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Ordering process in Fe-Al28Cr5 alloys studied by Mössbauer spectroscopy

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Abstract. In the paper, studies of ternary Fe-Al28Cr5 alloys directed to characterization of mechanisms of the formation of ordered intermetallic phases influencing the possibilities of their practical application are shown. Also, a role of chromium as a modifier in kinetics of the formation of ordered phases is determined. Among the research method used, Mössbauer spectroscopy for the determination of hyperfine structure parameters was adopted. These parameters, sensitive to changes in spin and charge electron densities in the nearest neighbourhood of a Mössbauer isotope nucleus, caused by specific configurations of atoms, are directly connected with the degree of ordering of a compound. Spectral analysis has been carried out using the authors' software developed based on a theoretical model relating the shape of a Mössbauer spectrum to the sample microstructure. It has been shown that Mössbauer spectroscopy enables quantitative evaluation of the degree of ordering of phases occurring in samples characterized by large graining, in the case of which it is not possible to determine the long-range order parameter by X-ray diffraction.

Key words: Fe-Al28Cr5 alloys • formation of D0_3 phases • Mössbauer spectroscopy

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Introduction

The alloys based on ordered intermetallic phases because of their peculiar physical and chemical properties, are of increasing interest in many scientific centres all over the world. These materials, while connecting high resistance and structural stability at elevated temperatures and corrosion resistance in aggressive media, or properties characteristic of ceramics, with properties typical of metallic materials – formability and plasticity (here in a limited degree) – are a promising alternative for conventional steels and high-temperature creep resisting alloys used in industry so far. Lack of necessity to use expensive alloy additions (such as chromium or nickel) in large quantities, as it is the case for alloy steels with similar properties, makes these materials competitive also for the sake of their price. These materials are also particularly interesting because of their high resistance to carburization, oxidation or sulfurization, their electrical resistance significantly higher than in heating elements used so far, and also their resistance to abrasive, erosion and cavitation wear. All these properties make intermetals attractive for application [4, 5].

A review of known properties of Fe-Al alloys indicates that a complete knowledge of the mechanism of order-disorder phase transitions, leading to the forma-

Table 1. Thermal treatment of the investigated samples

Abbreviation	Treatment
FC	homogenization for 48 h at 1000°C in air, slow cooling with furnace
Q-Air	homogenization for 48 h at 1000°C in air, quenching in air
Q-Oil	homogenization for 48 h at 1000°C in air, quenching in oil
Q-Air/500° 0.5 h	Q-Air + annealing at 500°C for 0.5 h / slow cooling with furnace
Q-Oil/500° 0.5 h	Q-Oil + annealing at 500°C for 0.5 h / slow cooling with furnace
Q-Air/500° 2 h	Q-Air + annealing at 500°C for 2 h / slow cooling with furnace
Q-Oil/500° 2 h	Q-Oil + annealing at 500°C for 2 h / slow cooling with furnace

tion of Fe_3Al and FeAl intermetallic phases [6], requires application of several research methods, sensitive both to a change in degree of atomic ordering, and to a change in electronic and defect structures. Within the framework of this paper, traditional structural studies carried out by X-ray diffraction have been expanded with investigations performed by Mössbauer spectroscopy.

In this work the Mössbauer spectroscopy method for determination of the level of long range ordering in the alloys characterized by $D0_3$ superstructure is described. In the presented approach, possible atomic configurations around ^{57}Fe probe are the basis for reconstruction of a Mössbauer spectrum. The degree of ordering is expressed by a sum of populations of selected atomic configurations characteristic of completely ordered structure. The influence of Cr addition on stabilization of ordered intermetallic phases has been examined also. The determined results are correlated with the results of *ab-initio* calculations.

Experimental

The investigated Fe-Al28Cr5 alloys were produced by vacuum induction melting of the nominal composition 66.64 at.% Fe, 28 at.% Al, 5 at.% Cr and small amounts of other additives (Mo-0.2, C-0.1, Zr-0.05, B-0.01 at.%) introduced in order to improve their thermal and mechanical properties. The samples were examined after different thermal treatment defined in Table 1.

X-ray diffraction analysis of the investigated samples indicated the presence of $D0_3$ phase (basing on the BCC lattice) depending on the sample compositions and the type of thermal treatment they underwent, too (Table 1).

Mössbauer spectroscopy studies performed in the standard transmission geometry were carried out for thin foils about 40 μm thick at room temperature using a constant acceleration drive. The source was $^{57}Co(Rh)$ with an activity of about 50 mCi. For the numerical analysis of the spectra, specially created software was used which implemented a theoretical model appropriate to solve the problem [5].

Theoretical model of spectrum and data analysis

Theoretical model of spectrum described in paper [5], pertains, in principle, to binary alloys. However, an attempt to apply it to ternary Fe-Al28Cr5 has been made. One may presume that from the point of view of a Mössbauer nuclide, Cr atom, as a non-magnetic one, while introduced to the neighbourhood of this nuclide, causes a similar change of hyperfine field to that of Al atom in the same location. That is why during calculations, the investigated alloy has been treated as it would contain two types of atoms, i.e. Fe atoms and X atoms, where X is Al atom or Cr atom.

The spectra have been analysed with an assumption that they contain a broadened doublet, corresponding to a non-magnetic phase – containing iron and high aluminium concentration, and a magnetic phase described by many overlapping sextets of lines. It was assumed that each sextet relates to a specific atomic configuration in two nearest neighbouring shells of ^{57}Fe. The influence of the nearest neighbouring shells is determined by a number of various atoms in those shells, but not by their space arrangement. Taking into account the above assumptions and the fact that for the BCC structure there are 8 sites in the first and 6 sites in the second shell, the cross-section $S(v)$ of the resonant absorption may be described by the following formula:

$$S(v) = \sum_{m=0}^{8}\sum_{n=0}^{6} P(m,n)L_6(v,m,n) \tag{1}$$

where v is the relative velocity of source-absorbent and m,n denote the numbers of Al and Cr atoms in the nearest and the next nearest shell of ^{57}Fe, respectively.

$P(m,n)$ is the frequency of the appearance of the (m,n) configuration and $L_6(v,m,n)$ is the Zeeman sextet relating to this configuration.

The positions of lines in each sextet are calculated via respective hyperfine parameters: the hyperfine magnetic field $H(m,n)$, isomer shift $\mathrm{IS}(m,n)$ and quadrupole shift $\mathrm{QS}(m)$.

In order to reduce the number of free parameters in Eq. (1), the following constraints have been imposed: $H(m,n) = H(0,0) - m\Delta H_{\mathrm{I}} - n\Delta H_{\mathrm{II}}$ where $H(0,0)$, ΔH_{I}, ΔH_{II} are constant values [1–3, 5], $\mathrm{IS}(m,n)$ is calculated as a linear function of the hyperfine field $\mathrm{IS}(m,n) = \mathrm{IS}_0 + \beta H(m,n)$. $P(m,n)$ in (Eq. (1)) is approximated as a product $P(m,n) = p_{\mathrm{I}}(m)p_{\mathrm{II}}(n|m)$ where $p_{\mathrm{I}}(m)$ is the probability of finding m atoms of Al or Cr in the first coordinative shell of the Mössbauer probe and $p_{\mathrm{II}}(n|m)$ is the conditional probability of finding n atoms of Al or Cr in the second shell given the presence of m atoms Al or Cr in the first shell. For further reduction of free parameters and to obtain smooth changes of $p_{\mathrm{II}}(n|m)$, the conditional probability is approximated by binomial distribution $p_{\mathrm{II}}(n|m) = C_n^6 p_m^n (1 - p_m)^{6-n}$ where p_m is a parameter different for different m.

The experimental spectra after different thermal treatment were fitted simultaneously. The searched values of parameters $H(0,0)$, ΔH_{I}, ΔH_{II}, IS, β, δ and $\mathrm{QS}(m)$, were assumed to be common for all the spectra fitted together.

Table 2. The determined values of some hyperfine structure parameters

ΔH_I (T)	ΔH_{II} (T)	$H(0,0)$ (T)	IS_0 (mm/s)*	β (mm/s T^{-1})
10.4	3.19	25.0	0.353	–0.00926

* in relation to α-Fe standard.

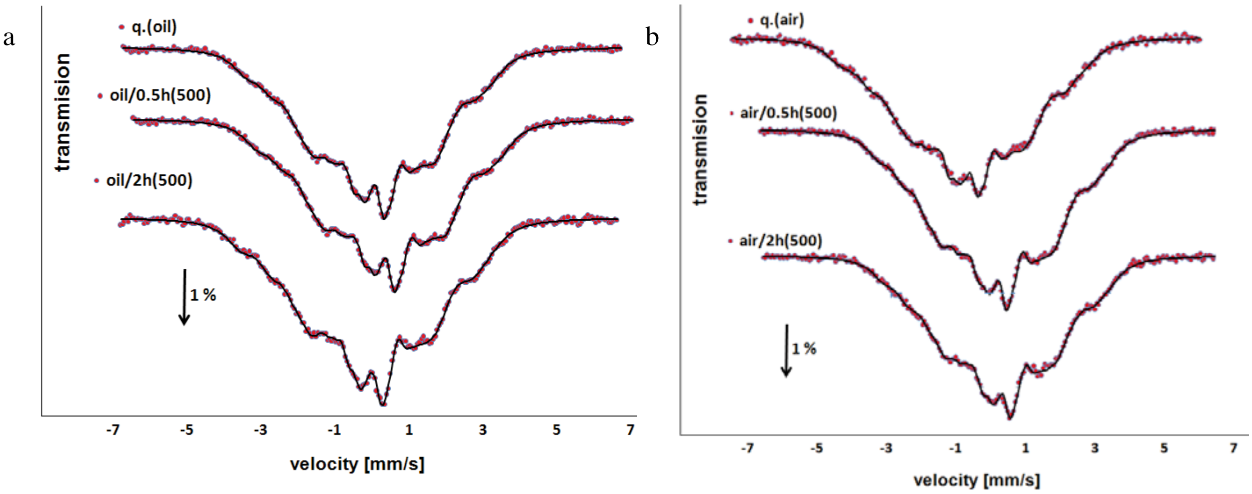

Fig. 1. The Mössbauer spectra (points) and theoretical fits (lines) for Fe-Al28Cr5 after different thermal treatment. All the spectra were fitted simultaneously with correlations between selected fitting parameters.

Results and discussion

Despite the relatively strong constraints imposed on the model parameters, very good fits were obtained. The determined values of the common parameters are presented in Table 2.

Figure 1 shows the experimental spectra and theoretical fits to the data, and Figs. 3 and 4 – the distributions of $P(m,n)$ (Eq. (1)) determined for each spectrum. According to the phase diagram for the Fe-Al system [6], if the concentration of Al is close to 28 at.%, the $D0_3$ phase is the equilibrium phase. Indeed, the XRD patterns related to all investigated Fe28Al [5] samples indicated the presence of $D0_3$ phase in various amounts. X-ray patterns of Fe-Al28Cr5 samples (Fig. 2) subjected to analogous thermal treatments differ distinctly from X-ray patterns of samples with no chromium addition corresponding to them. X-ray patterns obtained for samples directly after fast quenching process do not contain reflections characteristic of $D0_3$ superstructure. However, reflections of $D0_3$ superstructure occur in X-ray patterns of the discussed samples after the samples have been annealed for 0.5 h at 500°C, and they become even more distinct after additional annealing at the same temperature for 2 hours.

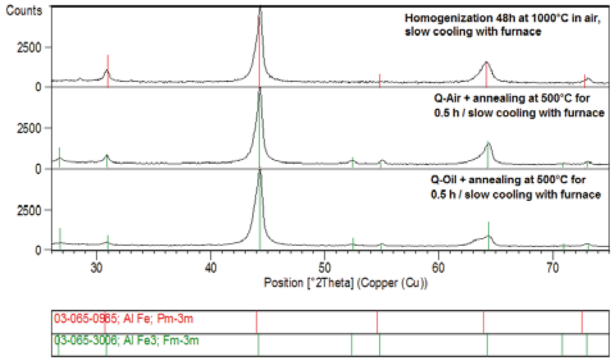

Fig. 2. X-ray diffraction patterns of Fe-Al28Cr5 samples annealed at 1000°C for 48 h and 1) cooled slowly with a furnace (FC), 2) quenched in oil (Q-oil), 3) quenched in air (Q-air).

In the completely ordered structure of $D0_3$, there are only two configurations of Al atoms in the two first coordination shells of Fe atom, namely configuration ($m = 4, n = 0$) with frequency $P(4,0) = 2/3$, and configuration ($m = 0, n = 6$) with frequency $P(0,6) = 1/3$.

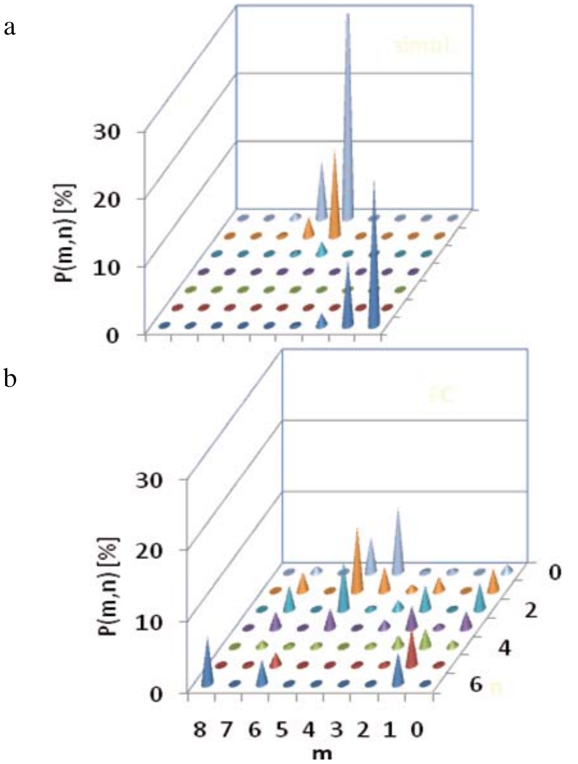

Fig. 3. (a) The simulated distribution of $P(m,n)$ for completely ordered Fe28Al crystallite of $D0_3$ superstructure, (b) the $P(m,n)$ distribution determined from Mössbauer spectrum of the furnace-cooled sample Fe-Al28Cr5 (FC).

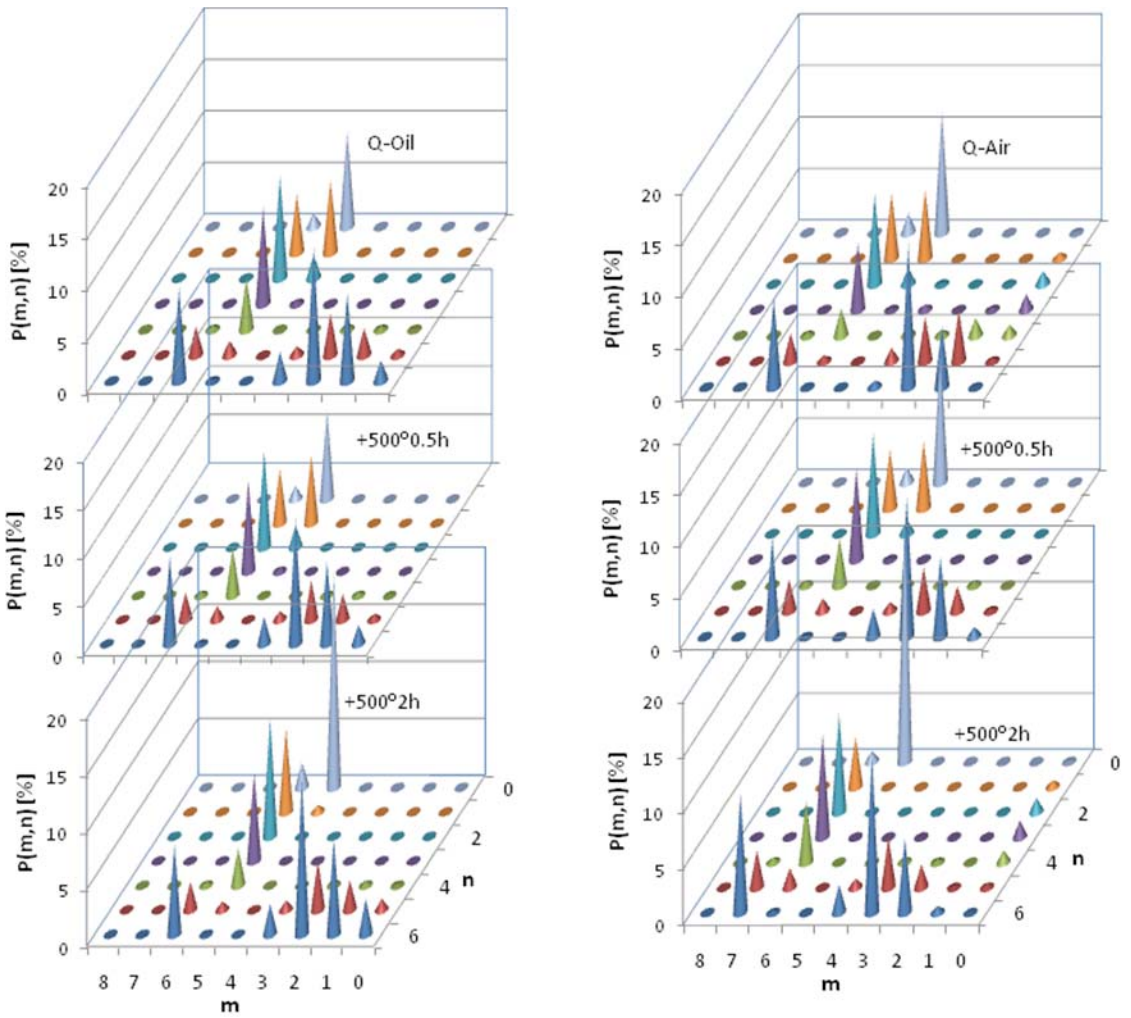

Fig. 4. The $P(m,n)$ distributions determined from Mössbauer spectra of samples that underwent various thermal treatment.

The alloys Fe-Al28Cr5 is not stoichiometric, so even in the completely ordered phase, some additional configurations beside the two mentioned above have to exist. Figure 3a shows a predicted contribution $P(m,n)$ for Fe28Al crystallite of $D0_3$ superstructure.

In the case of our samples, the ideally ordered structure is impossible to obtain because the samples are not in the equilibrium state, they have a non-stoichiometric composition, and contain defects and antiphase domains. Because of this, one may expect a number of various atomic configurations (m,n). Indeed, the experimentally obtained $P(m,n)$ distributions are quite complex (see Fig. 4), however almost all of them contain peaks at (4,0) and (0,6). This is especially seen in the diagram of determined $P(m,n)$ for the furnace cooled sample (Fig. 3b).

To determine precisely the level of alloy ordering, one would have to make such a simulation of its structure that would reflect the determined $P(m,n)$ distribution. Such a procedure is very complex and difficult to be carried out. Below, a simple method is presented, which, we hope, to be able to determine the ordering level. As a temporary measure of ordering, we propose the parameter S defined in [5]. The S parameter makes use of the populations of configurations $P(m,n)$ that are characteristic of $D0_3$ structure. $P_{max}(m,n)$ denote the values of the populations for the completely ordered $D0_3$ structure determined by the modelling (Fig. 3a). Figure 5 shows the changes of S parameter calculated on the basis of experimentally determined $P(m,n)$ distributions for Fe-Al28Cr5 samples that underwent different heat treatment. The values of the ordering degree of $D0_3$ type in all studied samples, irrespective of method of their cooling from high temperature, proved to be similar. This fact may be explained by reciprocal cancelling out of factors influencing the ordering process: on the one hand, fast quenching limits the time of alloy ordering, but on the other hand, high cooling rate leads

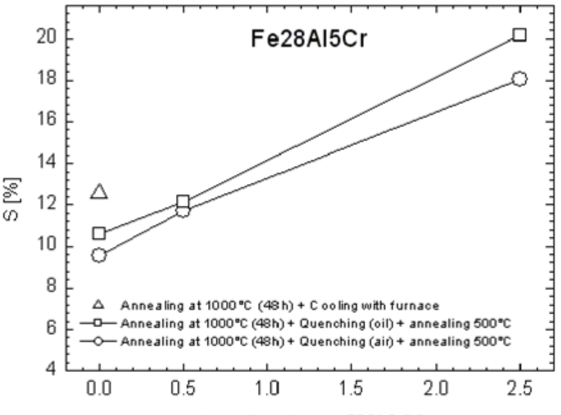

Fig. 5. The changes of S parameter for the investigated samples.

to a high concentration of frozen vacancies, favouring an increase in ordering rate. The determined *S* values are significantly lower than the analogous values obtained in the case of Fe28Al samples quenched in air or furnace cooled [5]. Basing on the above, one may conclude that the addition of chromium causes slowing down of B2 → $D0_3$ transition, which is consistent with the literature data. Annealing of fast quenched samples at 500°C, leads to a gradual increase in the degree of order of $D0_3$ type.

Conclusions

The results of Mössbauer and structural studies for Fe-Al28Cr5 samples after homogenization process at 1000°C, furnace cooled and fast quenched in oil or in air, and then additionally annealed at 500°C allow to conclude that:

- Fe-Al28Cr5 samples in furnace cooled after homogenization process at 1000°C, and in samples fast quenched in oil or in air, occurrence of B2 superstructure has been ascertained;
- introduction of a chromium additive leads to stabilization of the ordered B2 superstructure;
- thermal treatment of fast quenched Fe-Al28Cr5 samples, consisting in annealing at 500°C for 0.5 h and additional annealing at this temperature for 2 h, allows to obtain an ordered $D0_3$ superstructure.

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References

1. Błachowski A, Ruebenbauer K, Żukrowski J (2004) Charge and spin density perturbation on iron atom due to osmium impurity in metallic iron. Nukleonika 49:67–70
2. Dubiel SM, Cieślak J (1995) Influence of tin on spin- and charge-density waves in chromium. J Magn Magn Mater 148: 384–386
3. Dubiel SM, Zinn W (1982) Mösbauer effect study of spin- and charge-density changes in Fe-Al alloys. Phys Rev B 26:1574–1589
4. Jordan JL, Deevi SC (2003) Vacancy formation and effects in FeAl. Intermetallics 11:507–528
5. Kansy J, Hanc A, Giebel D (2011) Influence of heat treatment on ordering process in Fe72Al28 alloy studied by Mössbuer spectroscopy. Acta Phys Pol A 119:44–47
6. Kubashewski J (1982) Iron-binary phase diagrams. Springer, Berlin