительной области расслоения, обусловленной магнитным взаимодействием в системе. В рамках данного подхода получен обобщенный критерий существования такой области расслоения.

1. Introduction

Currently transport and magnetic properties of multilayered film are investigated intensively. Recently a thermocontrolled trilayer *F*/*f*/*F* structure was proposed [1] and implemented [2, 3]. This structure contains two layers of strong ferromagnets *F* and single inner layer (spacer) of a weak ferromagnet *f* with a low value of the Curie temperature, typically in the range of 300 – 500 K.

It was shown [2, 3] that the spacer *f* mediating magnetic exchange in *F*/*f*/*F* structures can be implemented as a thin film of diluted ferromagnetic Ni_cCu_{1-c} alloy. The film must be homogeneous in composition and should not contain additional phases originating from decomposition. In this regard, an in influence of Ni magnetic properties on phase equilibria in bulk Ni_cCu_{1-c} alloys is not well investigated neither experimentally nor theoretically.

Bulk Ni_cCu_{1-c} alloys are *fcc* binary substitution solid solution (α-phase) in which Ni and Cu are miscible at all compositions above temperature 627.7 K, where at $c = 0.673$ α-phase separates into two phases α_1 and α_2 as it was shown by Chakrabarti et al. [4]. In [4] it was predicted, that in Ni_cCu_{1-c} alloy ($0.86 < c < 0.91$) a metastable miscibility gap should exist due to magnetic contribution into free energy of the alloy (Fig. 1, lines $ab - ab'$). There is no direct experimental confirmation to this statement yet. It is difficult for the required temperatures to reach the equilibrium conditions experementally, if possible at all. For description of the magnetic contribution the paper authors [4] used a model proposed by Chuang [5, 6]. The model contains an empirical expression for magnetic capacity of ferromagnetic alloy. To investigate whether such miscibility gap can exist it is important to construct theoretically and independently solid

state part of the phase diagram of Ni_cCu_{1-c} system using first-principle calculation of interatomic interactions.

2. Calculation of phase equilibria in Ni_cCu_{1-c} alloy

In the present paper a simple model Hamiltonian with magnetic interactions for description of Ni_cCu_{1-c} bulk alloy is exploited. The Hamiltonian is similar to one used in the paper [7] for description of Fe_cNi_{1-c} system. The approach relies on a lattice model with site i of *fcc* lattice being occupied either by Ni atom ($c_i = 1$) or by Cu atom ($c_i = 0$). Magnetic interactions between Ni atoms are described by classical isotropic Heisenberg model. Since the local magnetic moment of Cu atoms is small, magnetic interactions Cu–Cu and Cu–Ni may be omitted. The model Hamiltonian is the following:

$$E=\frac{1}{2}\sum_{ij}\upsilon_{ij}c_ic_j+\frac{1}{2}\sum_{ij}J_{ij}c_ic_j\mathbf{s}_i\mathbf{s}_j, \qquad (1)$$

where υ_{ij} — mixing pair potentials corresponding to "chemical" interaction between atoms, J_{ij} — pair magnetic exchange interactions of Ni atoms that do not depend on Ni concentration c, $\mathbf{s}_i$ — vectors of unit length corresponding to local magnetic moments of Ni atoms.

To calculate interactions υ_{ij}, J_{ij} we used cluster expansion (CE) technique [12]. In this approach equation (1) is mapped onto set of ordered structures that have different distributions of c_i, s_i. The total energies E of structures are calculated by *ab initio* method, and υ_{ij}, J_{ij} are obtained by solving system of linear equations (1).

A small set of ordered superstructures representing Ni_cCu_{1-c} alloy was constructed. Since the most interesting part for us is the part of the phase diagram with high compositions of Ni, 5 superstructures of composition $CuNi_7$ (32 atoms per unit cell, ferromagnetic ordering) and 3 structures of pure Ni with ferromagnetic and antiferromagnetic collinear ordering were selected. These structures allow to find values of interactions υ_{ij} for 4 coordination shells of *fcc* lattice and J_{ij} for 2 shells.

The total energies of the structures were calculated within electron density functional (DFT) theory [13,14] by FLAPW method (Wien2k package [8]). Exchange correlation potential was used in generalised gradient approximation (GGA) according to [9]. Muffin-tin radii for Cu and Ni were equal to 2.2 a.u.. The electron density was calculated using 500 k-points in the first Brillouin zone. The structure relaxation was performed for lattice parameters and atomic positions. Atomic positions were changed until the forces on nuclei were smaller than 1 mRy/Bohr. Accuracy of the total energy was 0.1 mRy. Calculated values of interactions (in meV) are following: $\upsilon_{ij} = \{-16.37, 32.55, -7.72, -2.52\}$, $J_{ij} = \{-6.78, -18.27\}$.

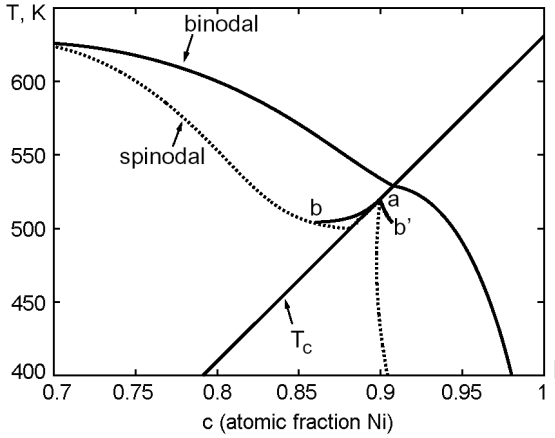

Fig. 1. Part of phase diagram according to [4]. Lines $ab - ab'$ correspond to metastable equilibria.

Calculation of phase equilibria for Ni_cCu_{1-c} system was performed within mean-field approximation for Hamiltonian (1). It was supposed that all Ni atoms have the same value of magnetisation $\mathbf{m} = (0, 0, m)$. In this case m can be calculated from the equation [10]: $m = L(H/k_BT)$, where $H = -(\sum_j J_{1j})mc$ — effective magnetic field, k_B — Boltzmann constant, T — absolute temperature, $L(x)$ — Langevin function. Free energy is given by the expression:

$$F = \frac{1}{2}\left(\sum_j \upsilon_{1j}\right)c^2 + k_BT(c\ln c + (1-c)\ln(1-c)) + \frac{1}{2}Hmc - k_BTc\ln\frac{\sinh(H/k_BT)}{H/k_BT}. \qquad (2)$$

Phase equilibria were calculated by standard common tangent method. Obtained phase diagram of solid Ni_cCu_{1-c} system is shown in Fig. 2. The shown lines are binodal, spinodal, metastable equilibria and dependence of the Curie temperature T_c upon the composition. Curie temperature below binodal line corresponds to homogeneous solid solution. Metastable equilibria $b''d' - bd$ and $bc - b'c'$ are shown in dash. The phase diagram contains stable miscibility gap (lines $ab - ab'$) due to magnetic

transformations in the alloy. Similar miscibility gap exists in Fe–Ni system (phases γ_1, γ_2 [6]). Presence of this miscibility gap in Ni_cCu_{1-c} system results in additional equilibria of phases with close compositions but different magnetic properties and, that is important, different Curie temperatures. This should result in broadening of magnetic transition.

Since we do not include dependence of Ni local magnetic moment upon the composition, theoretical dependence of T_c on Ni composition (Fig. 2) deviates from experimental one [11]. It should be mentioned, that in disagreement with the results of paper [4] our calculations show that additional miscibility gap is *stable*. Therefore, our calculations, which are not relying on numerical experimental measurements, show additional phase equilibria in Ni_cCu_{1-c} system at high composition of Ni. These equilibria are driven by ferromagnetic transformations.

It is possible to obtain a general condition for existence of the additional miscibility gap using the expression for free energy (2). It is convenient to introduce the following quantities: $V_0 = \sum_j \upsilon_{1j}$, $J_0 = \sum_j J_{1j}$. The lines of spinodal and magnetic transformation intersect at point a (Fig. 2), that gives two equations: $\partial^2 F/\partial^2 c = 0$; $T = T_c$. Combining the expression for spontaneous magnetisation near T_c: $m = \sqrt{5/3}\sqrt{T_c - T)/T_c}$; and the equation for the Curie temperature $T_c = -J_0 c/3k$, the following equation for concentration at point a can be derived:

$$\frac{\partial^2 F}{\partial^2 c} = V_0 - \frac{1}{3(1 - c_a)} J_0 + \frac{5}{6} J_0 = 0. \qquad (3)$$

The solution is:

$$c_a = \frac{6 + 3J_0/V_0}{6 + 5J_0/V_0}. \qquad (4)$$

Condition $0 < c_a < 1$ yields the restriction on interaction parameters: $J_0/V_0 > 0$, that narrows possible concentration range for the miscibility gap: $3/5 < c_a < 1$. Therefore, for binary alloys with decomposition ($V_0 < 0$) and one specie being ferromagnet ($J_0 < 0$), additional miscibility gap must exist.

3. Conclusions

Performed calculations of phase equilibria in Ni_cCu_{1-c} bulk alloys demonstrated existence of miscibility gap due to magnetic interactions between Ni atoms. Within mean-field approximation for model Hamiltonian the general condition on chemical and magnetic interactions was obtained, that indicates a presence of the phase separation. Our analysis shows that the phase separation in the concentration range of interest is due to Ni–Ni exchange interaction, which favors clustering of Ni and, thereby, compositional gradients in the alloy. This can additionally lead to a significantly non-linear dependence of the Curie temperature on the alloy concentration. In our opinion, additional experimental efforts are desired to resolve the issues of gap existence and stability. Effect of presence of additional phases with close compositions but different Curie temperatures should be taken into account in construction of magnetic multilayer systems. Since phase separation might significantly change magneto-structural properties of CuNi spacer, this would worsen properties of thermocontrolled spin devices.

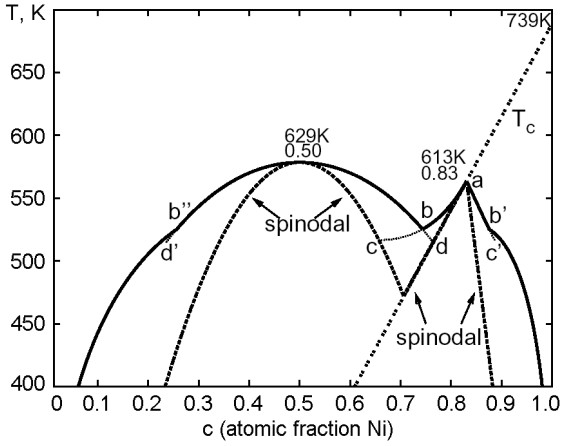

Fig. 2. Calculated solid state part of phase diagram for Ni_cCu_{1-c} system.

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Про існування додаткової області розшарування у сплаві Ni_cCu_{1-c}

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Ab initio методом лінеаризованих приєднаних плоских хвиль обчислено параметри магнітної і міжатомної взаємодії у сплаві Ni_cCu_{1-c}. Використовуючи ці параметри, побудовано частину фазової діаграми системи у наближенні середнього поля з гамільтоніаном, що містить як хімічні так і магнітні взаємодії. Обчислення показали наявність додаткової області розшарування, що обумовлена магнітною взаємодією у системі. В рамках даного підходу отримано загальний критерій існування такої області розшарування.