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Mössbauer monitoring of alloys homogeneity

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Abstract The possibility of monitoring structure homogeneity has been studied by the method of Mössbauer spectroscopy with a resonance detector on the example of beryllium alloys, containing from 0.09 to 0.8 wt.% iron and other metallic impurities with a total amount of 0.04 to 0.14 wt.%. The quality of the obtained spectra description has been improved using methods which have a different degree of complexity and effectiveness.

Keywords Mössbauer spectroscopy · Resonance detector · Be alloys homogeneity

1 Introduction

Beryllium alloys are used in nuclear reactors and instrumentation. They contain various impurities, including iron. As the result of prolonged exposure to radiation, impurities can be redistributed between the solid solution and secondary phases [1]. Temperature fluctuations can also lead to this. This redistribution deals with the structure-phase state of the alloys and can affect the properties of the alloys. Mössbauer spectroscopy allows studying the iron atom redistribution and the structure-phase state change in the beryllium [2, 3]. However, the homogeneous state, which is a solid solution, has not been studied well enough for different compositions of impurities. To control the homogeneity of alloys it is necessary to obtain accurate data of all Mössbauer parameters since each of them carries characteristic physicochemical information.

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Table 1 The quality of spectra processing by means of different methods

Alloy	Iron, wt. %	Parameter χ^2				
		L	*V*	*LM*	L^2	3L
Series *B*: alloys with the iron enriched with isotope ^{57}Fe						
*B*1	0.11	20.4	2.4	3.3	2.1	1.9
*B*2	0.11	54.0	3.3	10.7	3.5	9.0
*B*3	0.11	38.6	2.6	2.3	2.5	6.4
*B*4	0.11	92.7	9.8	11.5	7.7	7.1
Series *E*: alloys with the natural iron						
*E*1	0.09	8.1	2.5	1.5	2.4	1.3
*E*2	0.09	9.4	2.7	1.2	2.3	1.4
*E*3	0.09	6.1	2.1	1.4	2.0	1.3
*E*4	0.09	28.5	6.0	2.5	5.7	2.3
*E*5	0.09	16.6	3.3	1.7	2.9	2.1
*E*6	0.09	14.4	4.5	2.0	7.9	1.4
*E*7	0.09	27.2	5.7	2.5	5.1	2.2
*E*8	0.09	30.6	7.2	2.8	6.6	2.7
*E*9	0.09	17.0	6.3	1.9	10.0	1.5
*E*10	0.09	34.3	7.8	2.3	16.9	2.3
*E*11	0.17	17.9	6.6	2.1	5.4	2.1
*E*12	0.17	36.8	6,2	2.7	5.2	2.4
*E*13	0.32	43.0	15.7	11.3	20.8	8.0
*E*14	0.32	22.6	4.8	2.0	4.2	1.8
*E*15	0.32	27.6	5.7	3.1	5.0	1.9
*E*16	0.80	20.1	19.7	4.0	8.1	2.8
*E*17	0.09	51.8	4.6	6.3	17.3	11.5

Mössbauer spectroscopy in transmission mode using resonant detectors allows to obtain spectra with a better resolution of spectral lines. These spectra, however, contain specific distorted shapes caused by the detector, which complicate the calculations. Different methods of fitting can be used to obtain more precise information [4–11].

This paper deals with choosing the best method for the fitting of Mössbauer spectra registered using a resonant detector for effective control of the homogeneity of beryllium alloys.

2 Experimental

The list of alloys studied is presented in Table 1.

The alloys of the *B* and *E* series were prepared by arc melting. The iron in the *B* series was enriched with the ^{57}Fe isotope by 50%. The alloys also contain Al, Mn, Cr, Ti and other metallic impurities at the level of technical purity. The impurities amount to 0.09% in the *B* alloys, 0.14% in the *E*1-*E*10 alloys and 0.043% in the *E*11-*E*17 alloys. Homogenization of all alloys was carried out at 1000 °C.

Mössbauer spectra were registered in transmission mode on a spectrometer MS1101E with a resonant detector RSDU (Rostov). A ^{57}Co in chromium γ radiation source (Ritvertz) was used. The γ radiation source, the detector and a sample were placed in a thermostat with constant temperature of 25.00 ± 0.05 °C.

Each chosen sample contained such an amount of ^{57}Fe and was of such dimension that it can be considered a sufficiently thin absorber [4]. All spectra were registered at nearly the same conditions. The number of counts per channel was predominantly at least 1 million. Total time of the experiment was a year.

3 Spectra fitting methods

The spectra were fitted by various methods. We used the methods of a linear combination of the Lorentz and Gauss functions, the linear combination of the Lorentz function and its square, the Voigt function, the modified Lorentz function, and the convolution method of three Lorentzians.

These methods have been chosen based on the following reasons. The method of a linear combination of the Lorentz and Gauss functions, the Voigt function and the modified Lorentz function are usually applied for Mössbauer spectra fitting [5]. They must provide a better mathematical description of the spectrum in comparison with the fitting by Lorentz functions. The method of convolution of three Lorentzians directly takes into account the features of the resonant detector [8]. The linear combination of the Lorentzian and its square [9] also takes into account the specificity of the resonant detector. This method can be derived from the method of the convolution of three Lorentzians [8] or from Odeurs' method [10, 11] but it is easier to use.

The methods for solving extremum problems have been used for processing the spectra. The value of χ^2 was calculated as:

$$\chi^2 = \sum_i w_i \frac{(f_{ei} - f_i)^2}{f_i}, \tag{1}$$

where f_{ei} is the quantity of counts in the ith spectrometer channel from the experiment, f_i—the theoretical value of the quantity of counts in the ith spectrometer channel. The weight function w_i represents the regularized useful signal normalized to one. It is chosen to take into account the specifics of the absorption spectra calculation and to reflect the fitting quality of the experimental Mössbauer spectrum:

$$w_i = \delta_i / \sum_j \delta_j. \tag{2}$$

Here δ_i—the useful regularized signal in the ith channel:

$$\delta_i = \begin{cases} b_i - f_{ei}, & b_i - f_{ei} \geq \sigma \\ \sigma, & b_i - f_{ei} < \sigma \end{cases} \tag{3}$$

where b_i—the theoretical value of the base level in the ith channel of the spectrometer, σ—standard deviation of the quantity of counts in the base level calculated far from the resonances. Summation is carried out from the 1st to the nth channel (there are 1024 channels).

Table 1 shows the values of the parameter χ^2 obtained with the use of the Lorentzian (L), the Voigt (V), the modified Lorentzian (LM), the linear combination of the Lorentzian and its square (L^2), and the convolution of three Lorentzians ($3L$) methods. The values obtained

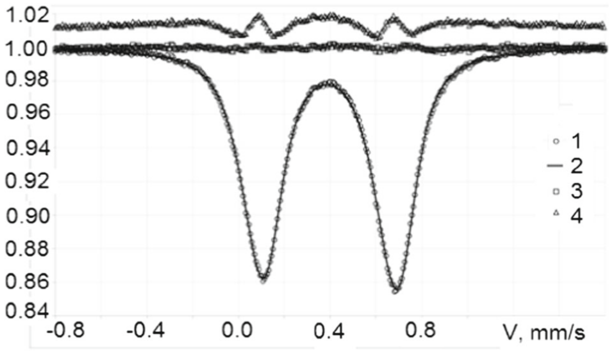

Fig. 1 The Mössbauer spectrum of the beryllium alloy with 0.32% iron: 1—the experimental spectrum; 2—its description by $3L$method; 3—a difference spectrum from $3L$; 4—a difference spectrum when processing by a simple Lorentzian (it is displaced up for descriptive reasons)

by means of linear combination of the Lorentz and Gaussian functions are 10–15% higher than those obtained with the use of the Voigt function; they are not included in the table.

4 Results, analysis and discussion

The Mössbauer spectrum of the beryllium alloy with 0.32% iron ($E14$) is presented in Fig. 1.

We can note that the methods used have improved the degree of quality of the spectra description in comparison with the fitting by Lorentz functions.

Fitting by a linear combination of the Lorentz and Gauss functions method or by the Voigt function method partially eliminated the influence of random factors obeying the law of normal distribution. This was more precisely done with the use of the Voigt function. However, for its application direct numerical calculations were required which is quite laborious. At the same time, the method of the modified Lorentz function was more effective for spectra fitting. All of these three methods, however, did not take into account the nature of the distortion of the spectra introduced by the resonant detector. They make it possible to calculate the isomeric shift and quadrupole splitting, but underestimate the line width.

The method of convolution of three Lorentzians is on the average better than other methods with respect to the χ^2 parameter; it is, however, laborious. For its application, it was necessary to complicate the measurement procedure. Figure 1 shows an example of the description by the aforementioned method. All Mössbauer parameters are most reliably calculated using this method.

It is worth to note that the difference of the methods mentioned above was only noticeable in the values of the width and amplitude of the lines for the selected group of alloys and the given measurement conditions in the experiment.

The $3L$ and L^2 methods yielded the same width and amplitude values.

The method of a linear combination of Lorentz function and its square is relatively simple and eliminates the distortion of the experimental line form introduced by the resonant detector to high degree. This method spends time to spectra fitting no more than the debugged program UNIVEM does. In our opinion, this makes it possible to trace the line width, the magnitude of the effect and the asymmetry of the lines characteristic of beryllium and some other noncubic matrices reliably.

By applying the method of linear combination of the Lorentz function L and its square L^2 in [9, p.92#3] we introduced an accounting coefficient k connected with the normalizing coefficients A_1 and A_2 as

$$A_2 = k\ A_1. \tag{4}$$

The coefficient k characterizes the contribution of L^2. To adjust it, like fine-structure parameters, we implemented the minimization of the average squared displacement using the method of coordinate descent in the LabView. The values of the accounting coefficient k were from 1.16 to 3.38. This indicates a significant contribution of the specific features of the resonant detector to the shape of the spectral line.

The following pattern has been found for samples of alloys under the same-type experimental conditions:

$$k = a/H^2 + b. \tag{5}$$

Here H is the average amplitude of the doublet lines, the empirical constants $a = (7.1 \pm 1.0) \cdot 10^{-5}$, $b = 1.27 \pm 0.05$. This pattern is satisfied with an error of about 5% for most samples of the investigated alloys. For lines with a small magnitude of the effect the error increases and amounts to more than 15% in some cases. This reduces the quality of the description of the spectra. As a result, for the alloys considered, a satisfactory quality of the description of the spectra is achieved with a value of the coefficient k not exceeding 3.2. The average amplitude of the spectral lines is not lower than 0.06. Thus, the method has some limitations in its application. These limitations can be established experimentally, which is quite acceptable for a method that has not yet been sufficiently developed.

After homogenization all iron is in solid solution in beryllium [12].

The calculated parameters of the fine structure of alloys coincided with the literature data for pure solid solutions [2, 3, 8, 13, 14] within the permissible error. The low solubility of impurities did not affect the value of these parameters. Other iron-containing phases were not detected. The samples can be considered homogeneous. The influence of undissolved impurities is negligible.

The calculated line width average is 0.31 ± 0.02 mm/s. The range of the quantity practically does not exceed the limits of the indicated error. Therefore the influence of various broadening factors is negligible and we can claim that the homogenization of alloys is adequate.

In general, the investigated alloys had a weakly expressed texture. Therefore, in accordance with the known anisotropy of the effect in a solid solution based on beryllium many spectra were in the form of asymmetric doublets. Under certain temperature conditions, which do not lead to recrystallization and reorientation of the grains, the asymmetry of the solid solution can be maintained.

Thus, the whole complex of Mössbauer data can be used to control the homogeneity of alloys and monitor of structural-phase transformations, while preserving the identity of the measurement conditions.

5 Conclusions

Mössbauer spectra of 21 beryllium alloys containing from 0.09 to 0.8% of iron were fitted in order to estimate the homogeneity of their structure. It has been shown that:

a) Homogenized Be-Fe alloys with 0.04–0.14% impurities are characterized by the coincidence of the obtained Mössbauer parameters with the literature data for the pure solid solution and the absence of other iron-containing phases;

b) The method of a linear combination of the Lorentz function and its square is optimal for the working control of the homogeneity. It is quite simple and eliminates the distortion of the experimental line form, introduced by the resonant detector, to high degree.

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