Change of the defect structure in FeAl alloy as a result of its aging at ambient temperature

Jerzy Kansy,
Aneta Hanc-Kuczkowska,
Dawid Giebel

Abstract. Positron annihilation lifetime spectroscopy (PALS) was used to study the defect structure of stoichiometric FeAl samples after their slow cooling or quenching from the temperatures of 1000 and 540°C. The high value of positron lifetime in the quenched-in defects suggests that they are mainly of di-vacancy type. After long storage at ambient temperature, the concentration of defects in the samples strongly decreases and mono-vacancies predominate. Annealing at 540°C generates an additional amount of defects may be ascribed to the formation of $FeAl_2$ phase in the FeAl matrix.

Key words: PALS • FeAl • LT10 • defect structure

J. Kansy✉, A. Hanc-Kuczkowska, D. Giebel
University of Silesia,
Institute of Materials Science,
12 Bankowa Str., 40-008 Katowice, Poland,
Tel.: +48 32 349 7532, Fax: +48 32 349 7594,
E-mail: kansy@us.edu.pl

Introduction

Because of their peculiar physical and chemical properties, alloys based on ordered intermetallic phases enjoy an increasing interest in many scientific centres in the world. These materials combine high resistance and structural stability in increased temperatures and corrosion resistance in aggressive media. However, further studies directed towards plasticization of the intermetals are necessary. The mechanical properties of the materials are influenced by high concentration of vacancies which reaches the value of several atomic percent, the figure significantly higher than that in pure metals [1, 8, 11, 13]. The present work aims at characterizing the defect structure of an FeAl alloy with stoichiometric composition as a function of its thermal treatment. The characterization has been done with the use of the positron annihilation lifetime spectroscopy (PALS) and X-ray diffraction (XRD) technique [4]. PALS investigations of the defect structure in a Fe-Al system of the composition reaching about 50 at.% of Al were carried out in a number of works [2, 3, 7, 16]. All of them conclude that for an Al content larger than 40 at.% a complex defect structure consisting of vacancies, di-vacancies and antisite atoms is likely to be formed. In the present work we decided to confirm this thesis and, additionally, to check the thermodynamic stability of the defect structure. For the analysis of experimental data, we used the latest software [4–6, 9, 15]. The software allows simultaneous analysis of many PALS spectra with correlated values of their parameters. Thanks to this the results are more reliable and unambiguous.

Table 1. Thermal treatment scheme for individual samples of FeAl alloy

| Sample no.	Designation	Thermal treatment
1	D2	homogenization at 1000°C for 20 h (homogenization) and slow cooling
2	D3	homogenization + annealing at 1000°C for 4 h and slow furnace cooling
3	D4	homogenization + annealing at 1000°C for 4 h and quenching to oil
4	D5	homogenization + annealing at 540°C for 4 h and slow furnace cooling
5	D6	homogenization + annealing at 540°C for 4 h and quenching to oil
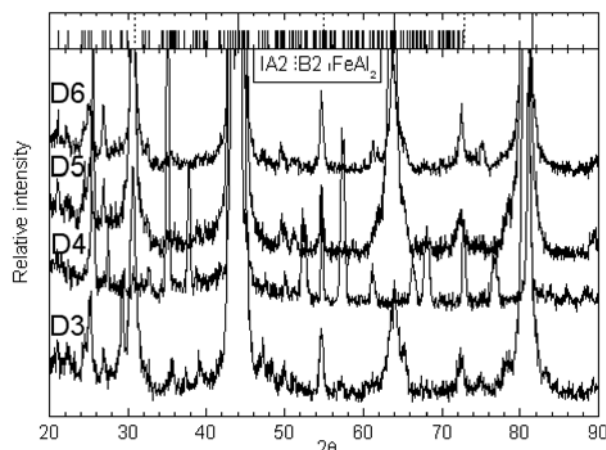
Fig. 1. X-ray patterns of the FeAl samples after slow cooling from 1000°C (D3), quenching to oil from 1000°C (D4), slow cooling from 540°C (D5) and quenching to oil from 540°C (D6). The solid (long) lines at the top of the figure indicate positions of XRD reflections related to A2 phase, the dotted lines – to B2 phase and the solid (short) lines – to $FeAl_2$ phase.

Investigated material and its heat treatment

ARMCO iron with a purity of min. 99.98% and aluminium with a purity of min. 99.98% have been used for the production of casts. Using the aforementioned components, an alloy with composition $Fe_{49.2}Al_{50.8}$ has been obtained. (The subscripts stand for the atomic percent of the components). The cast has been carried out in a Balzers VSG-02 induction furnace in an Al_2O_3 crucible. The charge melting has been carried out in vacuum of ca. 10^{-3} hPa in a chamber previously flushed with argon, while the casting process has been carried out under argon with a pressure of 900 hPa. Five samples with the form of a disk (diameter: 30 mm, height: 10 mm) have been cut off from the ingot. The samples

have been homogenised for 20 h at 1000°C and then subjected to additional thermal treatment. The types of thermal treatments applied for the studied samples are defined in Table 1.

According to the phase diagram [12], an ordered B2 phase is the equilibrium phase in an FeAl alloy with an aluminium content close to 50 at.% at a temperature ranging from ca. 1100°C to ca. 550°C. Below 550°C, the $FeAl_2$ phase appears. In order to determine the phase composition of the investigated alloys, a series of X-ray patterns of the samples were carried out. The diffraction patterns are presented in Fig. 1. These patterns indicate the coexistence of two crystalline phases: FeAl of B2 structure (a dominated one) and $FeAl_2$. More distinctly formed $FeAl_2$ phase has been revealed in D5 and D6 samples, i.e. in the samples annealed at 540°C for 4 h.

For the sake of PALS studies, two plates with a thickness of ca. 1 mm have been cut off from the D2, D3, D5 and D6 samples. The unusually high brittleness of the D4 sample, (quenched from 1000°C) rendered its cutting impossible, which may, most likely, have been caused by a very high concentration of quenched-in vacancies. Therefore, only the samples slowly cooled from 1000°C (D2 and D3), and the samples after slow cooling and quenching from 540°C (D5 and D6) were analyzed by PALS.

PALS measurement

Positron annihilation lifetime spectroscopy measurements of the investigated samples were repeated three times. The first measurement was taken just after the sample production, the second about six months later and the third after another six-month interval. Between the measurements, the samples were kept in air at room temperature. A particular spectrum was measured in a

Table 2. Details concerning three series of measurement: source contributions, full width at half maximum (FWHM) of the resolution curve and average statistics of the summary spectrum

| Measurement no.	Time of measurement	Type of positron source / Source lifetimes and their relative intensities / Total source contribution	Resolution of spectrometer (FWHM for ^{22}Na) (ps)	Average statistics of a spectrum (M counts)
1	just after production of samples	^{22}NaCl with activity of ca. 10 μCi in 5 μm nickel 130 ps (98%), 307 ps (1.3%), 1.71 ns (0.7%) total 44%	285	20
2	about half year after production	^{22}NaCl with activity of ca. 15 μCi in 25 μm Kapton 144 ps (44.1%), 378 ps (50.8%), 1.47 ns (5.1%) total 39%	240	10
3	about a year after production	^{22}NaCl with activity of ca. 15 μCi in 15 μm Kapton 135 ps (64%), 361 ps (36%) total 32%	240	7
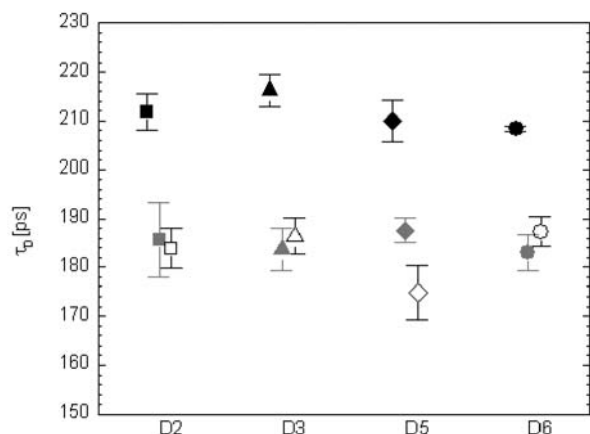
Fig. 2. The mean positron lifetime μ_D in defects (in ps) as a function of the age of samples. Black solid symbols indicate τ_D in "fresh" samples, gray solid symbols – τ_D in samples aged for half a year and empty symbols – τ_D in samples aged for a year.

one-hour interval for at least 24 h. Then, the one-hour spectra were added in order to obtain a "smooth" summary spectrum with high statistics (Table 2). During the procedure of adding a correction of spectrometer, "zero drift" was performed. The summary spectra were analyzed with LT10 software [15]. It should be emphasized that they were not analyzed one by one but all together in one computational procedure. During the calculations, the appropriate constraints and correlations between the parameters of the spectra were introduced.

Results and discussion

Initially, the spectra were analyzed with a simple 2-state-trapping model implemented directly to the LT10 code [10] described by the positron bulk lifetime τ_f, the lifetime in defects τ_D and the trapping rate by defects κ_D. Both τ_D and κ_D were fitted without any constrains while τ_f was assumed, according to theoretical predictions [3], as a constant value of 110 ps. The "apparatus" parameters relating to positron annihilation in the radioactive source and the parameters describing the resolution curve were assumed as common for all the spectra collected in the same measurement series (Table 2). Of course, they differed in various series. The source contribution was determined using the procedure described in detail in Refs. [4, 6].

The analysis indicates a change of τ_D, depending on the "age" of the sample. For the samples freshly obtained, τ_D was ca. 210 ps, while after half a year and after a year it decreased to ca. 185 ps (Fig. 2).

The observed changes in τ_D led to the assumption that the parameter is an average positron lifetime in at

least two types of defects whose relative concentrations vary with age of the sample. Therefore, in the next step, we fitted the spectra with two different defect lifetimes. The analysis of Fe-Al spectra with two components relating to defects, is not present in the literature because such an analysis involves a high scatter of results caused by the great number of degrees of freedom in calculations. Thanks to the new version of LT software, the number of degrees of freedom may be reduced by the application of a proper mathematical model of the spectrum and the applying proper constraints on the model parameters. In the present case we used a 3-state trapping model described by the bulk lifetime τ_f, two types of defect lifetimes τ_A and τ_B and two respective trapping rates by the defects κ_A and κ_B. As in the previous analysis, τ_f was assumed to be constant at 110 ps. The values of τ_A and τ_B were fitted free but common for all the analyzed spectra whereas κ_A and κ_B were entirely free. The positron lifetime in both types of defects obtained as a result of the analysis are $\tau_A = 211 \pm 1$ ps and $\tau_B = 184 \pm 1$ ps. For comparison, Table 3 contains theoretically calculated by other authors [3, 7] values of lifetimes for various types of defects which are expected in FeAl alloy of B2 structure, i.e. mono-vacancies in Fe and Al sub-lattices V_{Fe} and V_{Al}, di-vacancies $2V_{Fe}$ (the missing Fe atoms on the two adjacent Fe-sites as next nearest neighbours), di-vacancies $V_{Fe}V_{Al}$ (two vacancies on the nearest neighbouring Fe and Al sites) and triple defect $2V_{Fe}Fe_{Al}$ (two vacancies on the two adjacent Fe-sites plus Fe antisite atom).

Considering the theoretical predictions, one should presume that τ_A corresponds to a di-vacancy (most likely of $V_{Fe}V_{Al}$ type) or a triple defect $2V_{Fe}Fe_{Al}$. The value of τ_B lies between the values of defect lifetimes for V_{Al} and V_{Fe}, so it seems reasonable to assume that τ_B is a mean positron lifetime in both types of mono-vacancies.

On the ground of the determined values of trapping rates κ_A and κ_B, the defect concentrations of di- and mono-vacancy types were roughly estimated from the formula of $c_V = \kappa/\mu$. The trapping constant μ depends on the type of defects, however, because the exact values of μ are unknown, here we used $\mu = 4 \times 10^{14}$ s^{-1} determined for vacancies in an Fe$_3$Al alloy by Schaefer et al. [14] The values of c_V estimated in such a way are shown in Fig. 3. It can be seen that in "fresh" samples the di-vacancy type of defects predominates, but after long aging at ambient temperature the concentrations of both types of defects decreases and the concentration of mono-vacancies predominates.

As can be seen in Fig. 3, the sample cooled slowly from 540°C (D5) is characterized by a higher level of defects than the sample cooled slowly from 1000°C (D3). One attempt to explain this fact is to give consideration to the influence of the processes connected with the formation of an additional phase (FeAl$_2$) forming in this alloy (see the X-ray patterns in Fig. 1) during

Table 3 . Calculated values of positron lifetimes in different types of defects in B2 structure of FeAl

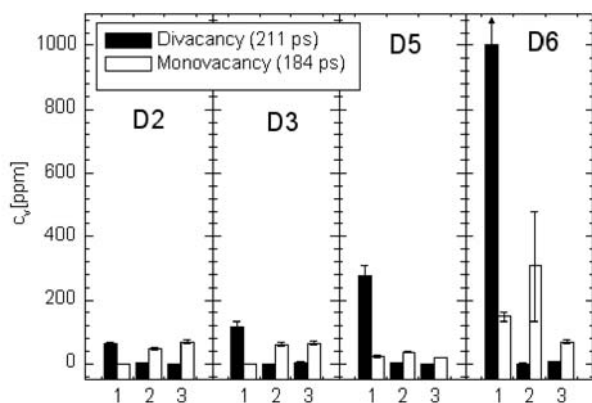| Type of defect	Haraguchi et al. [7]	Diego et al. [3]
Mono-vacancy at Al site V_{Al}	182.2	181
Mono-vacancy at Fe site V_{Fe}	195.3	189
Di-vacancy $2V_{Fe}$	201.9	
Di-vacancy $V_{Fe}V_{Al}$	211.1	205
Triple defect $2V_{Fe}Fe_{Al}$	206.7	195

Fig. 3. The estimated concentrations of two types of defects in the samples after different heat treatment (Table 1) No. 1 relates to "non-aged" samples; No. 2 – to samples aged for half a year and No. 3 – to samples aged for a year.

annealing at 540°C. This phase transition contributes to the reconstruction of crystalline lattice, which may generate additional number of vacancies.

Conclusions

The dominant defect in FeAl alloy of stoichiometric composition cooled from temperatures 540°C and 1000°C is di-vacancy (most likely of $V_{Fe}V_{Al}$-type).

Pure FeAl alloys are not stable at room temperature. After long storage of the samples, the concentration of quenched-in defects decreases with di-vacancies dissociating into mono-vacancies.

Annealing at 540°C cause additional amount of defects. This is probably connected with the formation of $FeAl_2$ phase in the FeAl matrix.

References

1. Chang YA, Pike LM, Liu CT, Bilbrey AR, Stone DS (1993) Correlation of the hardness and vacancy concentration in FeAl. Intermetallics 1:107–115
2. Čížek J, Lukáč F, Procházka I *et al*. (2012) Characterization of quenched-in vacancies in Fe-Al alloys. Physica B 407:2659–2664
3. de Diego N, Plazaola F, Jiménez JA, Serna J, del Río J (2005) A positron study of the defect structures in the D03 and B2 phases in the Fe-Al system. Acta Mater 53:163–172
4. Giebel D (2012) Complex analysis of positron lifetime spectra and its application in studies of defect structure of Fe-Al and Fe-Al-X (X=Cr,Ni) studies. PhD thesis, University of Silesia, Department of Computer Science and Materials Science, Katowice (in Polish)
5. Giebel D, Kansy J (2011) A new version of LT program for positron lifetime spectra analysis. Mater Sci Forum 666:138–141
6. Giebel D, Kansy J (2012) LT10 program for solving basic problems connected with defect detection. Physics Procedia 35:122–127
7. Haraguchi T, Hori F, Oshima R, Kogachi M (2001) A study of vacancy-type defects in the B2-phase region of the Fe-Al system by positron annihilation method. Intermetallics 9:763–770
8. Jordan JL, Deevi SC (2003) Vacancy formation and effects in FeAl. Intermetallics 11:507–528
9. Kansy J (1996) Microcomputer program for analysis of positron annihilation lifetime spectra. Nucl Instrum Methods A 374:235–244
10. Kansy J, Giebel D (2011) Study of defect structure with new software for numerical analysis of PAL spectra. J Phys Conf Series 265:012030
11. Kogachi M, Haraguchi T (1997) Quenched-in vacancies in B2-structured intermetallic compound FeAl. Mater Sci Eng A 230:124–131
12. Kubaschewski O (1982) Iron-binary phase diagrams. Springer, Berlin, p 5
13. Pike LM, Liu CT, Chang YA (1998) Effect of Ni on vacancy concentration and hardness in FeAl alloys. Metall Mater Trans A 29:1911–1915
14. Schaefer HE, Würschum R, Šob M *et al*. (1990) Thermal vacancies and positron-lifetime measurements in $Fe_{76.3}Al_{23.7}$. Phys Rev B 41:11869–11874
15. Software, available at http://prac.us.edu.pl/~kansy
16. Wolff J, Franz M, Broska A, Köhler B, Hehenkamp Th (1997) Defect types and defect properties in FeAl alloys. Mater Sci Eng A 239:213–219