

Point defect structure and ^{57}Fe hyperfine parameters of Fe-Al powders doped with Ni, Cu and Cr additions

Aneta HANC^{1*}, Janusz E. FRĄCKOWIAK¹, Lucjan PAJAŁ², Grzegorz DERCZ²

¹ Institute of Materials Science, University of Silesia, 4 Uniwersytecka Street, 40-007 Katowice, Poland

² Institute of Materials Science, University of Silesia, 12 Bankowa Street, 40-007 Katowice, Poland

* Corresponding author. Tel.: +48-32-3591117; fax: +48-32-2596929; e-mail: ahanc@us.edu.pl

Received September 19, 2007; accepted June 2, 2008; available on-line September 10, 2008

In the present work Fe-Al-X (X=Cu;Ni;Cr) metallic powders produced by the self-decomposition method of Fe-Al doped alloys were examined by Mössbauer spectroscopy. The concentration of Fe vacancies and Fe atoms substituting for Al (Fe-AS) was determined from the intensities of the sub-spectra in the Mössbauer analysis connected with distinct Fe environments. The results show that nickel and copper produce an increase of the vacancy concentration in comparison with the values found for Fe-Al metallic powders, whereas chromium decreases the vacancy concentration, causing a significant increase of the anti-site atom Fe-AS concentration.

Iron aluminides / Defects / Point defects / Mössbauer spectroscopy / Fe-Al

1. Introduction

The mechanical properties of high temperature intermetallic alloys are related to point defects and their concentration. Iron aluminides around 50 at.% Fe show reasonable mechanical strength and good oxidation resistance from room to high temperature [1].

It is well known that upon rapid quenching from elevated temperatures iron aluminides retain a high concentration of thermal vacancies, which, frozen, increase the yield strength and hardness at room temperature [2]. However, the technical application of these alloys is presently restricted by the poor ductility at low temperatures and low fracture toughness [3].

It is expected that the concentration of vacancies can be strongly changed in the aluminides with variations of heat and mechanical treatment, combined with modifications of the composition of the aluminides by transition metal ternary additives [4].

In this paper Fe-Al-X (X=Cu;Ni;Cr) metallic powders produced by the method of self-decomposition [5] of Fe-Al doped alloys were studied using ^{57}Fe Mössbauer spectroscopy. The spectra were analyzed using a model according to which point defects in atomic shells close to the probe atom induce changes in the isomer shift and quadrupole interactions. The concentrations of Fe vacancies and Fe atoms substituting for Al (Fe-AS) were determined from the intensities of the corresponding sub-spectra in the Mössbauer analysis related to distinct Fe environments. The result of solute X (X=Cu;Ni;Cr)

addition effects in the investigated Fe-Al-X metallic powders is presented and discussed.

2. Experimental details

2.1. Samples

The investigated metallic powders were made by the self-decomposition method from Fe-Al based alloys with a high content of aluminum and carbon-enriched, in conditions of high humidity. It has been found that the products of the chemical reaction of formed Al_4C_3 with water are responsible for the self-decomposition process. The products of this reaction deform the surface layer due to a higher specific volume than the volume of Al_4C_3 . This phenomenon, as well as casting stresses, influences the appearance of the complex stress state in that area. An initial crack occurs when the stress value exceeds the critical stress, which depends mainly on the matrix fracture toughness [5]. As a consequence of the self-decomposition process, powdered material has been obtained with a grain size of about 30-200 μm , selected by grain fraction. In the present paper powdered samples with an average size of 40-60 μm have been studied.

The chemical compositions of the investigated materials were determined by classical chemical analysis, and are listed in Table 1. The results of the chemical analysis indicated that all the investigated samples are characterized by aluminum concentrations of over 50 at.%.

Table 1 The chemical composition of the investigated materials.

Contents [at.%]	Fe-Al	Fe-Al	Fe-Al-Ni	Fe-Al-Ni	Fe-Al-Cu	Fe-Al-Cr
	I	II	I	II		
Fe	46.1	43.9	13.5	10.9	18.7	14.1
Al	53.9	56.1	53.8	56.6	56.1	64.6
Ni	—	—	32.7	32.5	—	—
Cu	—	—	—	—	25.1	—
Cr	—	—	—	—	—	21.3

Table 2 Phase composition of the investigated metallic powders determined by qualitative and quantitative structural analysis with X-ray diffraction and scanning electron microscopy.

Investigated material	Estimated phase composition	Phase content in the sample
Fe-Al	$\text{Fe}_{46}\text{Al}_{54}$	100%
	$\text{Fe}_{43}\text{Al}_{56}$	100%
Fe-Al-Ni	$\text{Fe}_{32}\text{Al}_{54}\text{Ni}_{14}$	70%
	$\text{Fe}_{12}\text{Al}_{53}\text{Ni}_{35}$	30%
	$\text{Fe}_{30}\text{Al}_{53}\text{Ni}_{17}$	65%
	$\text{Fe}_{10}\text{Al}_{53}\text{Ni}_{37}$	35%
Fe-Al-Cu	$\text{Fe}_{40}\text{Al}_{52}\text{Cu}_8$	77%
	$\text{Fe}_8\text{Al}_{53}\text{Cu}_{39}$	23%
Fe-Al-Cr	$\text{Fe}_{35}\text{Al}_{54}\text{Cr}_{11}$	60%
	$\text{Fe}_9\text{Al}_{53}\text{Cr}_{38}$	40%

2.2. Measurements

Qualitative and quantitative phase analysis was carried out by applying X-ray diffraction and scanning electron microscopy (SEM). The phase composition of the investigated metallic powders is shown in **Table 2**. The FeAl samples are single-phase materials with B2 structure. Alloying additions modify the phase composition and the Fe-Al-X samples are two-phase systems in which the main phase is of FeAl(X) type, while the second phase, containing iron as an impurity, is of XAl(Fe) type. All the phases that exist in the examined materials contain high concentrations of aluminum (over 50 at.%) and have an ordered B2 structure [6].

No equilibrium of the amount of FeAl_2 and Fe_2Al_5 intermetallic phases was detected. It is worth noticing that saturation of FeAl in aluminum by traditional methods always leads to precipitation of these phases.

^{57}Fe Mössbauer spectra were recorded in transmission geometry by means of a constant spectrometer of standard design. The 14.4 keV gamma rays were provided by a 50 mCi source of $^{57}\text{Co}/\text{Rh}$.

The spectra of the samples immediately after the process of self-decomposition and heat treatment (heating at 823 K for 5h) were recorded at room temperature. Selected spectra are presented in **Fig. 1** and **Fig. 2**. The hyperfine parameters of the investigated spectra were compared with an α -Fe standard. The shape of the experimental spectrum was described with a transmission integral calculated according to the numerical Gauss-Legendre's procedure [7]. This made it possible to determine with

high precision the value of the isomer shift, the quadruple splitting and the intensities of the fitted components. In the Mössbauer effect investigation, samples prepared as pellets were used with Li_2CO_3 as a binder, in which the investigated material was placed uniformly. The uniformity of the samples was confirmed by microscopic methods.

3. Results and discussion

The Mössbauer spectra presented in this work (**Fig. 1**) were fitted based on the model proposed in the work [8], taking into account the presence of point defects (vacancies) and anti-site atoms (Fe-AS) in the Mössbauer probe environments. According to this model each crystal phase was characterized by four components describing the local environment of a Mössbauer nuclide. The first of these components-(I) - a single line - is related to the undistorted B2 structure. The next single line-(II) represents the case when an Fe atom is located in an Fe-AS position. The third component-(III) - a quadrupole doublet of lines - is allocated to the case when the Mössbauer Fe nuclide located in the corners of a cubic centered unit cell has in its environment an Fe atom found in the Fe-AS-corner. The fourth component-(IV), being also a quadruple doublet of lines, defines the case where there is a vacancy in the Fe environment. Single-phase samples of the FeAl type were analyzed using four components, while samples of the FeAlX (X=Cu;Ni;Cr) series were investigated as two-phase

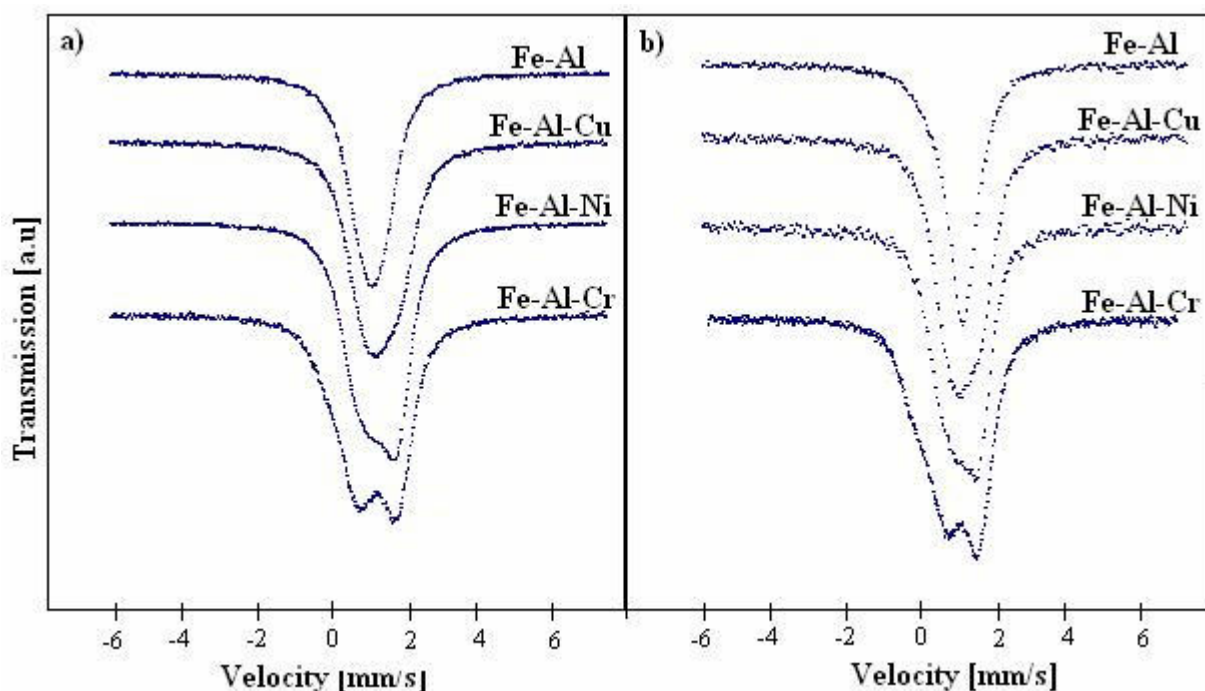


Fig. 1 Selected ^{57}Fe Mössbauer transmission spectra for Fe-Al-X (X=Cu;Ni;Cr) metallic powders obtained by the method of self-decomposition (a), self-decomposition followed by thermal treatment (b).

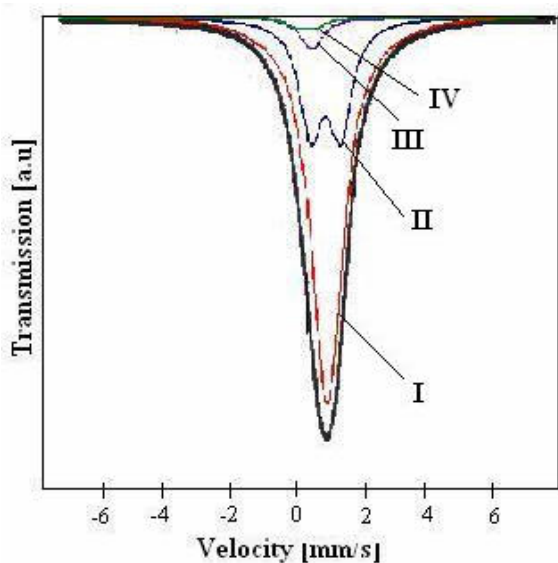


Fig. 2 Mössbauer transmission spectrum for Fe-Al metallic powders obtained by the self-decomposition method. The best fit and component spectra are drawn with lines, points are experimental data.

systems with the dominant phase of the FeAl(X) type and the second one an AlX(Fe) phase with low Fe concentration. For the two-phase samples the analysis was carried out by fitting the two sub-spectra (each

sub-spectrum was characterized by four components). The relative intensity ratio of the two sub-spectra was constrained by the ratio of the relative content of the phases in the sample.

The values of the vacancy and anti-site atom concentrations found using the described procedure are shown in [Tables 3 and 4](#). The values obtained for the point defect concentrations show that the investigated materials are characterized by higher concentrations of point defects than those described in the literature [2,8,9]. This is related to the preparation by the self-decomposition method, and the easier generation of vacancies in Al-rich alloys, caused by a lowering of the energy of formation [10].

Applying alloy additions in the investigated materials Fe-Al-X (X=Cu,Ni,Cr) causes a modification of the electron structure [11] and defect microstructure. The strongest increase of the vacancy concentration with a decrease of the concentration of anti-site atoms was found for systems containing nickel and copper. The use of chromium as a solute atom causes both a decrease of the vacancy concentration in comparison with the Fe-Al system and the highest increase of the anti-site atom concentration. A comparison of the concentrations of point defects found for samples analyzed immediately after the self-decomposition process and for samples thermally treated at 823 K shows a decrease of the point defect concentration by 40% after the thermal treatment. It is a consequence of the high enthalpy of migration of vacancies, which makes it difficult to reach thermal equilibrium at low temperature.

Table 3 Values of vacancy concentrations in samples of Fe-Al and Fe-Al-X (X=Cu;Ni;Cr) metallic powders, determined by Mössbauer spectroscopy.

Investigated material	Estimated phase composition	Vacancy concentration [%]* [material after self-decomposition process]	Vacancy concentration [%]*[material after thermal treatment]
Fe-Al	$\text{Fe}_{46}\text{Al}_{54}$	0.08	0.05
Fe-Al-Ni	$\text{Fe}_{43}\text{Al}_{56}$	0.10	0.06
	$\text{Fe}_{32}\text{Al}_{54}\text{Ni}_{14}$	0.12	0.09
	$\text{Fe}_{12}\text{Al}_{53}\text{Ni}_{35}$	0.14	0.10
	$\text{Fe}_{30}\text{Al}_{53}\text{Ni}_{17}$	0.11	0.08
Fe-Al-Cu	$\text{Fe}_{10}\text{Al}_{53}\text{Ni}_{37}$	0.12	0.10
	$\text{Fe}_{40}\text{Al}_{52}\text{Cu}_8$	0.11	0.06
	$\text{Fe}_8\text{Al}_{53}\text{Cu}_{39}$	0.09	0.07
Fe-Al-Cr	$\text{Fe}_{35}\text{Al}_{54}\text{Cr}_{11}$	0.06	0.04
	$\text{Fe}_9\text{Al}_{53}\text{Cr}_{38}$	0.05	0.03

* Error estimated from the fitting procedure is equal ± 0.005 **Table 4** Values of anti-site atom Fe-AS concentrations in samples of Fe-Al and Fe-Al-X (X=Cu;Ni;Cr) metallic powders, determined by Mössbauer spectroscopy.

Investigated material	Estimated phase composition	Fe-As atom concentration [%]* [material after self-decomposition process]	Fe-A atom concentration [%]* [material after thermal treatment]
Fe-Al	$\text{Fe}_{46}\text{Al}_{54}$	2.50	1.80
Fe-Al-Ni	$\text{Fe}_{43}\text{Al}_{56}$	2.55	2.10
	$\text{Fe}_{32}\text{Al}_{54}\text{Ni}_{14}$	0.97	0.62
	$\text{Fe}_{12}\text{Al}_{53}\text{Ni}_{35}$	0.85	0.55
	$\text{Fe}_{30}\text{Al}_{53}\text{Ni}_{17}$	1.05	0.85
Fe-Al-Cu	$\text{Fe}_{10}\text{Al}_{53}\text{Ni}_{37}$	1.02	0.80
	$\text{Fe}_{40}\text{Al}_{52}\text{Cu}_8$	0.90	0.76
	$\text{Fe}_8\text{Al}_{53}\text{Cu}_{39}$	0.97	0.84
Fe-Al-Cr	$\text{Fe}_{35}\text{Al}_{54}\text{Cr}_{11}$	3.10	2.40
	$\text{Fe}_9\text{Al}_{53}\text{Cr}_{38}$	3.60	2.80

* Error estimated from the fitting procedure is equal ± 0.01

According to the classification based on the preferred type of point defect, applied in work [2], all materials belong to compounds of the TRD type characterized by triple defects, i.e. two vacancies and one anti-site atom in the Fe sub-lattice. The results of theoretical calculations [12] and experimental research [2,8,9] indicate a high increase of the concentration of point defects with increasing aluminum concentration.

In addition, the results presented in this paper show distinctive changes in the point defect concentrations caused by the presence of admixture atoms. It can be assumed that materials enriched by alloy additions will exhibit better mechanic properties. These are also significantly influenced by the defect structure of the material. The existence of a second phase improves the mechanical properties as well.

4. Conclusions

In this work point defect concentrations were determined for a series of intermetallic compound samples FeAl and FeAlX (X=Cu;Ni;Cr), obtained by the self-decomposition method, applying Mössbauer spectroscopy.

It was found that the investigated materials contain high concentrations of point defects, which increase significantly with increasing aluminum concentration. This is a result of the lowering of the energy of formation of vacancies with increasing aluminum concentration.

The applied alloy additions modify the defect structure and the phase composition of the studied materials. Nickel and copper cause an increase of the vacancy concentration in comparison with the values

found for Fe-Al metallic powders, whereas chromium decreases the vacancy concentration, causing a high increase of the concentration of anti-site atoms Fe-AS.

References

- [1] C.G. McKamey, in: *Physical Metallurgy and Processing of Intermetallic Compounds*, Chapman Hall, 1996, p. 351.
- [2] J.L. Jorda, S.C. Deevi, Vacancy formation and effects in FeAl, *Intermetallics* 11 (2003) 507-528.
- [3] M. Kogachi, T. Haraguchi, S.M. Kim, Point defect behavior in high temperature region in the B2-type intermetallic compound FeAl, *Intermetallics* 6 (1998) 499-510.
- [4] M. Hillert, M. Selleby, Point defects in B2 compounds, *J. Alloys Compd.* 329 (2001) 208-213.
- [5] F. Binczyk, *Technol. Samorz. Rozp. Inz. Mater.* 4 (1989) 51-57 (in Polish).
- [6] A. Hanc, G. Dercz, J.E. Frąckowiak, L. Pająk, F. Binczyk, Structural studies on metallic powders from Fe-Al and Fe-Al-X (X=Cu;Ni;Cr) systems obtained by self-decomposition method, *Proc. XIX Conf. Appl. Crystallogr.*, Kraków, Poland, 2004, pp. 312-316.
- [7] A. Ralston, *A first course in numerical analysis*, McGraw-Hill Book Company, London, 1975.
- [8] S. Gianella, R.S. Brua, W. Deng, F. Marino, T. Spataru, G. Principi, Defect structures in FeAl B2 alloys, *J. Alloys Compd.* 317-318 (2001) 485-490.
- [9] J. Bogner, W. Steiner, M. Reissner, P. Mohn, P. Blaha, K. Schwarz, R. Krachler, H. Ipser, B. Sepiol, Magnetic order and defect structure of $\text{Fe}_x\text{Al}_{1-x}$ alloys around $x=0.5$: An experimental and theoretical study, *Phys. Rev. B* 58 (1998) 14922-14933.
- [10] P.R. Munroe, Nickel and iron aluminides: processing, properties and applications, *Proc. ASM*, 1996, pp. 95-113.
- [11] T. Michalecki, J. Deniszczuk, J.E. Frąckowiak, First principles study of the isomer shift in $\text{Fe}_{44}\text{M}_6\text{-Al}_{50}$ (M=Ti,V,Cr,Co,Ni,Cu) alloys with B2 structure, *Nucleonica* 49 (2004) S3-S6.
- [12] X. Ren, K. Otsuka, A unified model for point-defect formation in B2 intermetallic compounds, *Philos. Mag. A* 80 (2000) 467-491.

Proceeding of the X International Conference on Crystal Chemistry of Intermetallic Compounds, Lviv, September 17-20, 2007.