THE FORMATION OF SURFACE LAYERS IN Zr-Fe ALLOYS UNDER ION IRRADIATION

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The study of phase transformations in intermetallic phases, which are released in the form of fine-dispersed inclusions in binary alloys based on zirconium Zr - 1.03 at. % Fe; Zr - 0.51 at. % Fe; after ion irradiation and subsequent isothermal annealing was carried out. Mössbauer spectroscopy on 57Fe nuclei in backscattering geometry with registration of internal conversion electrons, X-ray spectral analysis, X-ray diffraction analysis and electron microscopy were used. As a result, the observed segregation and phase composition of the intermetallic phases in the surface layer change under ion irradiation. Subsequent isothermal annealing after irradiation leads to a change in the concentration of intermetallic phases and phase modification in the surface layer.

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The purpose of this work is the research after ion irradiation of surface layers of zirconium alloys with Fe\(^{57}\) additions by Mossbauer spectroscopy on Fe\(^{57}\) nuclei.

**EXPERIMENTAL METHODS**

For the study alloys Zr - 1.03 at. % Fe, Zr - 0.51 at. % Fe was made. The procedure for their preparation is described in [6]. Mössbauer spectroscopy on \(^{57}\)Fe nuclei was used in the backscattering geometry with registration of internal conversion electrons (CEMS). An X-ray spectral analysis of the surface of annealed zirconium alloy samples was carried out on a Camebax MBX 268 spectrometer. X-ray study of alloys was carried out on the DRON-3.0. X-ray diffraction analysis showed that at all stages of thermo mechanical processing of alloys the matrix phase composition is represented by the alpha-phase of Zr.

**RESULTS AND DISCUSSION**

The solubility limit of Fe in \(\alpha\)-Zr decreases from value 0.015±0.001 % at 943 K to value 0.004±0.001 % at 713 K [7,8]. Consequently, when doping zirconium with iron in the metallic matrix of alloys the precipitates of intermetallic phases of complex composition are formed. In a binary Zr-Fe system 5 intermetallic compounds was found: Zr\(_4\)Fe, Zr\(_3\)Fe, Zr\(_2\)Fe, ZrFe\(_2\), and ZrFe\(_3\) [9]. The equilibrium Zr-Fe phase diagram is shown in Fig. 1 [10].

![Fig. 1. The equilibrium Zr-Fe phase diagram](image)

Parameters of Mossbauer spectra of formed intermetallic phases in Zr-Fe system are given in the Table.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Isomer shift, (\delta), mm/s</th>
<th>Quadruple splitting, (\Delta), mm/s</th>
<th>Composition, at. % Fe</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrFe(_2)</td>
<td>-0.22(1)</td>
<td>0.46(1)</td>
<td>67</td>
<td>C15 type</td>
</tr>
<tr>
<td>Zr(_2)Fe</td>
<td>-0.31(1)</td>
<td>0.75(1)</td>
<td>33</td>
<td>CuAl(_2) type</td>
</tr>
<tr>
<td>Zr(_3)Fe</td>
<td>-0.12(1)</td>
<td>0.30(1)</td>
<td>33</td>
<td>TiNi type</td>
</tr>
<tr>
<td>ZrFe</td>
<td>-0.33(1)</td>
<td>0.91(1)</td>
<td>25</td>
<td>Re(_3)Ni type</td>
</tr>
<tr>
<td>(\alpha)-ZrFe</td>
<td>-0.34(1)</td>
<td>0.85(1)</td>
<td>20</td>
<td>hexagonal structure</td>
</tr>
<tr>
<td>(\beta)-ZrFe</td>
<td>-0.3(1)</td>
<td>0.75(1)</td>
<td>20</td>
<td>orthorhombic structure</td>
</tr>
<tr>
<td>ZrFe (solid solution)</td>
<td>0.04(1)</td>
<td>-</td>
<td>0.02</td>
<td>(\alpha)-phase</td>
</tr>
</tbody>
</table>

CEMS scattering spectrum of the surface of the Zr-1.03 at % Fe alloy after annealing at 970 K for 5 h is shown on Fig. 2. The spectrum has a doublet structure with doublet parameters characteristic for the phase Zr\(_3\)Fe.
According to experimental data the stable phase Zr3Fe is formed after high temperature annealing (1100-1200 K) and has the orthorhombic Re3B type structure with $a=3.326\,\text{Å}$, $b=10.988\,\text{Å}$, $c=8.807\,\text{Å}$. Fe atoms in this structure have only one position and with 6 Zr atoms as nearest neighbors [9].

Deformed alloys characterized broadened X-ray reflexes due to the increase in the dislocation density in the surface layer, furthermore, the formation of segregations of a second phase on the formed defects.

Analysis of the scattering spectra of annealed deformed alloys in the Zr-Fe system leads to the conclusion that the surface layer is enriched with intermetallic inclusions, which contain in its composition Fe atoms. The degree of enrichment of the surface layer due to the creation of a gradient layer as a result of thermal annealing of deformed alloy is shown in Fig. 3. Experimental data are presented as the diagram in the coordinates C-T to describe the surface segregation of intermetallic phases inclusions, where C – concentration $^{57}$Fe atoms composed of intermetallic phase; T – the annealing temperature (Fig. 3). The concentration of $^{57}$Fe atoms increase with temperature of annealing emphasizing the greatest increase in iron concentration and consequently the presence of gradient of intermetallic phases in the surface layer.

The results of calculations using the program SRIM-2008.04 of damages cascade and ion profile of the distribution of iron atoms in the Zr-1.03 at. % alloy under irradiated with iron ions with an energy of 600 keV are shown in Fig. 4,5.

The results of the calculations indicate that there is a weak dependence of the diameter of the cascade band d and the energy ranges R on the alloy composition and the strong dependence on the ion energy.

The calculations carried out with the help of the SRIM-2008.04 program will make it possible to make an effective choice of ion irradiation regimes in imitation experiments. The results of calculations of the effect of ion irradiation of a layer of zirconium-iron alloy which contain 12 at% iron in a layer 300 nm and 600 nm deep, respectively, are shown in Fig. 6,7.

CEMS spectrum of Zr-1.03 at% Fe alloy surface layer, which enriched up to 12 at. % Fe, after iron ion irradiation with an energy of 600 keV and after addition annealing at 970 K for 5 h is shown in Fig. 8. This spectrum consists of two components belonging to the amorphous phase (with a smaller value of quadruple splitting), which was formed after irradiation and the crystalline phase into which the amorphous phase turns during annealing. The spectrum of the crystalline phase has a higher value of quadruple splitting.

The dependence of the concentration change $\Delta C$ in the 300 nm layer on the iron content C in the layer and the additional annealing temperature T after irradiation is shows In Fig. 9. This 3D –diagram demonstrate the dependence
of the iron content on the annealing temperature in the surface layer 300 nm deep after ion irradiation and after additive annealing. This data demonstrate the possibility of the controlled formation of gradient layers after thermal annealing and ion irradiation. Additional annealing reduces the spatial scale of the created gradient structures in the concentration range of 14-16% and the annealing temperature range of 670-720 K.

Another important problem is the amorphization of intermetallic phases in surface layer under the irradiation by ions of the amorphous state of alloys, metastable and crystalline phases are formed after further annealing, while the crystallization temperatures and the entropy of crystallization activation depend on the composition of the alloy.

Fig. 6. Distribution of iron ions in the zirconium-iron alloy layer with a layer depth of 300 nm

Fig. 7. Distribution of iron ions in the zirconium-iron alloy layer with a layer depth of 600 nm

Fig. 8. CEMS spectrum of surface of Zr-1.03 at% Fe alloy after iron ion irradiation with an energy of 600 keV and after annealing at 970 K for 5 h

Fig. 9. The dependence of the concentration change in the 300 nm layer on the iron content in the layer and the additional annealing temperature after irradiation

CONCLUSIONS

Thus, a layer of 300 nm depth enriched with intermetallic inclusions before irradiation of the surface of the zirconium-iron alloy was created by thermal annealing of the deformed alloys. Irradiation by Fe\textsuperscript{4+} ions with energy 600 keV of surface enriched layer leads to transformation of crystalline Zr\textsubscript{3}Fe to amorphous phase. It is possible to create multi component gradient structures under ion irradiation of the alloy surface. The growth and disintegration of inclusions under thermal annealing after irradiation is not controlled by bulk diffusion and the migration of iron atoms can be associated with the presence of inter phase boundaries was found.

REFERENCES