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PROCEEDINGS

Defect structure of Fe-Al and Fe-Al-X (X = Ni; Cu; Cr) metallic powders obtained by the self-decomposition method

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

Key words iron aluminides • defects • point defects • Mössbauer spectroscopy • Fe-Al

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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 [9].

It is well known that upon rapid quenching from elevated temperatures iron aluminides retain a high concentration of thermal vacancies, which frozen, increase their yield strength and hardness at room temperature [7]. However, the technical application of these alloys is restricted presently by poor ductility at low temperatures and low fracture toughness [8].

It is expected that the concentration of vacancies can be strongly changed in the aluminides with the variation of heat and mechanical treatment, together with the composition modification of the aluminides by transition metal ternary additives [6].

In the paper, the Fe-Al-X (X = Cu; Ni; Cr) metallic powders produced by the method of self-decomposition [2] of the Fe-Al doped alloys were studied using ^{57}Fe Mössbauer spectroscopy. Spectra were analyzed using a model according to which point defects in atomic shells close to probe atom induce changes in the isomer shift and quadrupole interactions. The concentration of the Fe vacancies and the Fe atoms substituting Al (Fe-AS) was determined from the intensities of the corresponding sub-spectra in the Mössbauer analysis related to distinct Fe enviroments. The result of solute X (X = Cu; Ni; Cr) addition effects in the investigated Fe-Al-X metallic powders is presented and discussed.

Experimental details

Samples

The investigated metallic powders were made by self-decomposition method of the 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 chemical reaction of formed Al_4C_3 with water are responsible for 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. The initial crack occurs when the stress value exceeds the critical stress, which depends mainly on the matrix fracture toughness [2]. As a consequence of the self-decomposition process, powdered material has been obtained with a grain dimension about 30–200 μm, selected by grain fraction. In the present paper powdered samples with 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 chemical analysis indicated that all investigated samples are characterized by aluminum concentration of over 50 at.%.

Measurements

Qualitative and quantitative phase analysis was carried out by applying X-ray diffraction and scanning electron microscopy (SEM). Phase composition of the investigated metallic powders is shown in Table 2. Fe-Al samples are a single phase material with the B2 structure. Alloying additions modify the phase composition and Fe-Al-X samples are a two-phase system in which the main phase is of FeAl(X) type, while the second phase containing iron as impurities is of XAl(Fe) type. All the phases that exist in the examined material contain high concentrations of aluminum (over 50 at.%) and have an ordered B2 structure [5].

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

The measurements of the ^{57}Fe Mossbauer spectra were performed 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}Co/Rh.

The spectra of the samples immediately after the process of self-decomposition and heat treatment (heating at 823 K for 5 h) were measured at room temperature. The selected obtained spectra are presented in Figs. 1 and 2. Hyperfine parameters of the investigated spectra were related to the α-Fe standard. Experimental spectrum shape was described with a transmission integral calculated according to the numerical Gauss-Legandre's procedure [11]. This made it possible to determine with high precision the value of isomer shift, the quadrupole splitting and the intensities of the fitted components. In the Mössbauer effect, investigation of the samples prepared as pellets were used with Li_2Co_3 as a binder, in which the investigated material was placed uniformly. The uniformity of samples was confirmed by microscopic methods.

Table 1. The chemical composition of the investigated materials.

Contents [at.%]	Fe-Al I	Fe-Al II	Fe-Al-Ni I	Fe-Al-Ni II	Fe-Al-Cu	Fe-Al-Cr
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	Percentage phase content in sample
Fe-Al	$Fe_{46}Al_{54}$ $Fe_{43}Al_{56}$	100% 100%
Fe-Al-Ni	$Fe_{32}Al_{54}Ni_{14}$ $Fe_{12}Al_{53}Ni_{35}$ $Fe_{30}Al_{53}Ni_{17}$ $Fe_{10}Al_{53}Ni_{37}$	70% 30% 65% 35%
Fe-Al-Cu	$Fe_{40}Al_{52}Cu_8$ $Fe_8Al_{53}Cu_{39}$	77% 23%
Fe-Al-Cr	$Fe_{35}Al_{54}Cr_{11}$ $Fe_9Al_{53}Cr_{38}$	60% 40%

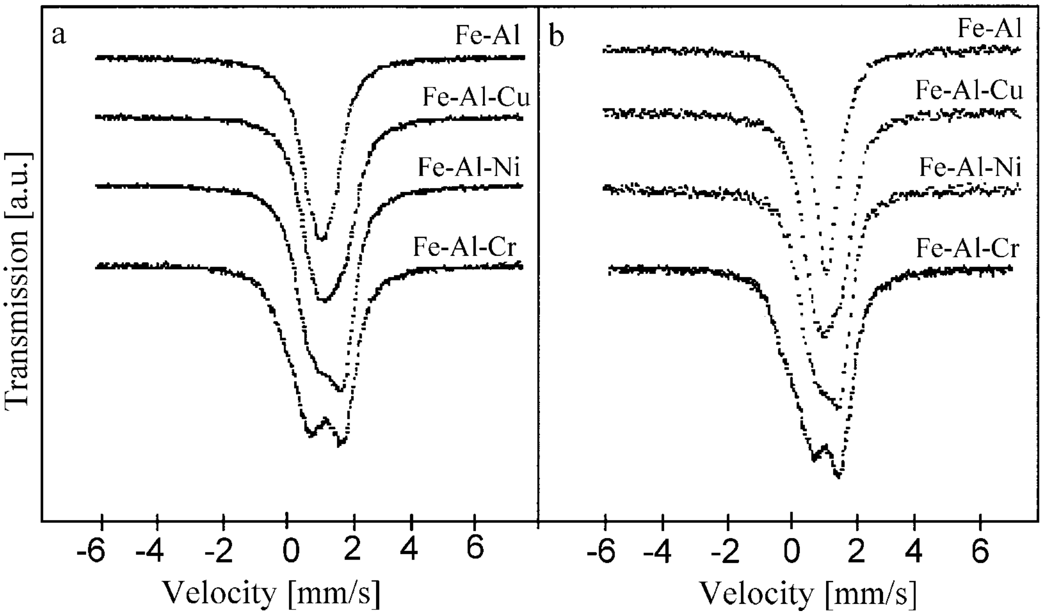

Fig 1. The selected ^{57}Fe Mössbauer transmission spectra for the Fe-Al-X (X = Cu; Ni; Cr) metallic powders obtained by the method of self-decomposition (a), self-decomposition followed after thermal treatment (b).

Results and discussion

The measured Mössbauer spectra presented in this work (Fig. 1) were fitted based on the model proposed in [4], 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 the 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 quadrupole doublet of lines, defines the case where there is a vacancy in the Fe environment. Single phase samples of the Fe-Al-type were analyzed using four components, while samples of the Fe-Al-X (X = Cu; Ni; Cr) series were investigated as two-phase systems with the dominant phase of the FeAl(X) type and the second AlX(Fe) phase with low Fe concentration. For the two phase samples, 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 percentage content of the phases in the sample.

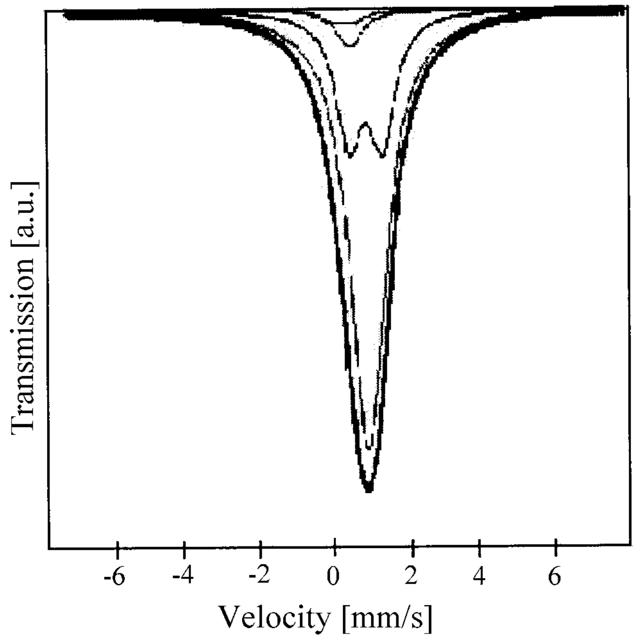

Fig 2. The Mössbauer transmission spectrum for the Fe-Al metallic powders obtained by the self-decomposition method. Solid dots – experimental data; thick solid line – fitted curve; dotted lines – sub-spectra described in the text.

The values of vacancy and anti-site atoms concentrations found using the described procedure are shown in Tables 3 and 4. The obtained values of point defect concentrations show that the investigated materials are characterized by higher concentrations of point defects than those described in the literature [3, 4, 7]. This is related to their preparation by self-decomposition method, and easier generation of vacancies in Al-rich alloys, caused by a lowering of the energy of formation [1].

Applying alloy additions in the investigated materials Fe-Al-X (X = Cu; Ni; Cr) causes the modification of the electron structure [10] and defect microstructure. The strongest increase of vacancy concentrations with the decrease of concentration of anti-site atoms was found for systems containing nickel and copper. Applying chromium as a solute atom causes both the decrease of vacancy concentration in comparison to the Fe-Al systems and the highest increase of anti-site atoms concentrations. Comparison of concentration values for point defects found for samples immediately after self-destruction process and samples thermally treated at 823 K, shows a decrease of point defect concentrations by 40% after thermal treatment. It is a consequence of a high enthalpy of migration of vacancies, making it difficult to reach thermal equilibrium at low temperature.

Using the classification according to the preferred type of point defects applied in work [7] all investigated

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

Investigated material	Estimated phase composition	Vacancy concentration [%][a] (material after self-decomposition process)	Vacancy concentration [%][a] (material after thermal treatment)
Fe-Al	$Fe_{46}Al_{54}$	0.08	0.05
	$Fe_{43}Al_{56}$	0.10	0.06
Fe-Al-Ni	$Fe_{32}Al_{54}Ni_{14}$	0.12	0.09
	$Fe_{12}Al_{53}Ni_{35}$	0.14	0.10
	$Fe_{30}Al_{53}Ni_{17}$	0.11	0.08
	$Fe_{10}Al_{53}Ni_{37}$	0.12	0.10
Fe-Al-Cu	$Fe_{40}Al_{52}Cu_{8}$	0.11	0.06
	$Fe_{8}Al_{53}Cu_{39}$	0.09	0.07
Fe-Al-Cr	$Fe_{35}Al_{54}Cr_{11}$	0.06	0.04
	$Fe_{9}Al_{53}Cr_{38}$	0.05	0.03

[a] Error estimated from the fitting procedure is equal to ±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 with Mössbauer spectroscopy.

Investigated material	Estimated phase composition	Fe-As atom concentration [%][a] (material after self-decomposition process)	Fe-A atom concentration [%][a] (material after thermal treatment)
Fe-Al	$Fe_{46}Al_{54}$	2.50	1.80
	$Fe_{43}Al_{56}$	2.55	2.10
Fe-Al-Ni	$Fe_{32}Al_{54}Ni_{14}$	0.97	0.62
	$Fe_{12}Al_{53}Ni_{35}$	0.85	0.55
	$Fe_{30}Al_{53}Ni_{17}$	1.05	0.85
	$Fe_{10}Al_{53}Ni_{37}$	1.02	0.80
Fe-Al-Cu	$Fe_{40}Al_{52}Cu_{8}$	0.90	0.76
	$Fe_{8}Al_{53}Cu_{39}$	0.97	0.84
Fe-Al-Cr	$Fe_{35}Al_{54}Cr_{11}$	3.10	2.40
	$Fe_{9}Al_{53}Cr_{38}$	3.60	2.80

[a] Error estimated from the fitting procedure is equal to ±0.01.

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 [3, 4, 7] indicate the high increase of concentration of point defects with increasing aluminum concentrations.

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

Conclusions

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

It was found that the investigated materials obtained by the self-decomposition method contain high concentrations of point defects, significantly increasing with increasing aluminum concentration. This is a result of the lowering of energy formation of vacancies with an increase of aluminum concentration.

Applied alloy additions modify the defect structure and the phase composition of the studied materials. Nickel and copper cause an increase of vacancy concentrations in comparison to the vacancy values found for Fe-Al metallic powders, whereas chromium decreases the vacancy concentrations causing the high increase of concentration of anti-site atoms Fe-AS.

References

1. Baker I, Munroe PR (1990) High-temperature aluminides and intermetallics. In: Whang SH, Liu CT, Pope DP, Stiegler JD (eds) Proc of the Symp on High Temperature Aluminides and Intermetallics, 1–5 October 1989, Indianapolis, USA. The Materials Society, Warrendale, PA, pp 95–114

2. Binczyk F (1989) The factors which determine the structure of the Fe-Al-C alloys with high content of aluminium and the analysis of the phenomena leading to their self-decomposition. Inżynieria Materiałowa 4:51–57 (in Polish)
3. Bogner J, Steiner W, Reissner M *et al.* (1998) Magnetic order and defect structure of Fe_xA_{1-x} alloys around $x = 0.5$: An experimental and theoretical study. Phys Rev B 58;22:14922–14933
4. Gianella S, Brua RS, Deng W, Marino F, Spataru T, Principi G (2001) Defect structures in FeAl B2 alloys. J Alloys Compd 317/318:485–490
5. Hanc A, Dercz G, Frąckowiak JE, Pająk L, Binczyk F (2004) Structural studies on metallic powders from Fe-Al and Fe-Al-X (X = Cu; Ni; Cr) systems obtained by self-decomposition method. In: Morawiec H, Stróż D (eds) Proc of the XIX Conf on Applied Crystallography, 3–7 September 2003, Kraków, Poland, pp 312–316
6. Hillert M, Selleby M (2001) Point defects in B2 compounds. J Alloys Compd 329:208–213
7. Jordan JL, Deevi SC (2003) Vacancy formation and effects in FeAl. Intermetallics 11:507–528
8. Kogachi M, Haraguchi T, Kim SM (1998) Point defect behavior in high temperature region in the B2-type intermetallic compound FeAl. Intermetallics 6:499–510
9. McKamey CG (1996) Iron aluminides. In: Stoloff NS, Sikka VK (eds) Physical metallurgy and processing of intermetallic compounds. Chapman & Hall, New York, chapter 9, pp 351–392
10. Michalecki T, Deniszczyk J, Frąckowiak JE (2004) First principles study of the isomer shift in $Fe_{44}M_6Al_{50}$ (M = Ti, V, Cr, Co, Ni, Cu) alloys with B2 structure. Nukleonika 49;S3:s3–s6
11. Ralston A (1975) A first course in numerical analysis. McGraw-Hill Book Co., London
12. Ren X, Otsuka K (2000) A unified model for point-defect formation in B2 intermetallic compounds. Philos Mag A 80:467–491