Solid-phase transformations in beryllium of technical purity with the participation of the Mössbauer iron isotope

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Abstract. New data on the redistribution of impurities in beryllium of technical purity were obtained by Mössbauer spectroscopy. The metal with 0.15% aluminum, 0.11% iron and other impurities was investigated. The introduction of iron enriched with isotope $^{57}$Fe in addition to natural iron as an impurity provided the magnitude of the Mössbauer effect, sufficient for resolving the experimental spectra and determining the parameters of the supersaturated solution that decomposed and the secondary phases that appear. Isothermal annealing at 600 °C leads first to the precipitation of the AlFeBe$_4$ phase, which predominates for 1,700 hours. During the solid-phase sequential reaction, the release of its final product of the FeBe$_{11}$ type gradually develops. Modifications of the process, the necessary level of enrichment, as well as the possibility of regulating the distribution of impurities that affect the properties of beryllium are discussed. The results obtained can be useful in analyzing the behavior of impurities during heat treatment and operation of reactor beryllium and other materials.

1. Introduction

Beryllium is used in a number of nuclear reactors and other types of equipment. In beryllium of technical purity, it is customary to take into account the separation of secondary phases and the interrelation of impurities [1-6]. Over time, the material gradually degrades, in particular, thermal conductivity deteriorates [7]. Among a number of factors that determine the stability of the properties of the material, the behavior of the impurities is quite important.

In the present paper, Mössbauer studies of technical beryllium with a limiting content of aluminum impurities were carried out to evaluate possible structural-phase changes during long-term operation of the metal at an elevated temperature.

2. Experimental

The Mössbauer spectra (i.e., the dependence of the Mössbauer effect on the velocity of the sample under study) are obtained for an alloy simulating the composition of technical beryllium. Measurements of the effect on transmission were carried out on a spectrometer MC1101E with a resonant detector of the RSDU type (Rostov), a $^{57}$Co radiation source in chromium (Ritvertz) was used. Samples were in the form of plates with a thickness of 1.5-2 mm. The gamma radiation source, detector and sample were placed in a thermostat in which a constant temperature of 25.00 ± 0.05 °C was maintained. The known Mössbauer parameters of the solid solution of iron in beryllium and the secondary phases of FeBe$_{11}$ and AlFeBe$_4$, and other possible iron-containing phases were used for identification [8-11]. The spectra were processed according to the methods [12, 13], developed with the participation of the authors.

Beryllium of technical purity usually has about 10 significant impurities [1-5], in particular in reactor beryllium [5], among important impurities can be noted oxygen - up to 2 wt. %, carbon - up to 0.1,
silicon - up to 0.03, iron - up to 0.17, aluminum - up to 0.14, magnesium and other metals - in total up to 0.05 wt. %. In the initial state (after preparatory technological annealing), such alloys have, as a rule, a Mössbauer spectrum consisting of doublet lines of a solid solution and one or two secondary phases, with characteristic parameters of the fine structure. In natural iron, 2% of the Mössbauer isotope $^{57}$Fe is contained. This small content does not always allow us to determine the phase composition, and to enhance the effect, iron needs to be enriched.

Earlier, processes of precipitation of various phases in beryllium of technical grade during heat treatment were observed [1, 3, 11, 13, 14]. In addition to the known data, let us consider the case when the aluminum content is 0.15 wt. %, that is, it is at the upper level of the interval typical for the technical metal. The material also contained 0.11 wt. % of iron enriched with the $^{57}$Fe isotope. This enrichment was obtained by fusing beryllium containing a small amount, about 0.05%, of natural iron, with the addition of iron, consisting of 90% of the Mössbauer isotope. The content of the remaining metallic impurities did not exceed 0.05 wt. %.

The alloy was homogenized at 1000 °C. Further, a long (more than 2,100 h) isothermal annealing at 600 °C was carried out. The temperature was chosen in order to accelerate diffusion processes. The spectra were taken at intermediate stages and upon completion of annealing with rapid cooling, fixing the high-temperature phase composition of the alloy.

3. Results and discussion

After homogenization, the Mössbauer spectrum of the investigated material showed only the presence of a solid solution of beryllium-iron, the other iron-containing phases were absent; the weak solubility of aluminum did not affect the spectrum.

At the beginning of isothermal annealing, as a result of the decomposition of the supersaturated solid solution, only the secondary phase of AlFeBe$_4$ was detected. Then, with some delay (not less than 50 hours), a phase of the FeBe$_{11}$ type began to appear. The spectrum of the sample after one of the annealing is shown in Fig. 1.

![Mössbauer transmission spectrum](image_url)

**Figure 1.** Mössbauer transmission spectrum for beryllium with 0.15% aluminum after 138 hours of annealing at 600 °C: 1 - experimental spectrum; 2 - doublet of a solid solution; 3 - doublet of the secondary phase of AlFeBe$_4$; 4 - doublet of the phase of the FeBe$_{11}$ type; 5 is the difference spectrum.

Long-time isothermal annealing has made major changes. Fig. 2 represents the iron content in different phases during the process.
Figure 2. The relative iron content in various phases of beryllium with isothermal annealing at 600 °C: 1 - in a solid solution; 2 - in the FeBe$_{11}$ phase; 3 - in the AlFeBe$_4$ phase.

The processing of the spectra made it possible to reveal the two secondary phases. The AlFeBe$_4$ phase with an isomer shift of 0.57 ± 0.01 mm/s and a quadrupole splitting of 0.28 ± 0.01 mm/s can be satisfactorily identified from literature data, the second iron-containing phase with an isomer shift of 0.54 ± 0.01 mm/s and a quadrupole splitting of 0.14 ± 0.01 mm/s, taking into account the literature data, we are approximately classed as FeBe$_{11}$ type, but it has a somewhat higher isomeric shift, which may indicate partial substitution of iron for other impurities and the complication of the lattice.

In beryllium, the precipitation of the AlFeBe$_4$ phase is the most rapid during annealing, and it has proved to be the most preferable for a long time. Only after 1,700 hours it yielded to another secondary phase, but even with an exposure of 2,167 hours it contained about 40% of the total amount of iron impurity. As a result, the relatively high content of the ternary phase was observed during a time interval exceeding the usual one corresponding to a reduced content of aluminum.

After passing through the maximum, the fraction of the triple phase began to decrease, which indicates that it plays the role of an intermediate in a multistage solid reaction. Apparently, the marked excess of the triple phase and its gradual decay are a characteristic feature for a given impurity composition, taking into account somewhat higher aluminum content.

During annealing, the phase of FeBe$_{11}$ type initially lagged behind, and then gradually became dominant. We applied a diffusion model developed earlier [13] to this process, and estimated the time of possible output to a constant phase ratio. It turned out that this could occur no earlier than 4,000 hours of annealing. This significantly distinguishes the material in question from those studied previously. Its properties, possibly, will be stable for a longer time of exploitation. In contrast, the behavior of ordinary beryllium of technical purity for various isothermal anneals, even with exposure to 500–1000 h [13, 14], was characterized by the establishment of a certain ratio of secondary phases. With longer exposures, this ratio was almost unchanged.
In this work, by the nature of the change in the relative iron content in different phases during the annealing (Figure 2), the entire process can be attributed to a successive solid-state reaction of the type

\[ A \rightarrow B \rightarrow C \]

The following notations are used here: A-system, which includes the initial supersaturated solid solution \((\text{Be} + \text{Fe})_0\) and an admixture of poorly soluble aluminum at the grain boundaries; B - system including AlFeBe type and depleted solid solution \((\text{Be} + \text{Fe})_2\); C is a system including a FeBe\(_{11}\) type phase, free aluminum and a depleted solid solution \((\text{Be} + \text{Fe})_2\). In the course of this multistage reaction, the following transformations occur gradually:

- first, with the inclusion of an admixture of iron diffusing from the solid solution to the boundary, that is, to aluminum, a triple phase is formed:

\[ (\text{Be} + \text{Fe})_0 + \text{Al} \rightarrow \text{AlFeBe}_4 + (\text{Be} + \text{Fe})_1; \]

- then, with the precipitation of a new phase containing iron, redistribution of iron and aluminum begins

\[ \text{AlFeBe}_4 + (\text{Be} + \text{Fe})_1 \rightarrow \text{FeBe}_{11} + \text{Al} + (\text{Be} + \text{Fe})_2. \]

Since other metal impurities from the solution (denoted by the letter M) can be reactive \([3]\), the reactions can also be represented as:

\[
\begin{align*}
(\text{Be} + \text{Fe} + \text{M})_0 + \text{Al} & \rightarrow \text{AlFeBe}_4 + (\text{Be} + \text{Fe} + \text{M})_1, \\
\text{AlFeBe}_4 + (\text{Be} + \text{Fe} + \text{M})_1 & \rightarrow (\text{Fe}, \text{M})\text{Be}_x + \text{Al} + (\text{Be} + \text{Fe} + \text{M})_2.
\end{align*}
\]

where the index \(x\) is close to 11.

The possibility of redistribution during long-time annealing helps to uncover the mechanism of complex processes during operation and to approach their management. With a decrease in the proportion of the triple phase, its effect on the physical and mechanical properties of the material is gradually weakened. Apparently, there is some critical portion of this phase that should be supported.

One can find this fraction with allowance for the thermodynamic conditions for the existence of phases in beryllium alloys \([1, 3, 15]\) and the features of successive reactions, and to maintain it, it should probably be ensured that the aluminum content exceeds the iron content.

It can be suggested in practice to test several alloys with reduced iron content to select the optimal process. We do not touch the fraction of the natural impurity and believe that the adopted technology does not allow it to be significantly reduced to a negligible value. At the same time, it is possible to preserve a sufficiently high value of the Mössbauer effect by providing the necessary minimum of enrichment with the Mössbauer isotope. To estimate this minimum, we use our experimental data on the quality of resolution of the spectra \([12]\). It has been established that, without enrichment, the difference spectrum is up to 10%, with an enrichment of 50%, it averages 3%. The 10% difference spectrum does not allow to properly resolve the complex spectrum, since it is necessary to single out 3 doublets with close lines. For an acceptable resolution, the difference spectrum should not exceed 5%.

Thus, with a decrease in enrichment, that is in the magnitude of the effect, the fraction of the difference spectrum that prevents resolution is growing. With a rough approximation, we can assume that the difference spectrum increases linearly with decreasing enrichment. Using the linear approximation, we find that the 5% difference spectrum is reached when enriching about 30%. Hence, to control the maintenance of the required amount of ternary phase, 30% enrichment of the iron with a Mössbauer isotope is sufficient. This value can be achieved with the preparation of alloys.

To simplify the preparation of samples with enriched iron, it is possible to use the ion implantation method based on the experience of introducing iron and aluminum from films into beryllium \([16]\) and taking into account the general mecanochemical regularities \([17]\). Iron has several chemical compounds with beryllium and a relatively high solubility \([1, 3]\). To interact with beryllium, therefore, it requires a smaller dose of mechanical energy. Iron is excited by an ion beam with low losses on atomization and is energetically introduced. During the implementation, it is usually expected that phases will be created according to the type of stable and metastable formations existing under normal conditions. For the Be-Fe system, this is a solid solution, as well as compounds of the FeBe\(_{11}\) and AlFeBe\(_4\) type. Aluminum is slightly soluble in beryllium, does not have binary compounds with it, but diffuses better at elevated temperatures than iron. When implantation, this or that penetration depth of aluminum is realized. It depends on the ratio of the number of atoms of iron and aluminum in the matrix.
and the film. Subsequent heat treatment can equalize the concentration of impurities by volume and create the necessary amount of a triple phase.

Similarly, reactor irradiation can act on the material prepared with the optimal composition, which gradually, with the accumulation of a dose [18], creates conditions for the movement and redistribution of impurities and, accordingly, changes in the properties of the material. Thus, in principle it is possible to obtain a material with long stable properties.

4. Conclusion

According to Mössbauer spectroscopy data, a long-term annealing of technical beryllium with an increased aluminum content leads to a sequential solid-phase reaction. This leads to a controlled redistribution of iron and aluminum impurities in favor of the intermediate secondary phase of AlFeBe$_4$, which has a significant amount for more than 2,100 hours.

The AlFeBe$_4$ phase is well identified with Mössbauer parameters, which coincide with the literature data. To control the maintenance of the required amount of triple phase, 30% enrichment of the iron with a Mössbauer isotope $_{57}$Fe is sufficient.

The results obtained can be useful in analyzing the behavior of impurities during heat treatment and long-time operation of reactor beryllium and other materials.

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