Thermal stabilization of Zr-Fe layered system obtained by ion-plasma sputtering

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Abstract. The samples of α-Iron after magnetron sputtering of Zirconium coating and consequent isothermal annealings at 700°C were investigated by methods of Mossbauer spectroscopy and X-ray diffraction. The sequence of phase transformations was established. The relative content of formed phases in the bulk of the sample is obtained. The possibility of obtaining thermal stabilization of spatially inhomogeneous layered system is shown.

1. Introduction
Ion-plasma depositions is active method for formation of surface layers with required chemical composition and make it possible to realize the idea of creation of physically and chemically compatible multilayer systems. The binary system Fe-Zr is of great interest for study the process of phase formation in layered systems obtained by the method of magnetron deposition. Iron is the main component of structural materials. Zirconium is an important structural metal used in nuclear plant. High values of corrosion resistance, mechanical strength, melting point and low effective cross-section for absorption of thermal neutrons have recently made wide use of zircalloys (Zirconium alloys with Iron and Tin) in reactor building. The phase diagram of the binary system Fe-Zr [1] includes several intermetallic compounds. The production of thin layered systems by the ion-plasma sputtering method and subsequent thermal treatment will create a thermally stable system with one phase on the surface and second phase in the bulk of the sample.

The study of phase-structure transformations in alpha-Iron with a Zirconium coating during thermal annealing at 700°C was performed.

2. Experimental
The substrates for the studies were prepared from a bar of armco iron (99.8% Fe) by rolling on a roll to a thickness of \( \approx 5 \pm 1 \) μm and subsequent homogenizing annealing at a temperature of 850°C for 2 hours. The deposition of Zirconium on Iron foil substrates was carried out by method of ion-plasma sputtering. Sequential isothermal annealing of two-layer Zr(2 μm)-Fe(5 μm) systems was carried out at a temperature of 700°C up to 20 hours in a vacuum surface with a residual pressure of 6×10^{-6} mm Hg. Samples were studied by Mossbauer spectroscopy (MS) method on \(^{57}\)Fe nuclei at room temperature. As a source of γ-quanta, \(^{57}\)Co(Rh) with an activity of \( \approx 10\mu\)Ci was used. The fitting of the experimental spectra was carried out using the DISTRI program [2] by reconstructing the distribution functions of the hyperfine parameters of the partial spectra. XRD of samples was carried out on the wavelength of...
CuKα with the D8 ADVANCE diffractometer. The measurements were made in Bragg-Brentano geometry on both sides of the specimen.

3. Results

Figure 1a shows the Mössbauer spectra of layered system subjected to successive isothermal annealing. After annealing at 700°C for 0.5 h, an appearance of a set of lines in central part of spectra is observed. The relative intensities of additional lines increase to a maximum after annealing for 5 h, followed by a decrease. On the other hand, after annealing for 3 h the lines of ferromagnetic phases with substantially smaller hyperfine fields are seen, which increase with the duration of annealing. The figure shows the positions of spectral lines of different phases present on the phase diagram of a given binary system. A good agreement of the lines makes it possible to classify newly formed phases with standard ones and to identify them. All spectra have the main component Zeeman sextet (figure 1a) referring to the 57Fe nuclei in the Armco-Iron substrate. Excluding high-intensity lines from α-Fe, partial spectra of intermetallic phases were obtained (figure 1b). It can be seen that the Mossbauer parameters of the obtained phases correlate well with the results of papers [3–6], according to which the newly formed phases can be attributed to paramagnetic (FeZr$_2$ and FeZr$_3$) and ferromagnetic intermetallides (Fe$_2$Zr and Fe$_3$Zr).

![Mössbauer spectra](image1.png)

![Partial spectra](image2.png)

**Figure 1.** Mössbauer spectra (a) and partial spectra (b) of intermetallic compounds of Zr-Fe layered system after annealings.
Three distribution functions of hyperfine parameters of Mossbauer spectra were reconstructed using DISTRI program [2]: one distribution function \( p(\varepsilon) \) of the quadrupole shift and two distribution functions \( p(H_n) \) of the hyperfine magnetic field in intervals \( \varepsilon \) and \( H_n \), characteristic for intermetallide phases and solid solution of Zirconium atoms in \( \alpha \)-Fe.

The analysis of the distribution functions of the quadrupole shift \( p(\varepsilon) \) and the effective magnetic field \( p(H_n) \) was performed and the dependence of the relative intensities \( I \) of the partial spectra for different phases versus the duration of isothermal annealing was obtained (figure 2). The obtained dependences can be interpreted as dependencies \( f \) the relative phase content in atomic units of Iron.

![Figure 2. The relative intensities of formed phases in Zr-Fe layered system versus duration of isothermal annealing.](image)

Figure 2 shows that already after the first annealing the content of \( \alpha \)-Fe in sample is decreased from 100% to 80%. Thus, isothermal annealing at 700°C of Zr(2 µm)-Fe(5 µm) layered system is characterized by the formation of intermetallic phases of FeZr\(_2\) and FeZr\(_3\), and then Fe\(_2\)Zr and Fe\(_3\)Zr.

Both sides of the sample were studied by method of X-ray diffraction (figure 3).

![Figure 3. The fragments of XRD spectra of Zr-Fe layered system after thermal annealing.](image)
In initial state on the surface of sample from Zirconium coating there are lines of $\alpha$-Zr and $\alpha$-Fe. X-ray phase analysis of samples side performed after 0.5 h annealing at 700°C showed the appearance of reflexes of FeZr$_3$. During subsequent thermal annealing, the lines of $\alpha$-Zr-coating and $\alpha$-Fe-substrate disappear. After 5 h annealing FeZr$_3$ reflexes are observed. At the same time, on the reverse side a set of $\alpha$-Fe lines with a certain texture is observed. This is evidence of the occurrence of thermally induced processes in the near-surface layer of the samples. Thus, we can say that under these thermal annealing conditions a spatially inhomogeneous system is formed: Iron zirconides (on the surface) and a solid solution of Zirconium atoms in $\alpha$-Iron (in bulk of sample).

4. Conclusion
As a result of the studies carried out, a sequence of phase transformations in layered Zr-Fe systems subjected to isothermal annealing was established; the relative content of formed phases in the bulk of the sample at each annealing step is obtained; the possibility of obtaining thermal stabilization of the intermetallic phases on an armco iron substrate is shown.

References
[1] Lyakishev N P 1997 *Diagrams of the state of double metal systems* (Moscow, 1997) (in Russian)
[2] Rusakov V S 2000 *Mossbauer spectroscopy of locally inhomogeneous system* (Almaty, INP NNC RK) (in Russian)
[3] Ghafari M et al 1982 *Nucl. Instr. Meth.* 199 197
[4] Aubertin F et al 1985 *Z. Metallkunde* Bd. 76 S237
[5] Congiu F et al 2004 *J. Magn. Magn. Mater.* 272-276 e1123
[6] Svechnikov V N et al 1963 *Zhurnal neorganicheskoy himii* 8 2118