Journal of Magnetism and Magnetic Materials 324 (2012) 2442–2451

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Site preference and magnetism of $Fe_{3-x}Cr_xAl_{0.5}Si_{0.5}$

A. Go [a,*], K. Rećko [a], L. Dobrzyński [b,c], J.J. Milczarek [b], M. Biernacka [a]

[a] Faculty of Physics, University of Bialystok, Lipowa 41, 15-424 Białystok, Poland
[b] National Centre for Nuclear Studies, 05-400 Otwock, A. Soltana 7, Poland
[c] Faculty of Mathematics and Natural Sciences, College of Sciences, Cardinal Stefan Wyszyński University in Warsaw, 01-938 Warsaw, Woycickiego 1/3, Poland

ARTICLE INFO

Article history:
Received 7 May 2011
Received in revised form
4 March 2012
Available online 15 March 2012

Keywords:
Transition metal alloy
Magnetism
DO_3-structure
Electronic structure
X-ray diffraction
Neutron diffraction

ABSTRACT

In order to gain better insight into the origin of the observed differences between $Fe_{3-x}Cr_xAl$ and $Fe_{3-x}Cr_xSi$, alloys of $Fe_{3-x}Cr_xAl_{0.5}Si_{0.5}$ ($x=0$, 0.125, 0.250, 0.375 and 0.5) were prepared and studied by means of X-ray and neutron diffraction as well as by magnetization measurements. Electronic structure calculations of these alloys have been performed by means of TB-LMTO-ASA method. It was expected, and experimentally verified, that the presence of silicon and aluminum atoms in 1:1 proportion will result in the independence of the lattice parameter on the iron/chromium concentration. All samples have been proved to be a single phase of the DO_3-type of structure. Theoretical and experimental results indicate that chromium atoms locate preferentially in B sublattice. Cr magnetic moments are oriented antiparallel to Fe magnetic moments. Neutron measurements show a linear dependence of the magnetic moments of Fe(A,C), Fe(B) and Cr(B) as a function of Cr concentration. However the calculated total magnetic moment decreases faster with chromium content than indicated by the experiment.

1. Introduction

Cr-doped Fe_3Al, Fe_3Si and $Fe_3Al_{0.5}Si_{0.5}$ alloys belong to DO_3-type structures (see Fig. 1) which can be thought of as consisting of four interpenetrating face centered cubic Bravais lattices originated at (0,0,0), (1/4,1/4,1/4), (1/2,1/2,1/2) and (3/4,3/4,3/4) positions, abbreviated as A, B, C and D, respectively. This results in diffraction patterns containing fundamental reflections whose structure factors are given by Eq. (1), and two types of superstructure lines of B2 and DO_3-types, whose structure factors are described by Eqs. (2) and (3), respectively.

$$(F^{(1)}_{hkl})_{eff} = 4(f_A + f_B + f_C + f_D) \quad \text{for} \quad h+k+l = 4n \tag{1}$$

$$(F^{(2)}_{hkl})_{eff} = 4(-f_A + f_B - f_C + f_D) \quad \text{for} \quad h+k+l = 4n+2 \tag{2}$$

$$(F^{(3)}_{hkl})_{eff} = 4(f_A \pm if_B - f_C \mp if_D) \quad \text{for} \quad h+k+l = 4n \mp 1 \tag{3}$$

where f_j is the effective scattering amplitude of the j-th site.

In ordered parent alloys A, B and C sites are occupied by iron atoms. The different nearest-neighbor configurations prejudge the equivalence of A- and C-positions and their in-equivalence with B-site (see Table 1 in [1]). D-sites are occupied exclusively by aluminum or/and silicon atoms. As a consequence of the above relationships the appropriate formulas of the structure factors can be simplified to

$$|F^{(1)}_{hkl}| = 4(f_{Fe_B} + f_{(Al/Si)_D} + 2f_{Fe_{A,C}}) \tag{1a}$$

$$|F^{(2)}_{hkl}| = 4(f_{Fe_B} + f_{(Al/Si)_D} - 2f_{Fe_{A,C}}) \tag{2a}$$

$$|F^{(3)}_{hkl}| = 4(f_{Fe_B} - f_{(Al/Si)_D}) \tag{3a}$$

The lattice parameters of parent alloys are markedly different, 565.5 pm and 573.0 pm for Fe_3Si and Fe_3Al, respectively. Chromium substituted for iron in the two alloys exhibits also different preference to the occupation of lattice sites. In addition, in real samples some disorder in occupation of sites may exist. Neutron experiments for Cr-doped Fe_3Si compounds [2] disclosed exclusively silicon nature of the occupation of D-sites. However, Mössbauer spectroscopy studies [3] indicated about ~3% of B-D type disorder. In Cr-doped Fe_3Al systems a small B-D disorder as well as (A,C)-D one were observed experimentally [4].

Noteworthy, the type of ordering in $Fe_{3-x}T_xSi$ and $Fe_{3-x}T_xAl$ alloys, when transition metal impurities (T) are added, is very sensitive to the heat treatment procedure [5]. Consistently, different type of in-site disordering and magnetic behavior, were found [1,2]. Observed small negative polarization of Si [6,7] can also complicate interpretation of the real origin of neutron magnetic signals which come from D-site of given alloy. According to early studies by Burch et al. [8], transition metal impurities on the left-hand side of Fe in the periodic table of elements (e.g. Mn or V) demonstrate strong preference for B site occupation, while the elements to the right of Fe (e.g. Co) enter

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[*] Corresponding author.
E-mail address: annago@alpha.uwb.edu.pl (A. Go).

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doi:10.1016/j.jmmm.2012.03.003

preferentially into the (A,C) sites. NMR spin-echo experiments carried out on $Fe_{3-x}T_xSi$ compounds brought same conclusion [9,10]. On the other hand, quite different site-occupancies and T–Fe magnetic interactions were discovered in $Fe_{3-x}T_xAl$ samples [3,4,11]. The first theoretical explanation of this fact was based on the electronic band structure calculations [12,13]. Reddy at al. [14] demonstrated that Co- and Ni-substituting for iron in $Fe_{3-x}T_xAl$ samples show preferential occupation of (A,C) positions, and ferromagnetic coupling between their and iron magnetic moments. In the case of Cr impurity, the ab-initio studies [14,15] fully confirmed that Cr atoms prefer rather B-sites than (A,C)—ones. According to the experimental observation [1–4,11], however, the chromium in $Fe_{3-x}Cr_xSi$ did not obey the aforementioned rule of preferential substitution, i.e. Cr atoms locate both into (A,C) and B sites. One should recall that the self-consistent band structure calculations disclosed the existence of strong preference of chromium to occupy the B-sites [16]. Only at large chromium concentration some of chromium atoms in $Fe_{3-x}Cr_xSi$ locate also in (A,C) sites. Moreover, according to [17], chromium in Fe_3Si perturbs strongly the magnetic moments of neighboring iron atoms. This perturbation is seen mainly at Cr atoms located in the first neighborhood of iron atoms. Although CPA (coherent potential approximation) calculation of $Fe_{3-x}Cr_xAl$ [18] did not show definite preference of Cr to the B-sites, recently published self-consistent TB-LMTO calculations [19] confirmed the existence of the strong preference of the B-position occupation by chromium. Because of the rapidly varying lattice parameters with chromium content, see Fig. 3, such situation required repetition of theoretical calculations with special emphasis on the effects introduced by the impurity when the average atomic volume in the alloys stays constant. The studies of $Fe_{3-x}Cr_xSi_{0.5}Al_{0.5}$ may be particularly interesting. It follows from [1,11] that these alloys should exhibit same lattice parameters, so at least a problem of an influence of the volume per atom varying with chromium concentration on magnetic and structural properties should be of less importance.

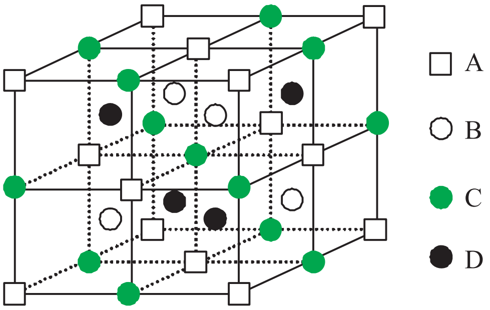

Fig. 1. Unit cell of the DO_3-type structure. A and C sites are chemically equivalent.

2. Calculation details

The electronic structure of $Fe_{3-x}Cr_xSi_{0.5}Al_{0.5}$ has been studied within the framework of the local spin-density approximation, using the self-consistent spin-polarized tight-binding linear muffin-tin orbital method [20] in the atomic sphere approximation. The exchange correlation potential was taken in the form of von Barth and Hedin [21]. The Langreth–Mehl-Hu non-local exchange correlation [22] was added. The scalar relativistic wave equation was solved. The values of the atomic sphere radii were chosen in such a way that the sum of all atomic sphere volumes was equal to the volume of the unit cell. The initial atomic configurations for every atoms were taken to be the same as for pure elements. We assumed for Fe: core(Fe)+$3d^64s^2$; for Cr: core(Cr)+$3d^44s^2$; for Si: core(Si)+$3s^23p^2$ and for Al: core(Al)+$3s^23p^1$. The tetrahedron method [23] was used for integration over the Brillouin zone. Calculations were carried out for at least 280 k-points in the irreducible wedge of the Brillouin zone. The iterations were repeated until the energy eigenvalues of the consecutive iteration steps converged to values stable within 0.01 mRy.

All electronic structure calculations were carried out using spin-polarized (ferromagnetic) approach for five values of the x parameter (0, 0.125, 0.25, 0.375, 0.5). The supercell structure with 32 atoms was used in calculations. It was obtained by the extension into the three dimensional space of the basic position of DO_3 structure along the main diagonal. Eight positions in the supercell were occupied by four silicon and four aluminum atoms (D-sites) positioned randomly, whereas Fe and Cr atoms occupied the remaining positions (A, B and C). A lot of different distributions of atoms were considered and results presented in the paper concern the most stable energetically ones. The used lattice parameters were the experimental ones. According to experimental data (see below) the volume of supercell does not change with chromium content in the investigated range of concentration x ($0 \leq x \leq 0.5$). Chemical disorder, introduced by replacing some Fe by Cr atoms, is changing the crystal symmetry. Thus for each supercell, new group of symmetry was found and calculations were carried out for new crystal symmetry.

3. Sample preparation

Appropriate proportions of Fe (99.97%), Cr (99.97%), Al (99.99%) and Si (99.999%) were mixed to make the $Fe_{3-x}Cr_xAl_{0.5}Si_{0.5}$ alloys with the concentration x=0, 0.125, 0.25, 0.375 and 0.5. The constituents were melted together in the induction furnance in argon atmosphere. Noteworthy, chromium and aluminum have a high vapor pressure values. For this reason, Cr and Al in the oven have been arranged at the bottom of the table and covered by the iron and silicon. This minimized the loss of two first volatile elements. In contrast with earlier used proce-

Table 1
Structural parameters for $Fe_{3-x}Cr_xAl_{0.5}Si_{0.5}$ alloys obtained from X-ray measurements at room temperature.

Chromium concentration x		0	0.125	0.25	0.375	0.5
Lattice parameter (pm)		572.13(9)	572.06(11)	572.02(11)	572.12(10)	572.00(8)
Debye–Waller factor $(\text{Å})^2$		0.376(12)	0.353(19)	0.357(14)	0.380(14)	0.344(18)
Site occupancy	A,[a]C[a]	0.998(7)	1.000(13)	0.994(13)	1.005(9)	1.002(8)
	B[a]	0.994(9)	0.990(14)	0.977(12)	0.975(8)	0.964(9)
	D[b]	1.043(23)	1.046(25)	1.050(19)	1.041(15)	1.039(17)
R_F		0.31	0.33	0.36	0.33	0.28
R_{Bragg}		0.23	0.37	0.34	0.29	0.24
χ^2		4.05	5.41	5.23	4.17	4.11

[a] Fe atomic scattering factor was used during the refinement.
[b] Al atomic scattering factor was used during the refinement.