

# Secondary particles precipitates in Be-Fe alloys

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**Abstract** Mössbauer spectra of monocrystalline Be-Fe alloy (0.85 % Fe) were obtained with the use of resonant detector after isothermal annealing at 600 °C for total duration of 2659 hours, and Mössbauer spectra of coarse-grained Be-Fe alloys (0,09-0,80 % Fe) samples were obtained after annealing at 500-600 °C for different durations. The alloys were prepared from the beryllium of different purity. Spectra of phases were fitted by a convolution equation of the three Lorentz lines. The coherent analysis of the solid solution decomposition process by means of the kinetic law classification and the secondary particles precipitate growth processes based on the diffusion models has been implemented. Nucleation on the numerous dislocation clusters and diffusion growth of the FeBe<sub>11</sub> nano-particles are the dominant processes in the analyzed materials. The phase distribution, the incubation period and the diffusion path were obtained. The dependence between the impurity concentration and Mössbauer parameters of the phases is discussed.

Keywords Mössbauer spectroscopy · Be alloys · Resonant detector · Shape of line

# **1** Introduction

Decomposition of an oversaturated solid solution and growth of the secondary particle precipitates (SPP) are the typical processes that take place upon thermal treatment or material's use. Mössbauer spectroscopy reveals fine details of structure and phase composition which give information about dissolution and precipitation processes.

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The resonant detectors employed in Mössbauer spectrometers have certain advantages, but make a typical spectral line shape distortion. We have introduced a mathematical description of the experimentally measured lines and found a number of regularities in the solid solution decomposition in several alloys of beryllium [1]. Under the conditions of no external vibrations, nonlinearity of the operation of the electric circuits in the spectrometer and vibrator, resonance self-absorption in the source, and inhomogeneity of the local atomic and resonant environment of Mössbauer nuclei in the source and the detector, the instrument function of the spectrometer is a product of the Lorentz lines of the source and the resonant detector. Thus, for each equivalent state of the absorber atoms the experimentally detected line  $\chi(E)$  can be described by the mathematical convolution of three generally different Lorentz lines:

$$\chi(E) = \frac{\Delta_{12}}{\pi^3} \cdot \frac{(E - E_1 - E_3)^2 \Delta_1 \Delta_3 + (E - E_2 - E_3)^2 \Delta_2 \Delta_3 + \delta^2 \Delta_1 \Delta_2 + \Delta_{12} \Delta_{23} \Delta_{13} \Delta_{123}}{\left((E - E_1 - E_3)^2 + \Delta_{13}^2\right) \left((E - E_2 - E_3)^2 + \Delta_{23}^2\right) \left(\delta^2 + \Delta_{12}^2\right)^2}, \quad (1)$$

where  $E_1$ ,  $E_2$ ,  $E_3$  are the energies of resonance transitions of the source, detector, and absorber, respectively;  $\delta = E_1 - E_2$  is the isomer shift between the source and resonant detector;  $\Delta_1$ ,  $\Delta_2$ ,  $\Delta_3$  are the half-widths of the source, detector, and absorber lines, respectively;  $\Delta_{ij} = \Delta_i + \Delta_j$ ,  $\Delta_{123} = \Delta_1 + \Delta_2 + \Delta_3$ . The unknown parameters  $\delta$ ,  $\Delta_1$ ,  $\Delta_2$  required for fitting the experimental spectra with (1) must be experimentally obtained. A comparative analysis of the spectra fitting quality with other techniques carried out. Complex spectra containing small intensity lines and doublets with a small quadrupole splitting were fitted and a coherent analysis of the solid solution decomposition according the kinetic law and the SPP growth based on the diffusion models has been implemented.

In this work, the Mössbauer spectra of the monocrystalline Be-Fe alloy and coarsegrained cast Be-Fe alloys were obtained after homogenization and after annealing for different durations, the mechanisms of the solid solution decomposition and the SPP growth were analyzed.

### 2 Experimental technique

Four coarse-grained beryllium alloys with natural iron content of 0.09 - 0.80 % (denoted as C1 – C4) and one monocrystalline beryllium alloy with natural iron content of 0.85 (denoted as S1) were prepared (Table 1). The samples for Mössbauer investigations were in the form of plates with a thickness of 2 to 10 mm.

Mössbauer transmission spectra were obtained at room temperature with a conventional constant acceleration system with a  ${}^{57}$ Co (Cr)  $\gamma$ -ray source. Velocity and isomer shift calibrations were performed with reference to sodium nitroprusside at room temperature. A resonant detector RSDU-2A (Ritverc) was used for the  $\gamma$ -ray detection. During the recording of the spectra, the vibrator, the  $\gamma$  radiation source, the detector, and the absorber were placed in a thermostat where a constant temperature of 25.00 ±0.05 °C was held. Mössbauer spectra of a solid solution of iron in beryllium after homogenization at 1100 °C and spectra with SPP after annealing at 500, 560 and 600 °C for different durations of more than 1000 hours were obtained.

The spectra were fitted by the convolution equation of the three Lorentz lines (1) as well as by other techniques. Applying (1) allowed a better approximate description of the spectra for both the initial solid solutions and the annealed materials: relative areas of the result

Graphic symbol	Method of preparation	Impurity content, mass %			
		Fe	Al	Sum of Ti, Cr, Mn	
C1	Melting of distilled beryllium with the addition of iron in an arc fur- nace	0.090	0.023	0.039	
C2		0.12	0.017	0.017	
C3		0.32	0.007	0.019	
C4		0.80	0.007	0.020	
S1	The monocrystalline part of the magnesium-reduced beryllium after annealing at 1200 °C in inert atmosphere	0.16	0.060	0.064	

#### Table 1 Analyzed materials

from subtracting the experimental spectrum and the mathematical processing (the difference spectrum) as well as  $\chi^2$  have generally the smallest values.

Figure 1 shows typical spectra of the alloys that were annealed at 600 °C. Note that in both cases the difference spectrum does not exceed the background level.

The fraction of iron in the different phases was determined from the relative area of the phase spectrum.

The process of the solid solution decomposition is characterized according the kinetic law [2]:

$$c_{\rm s} = \exp(-\mathbf{p} \cdot \mathbf{t}^{\rm n}) \tag{2}$$

where  $c_s$  – the relative amount of iron in solid solution at the annealing time t; p – empirical constant; n characterizes the decomposition mechanism. If simultaneously proceeding processes occur in a material, they can be described with a following linear combination:

$$c_{\rm s} = A_1 \cdot \exp(-p_1 \cdot t) + A_2 \cdot \exp(-p_2 \cdot t^{2/3}) + A_3 \cdot \exp(-p_3 \cdot t^{3.5}) + A_4 \tag{3}$$

According to the kinetic law classification, the exponents in (3) characterize the following processes respectively: 1) nucleation at the grain boundaries when other nucleation sites are exhausted; 2) precipitation on dislocations; 3) decomposition at a decreasing rate of nucleation of the new phase. Let  $A_1$ ,  $A_2$ , and  $A_3$  be the relative contributions from the corresponding process to the process of decomposition, and  $A_4$  be a quantity proportional to the limit of impurity solubility in a solid solution so that  $A_1 + A_2 + A_3 + A_4 = 1$ . The fitting of the experimentally obtained dependence  $c_s(t)$  using (3) can estimate the contributions from different processes. It was found in particular that the contribution from the process of decomposition to a decreasing rate of nucleation of the new phase is negligible for all of the investigated materials, i.e.,  $A_3 = 0$ .

The process of the SPP growth was analyzed using the models of diffusion from the grain to the boundary and inside the grain [1]. Due to the low diffusion coefficient and the coarse grains, the relative amount of the secondary phases precipitated at the grain boundary is negligibly small, i.e.,  $A_1 = 0$ .

In considering the diffusion equation inside the grain, the set of microstructure flaws serving as a sink for impurities was approximated by alternating parallel plate-like



nano-formations (dislocation clusters typical for beryllium). In this case, the solution of the diffusion equation takes the form:

$$c_2^i = k_2^i \cdot \left( 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp\left[ -\frac{(2n+1)^2 \pi^2 t D}{L^2} \right] \right)$$
(4)

here  $c_2^i$  – the relative amount of iron on the nano-formation plates inside the grain in the *i*th secondary phase (i = 1, 2, ...);  $k_2^i$  – the relative contribution to the SPP growth by means of the diffusion model; L – the average distance between layers of the nano-formation plates. Summation with respect to *n* carries from 0 to 90.

The total contribution from the diffusion precipitation of all secondary phases onto platelike formations is equal to the contribution to the decomposition of the solid solution on dislocations:

$$A_2 = \sum_i k_2^i \tag{5}$$

This is the particular case of the consistent solution for the models of the solid solution decomposition based on the kinetic law classification and the diffusion growth of the SPP based on the solution of the diffusion equation.

The consistent dependences of the relative amount of iron in the solid solution and in the SPP for the single crystal material on the annealing time at the temperature of 600 °C are shown in Fig. 2.

according the diffu	sion equatior	n solution; M	lössbauer ch	aracteristics	s of secondary ph	ISES	0		0	
Graphic symbol	$T, ^{\circ}C$	FeBe <sub>11</sub> ph	lase				Phase $\varepsilon$		Phase 8	
		$L, \mu m$	$t_{inc},h$	$k_2$	Is, mm· s <sup>-1</sup>	Qs, mm· s <sup>-1</sup>	$Is, \text{mm} \cdot \text{s}^{-1}$	$Qs, \operatorname{mm} \cdot \operatorname{s}^{-1}$	$Is, \text{mm} \cdot \text{s}^{-1}$	Qs, mm· s <sup>-1</sup>
C1	600	I	I	I	I	I	0.56	0.27	I	I
C2	500	1	8	0.17	0.49	0.13	Ι	I	I	I
C2	600	7	54	0.45	0.51	0.13	0.58	0.34	Ι	I
C3	500	1	82	0.88	0.51	0.12	Ι	I	0.70	0.47
C3	500	2	38	0.74	0.52	0.14	Ι	Ι	0.69	0.47
C4	009	2	2	0.82	0.51	0.14	Ι	Ι	0.66	0.41
S1	009	3	58	0.84	0.50	0.12	0.59	0.28	I	I

### **3** Discussion

For almost all of the investigated materials, the main SPP phase could be determined according to the consistency of the Mössbauer parameters (Table 2): FeBe<sub>11</sub>.

The spectrum of the FeBe<sub>11</sub> phase is a doublet with quadrupole splitting  $Qs = 0.13 \pm 0.02$  mm· s<sup>-1</sup> and isomer shift  $Is = 0.51 \pm 0.02$  mm· s<sup>-1</sup> consisting of two equal lines. These values are close to the literary data [3–5].

It was found that the relative amount of iron precipitated inside the grain in the FeBe<sub>11</sub> phase was up to 85 %. The remaining fraction of iron is in the solid solution, and in the most cases, partly in the third phase. The incubation period for this phase is usually a few tens of hours. The estimated distances between dislocation clusters are from 1 to 7  $\mu$ m. For comparison, we note that, according to [1], the phase FeBe<sub>11</sub> precipitates inside the grains and on the boundaries in the technical fine-grained hot-pressed material, but mainly inside the grains in the more pure material. Thus, the precipitation occurs in both the fine-grained and coarse-grained or single crystal materials. This can be explained by the known specificity of the usual technical beryllium saturated with the dislocation structure [6], which provides a small diffusion path (several micrometers) within the grains, the average size of which is almost always much greater.

The phase with isomer shift and quadrupole splitting close to that of AlFeBe<sub>4</sub> precipitates significantly in aluminum-enriched S1, C1 and C2 materials after annealing at the temperature of 600 °C.

For this materials and hot-pressed beryllium studied earlier, the spectrum of the AlFeBe<sub>4</sub> phase is a doublet with  $Qs = 0.30 \pm 0.03 \text{ mm} \cdot \text{s}^{-1}$  and  $Is = 0.57 \pm 0.03 \text{ mm} \cdot \text{s}^{-1}$  consisting of two equal lines. These values are close to the literary data [4, 5].

In other cases, the third phase is either absent or exists in a small amount, but with the Mössbauer spectra parameters that do not allow identifying it as AIFeBe<sub>4</sub>: values of isomer shift and quadrupole splitting is too high. We conditionally denote this phase as  $\delta$  and still find it difficult to identify it. The spectrum of this phase, that was detected only in the coarse-grained alloys, is a doublet with  $QS = 0.68 \pm 0.03 \text{ mm} \cdot \text{s}^{-1}$  and  $IS = 0.44 \pm 0.03 \text{ mm} \cdot \text{s}^{-1}$  consisting of two equal lines.

For comparison, we note that the phase  $\varepsilon$  with Mössbauer spectra parameters similar to those of the compound AlFeBe<sub>4</sub> precipitates in the fine-grained hot-pressed with the impurities of Al, Ti, Cr, Mn group, and the relative amount of the iron precipitated inside this phase was up to 69 % [1]. We associate this with a large total surface energy of the grain boundaries and with the increased chemical activity of impurities in the fine-grained material. Perhaps, the considered features of the secondary phases appear during the formation of physical and mechanical properties, which are known to differ markedly for the coarse and fine-grained, cast and hot-pressed materials. Note that the influence of some of the considered phases is already mentioned in the literature on the basis of other material science experiments [6, 7].

The results, we hope, will be useful for the analysis of solid-state processes during heat treatment and operation of beryllium materials.

### 4 Conclusions

1. Mössbauer spectroscopy with the use of the resonant detector together with the convolution equation of the three Lorentz lines allowed to reveal the small phases and to obtain kinetic and diffusion characteristics of the solid solution decomposition and the SPP growth processes.

2. The coherent analysis of the decomposition process by means of kinetic law classification and SPP growth processes based on diffusion models has been simplified for coarse-grained materials due to the absence of the precipitates on the grain boundaries.

3. In the monocrystalline and coarse-cast beryllium alloys, the overwhelming process during the annealing is the precipitation of the  $FeBe_{11}$  nano-phase on the clusters of dislocations. The precipitation occurs in both the fine-grained and coarse-grained or single crystal materials due to the specificity of the technical beryllium saturated with the dislocation structure, which provides a small diffusion path (several micrometers) within the grains.

4. AlFeBe<sub>4</sub> phase precipitates in the aluminum-enriched S1, C1 and C2 materials after annealing at 600  $^{\circ}$ C.

5. In the other coarse-grained alloys, a new phase was found with the doublet with  $Qs = 0.68 \pm 0.03 \text{ mm} \cdot \text{s}^{-1}$  and  $Is = 0.44 \pm 0.03 \text{ mm} \cdot \text{s}^{-1}$ .

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