East Eur. J. Phys. Vol.4 No.3 (2017) 43-47 DOI:10.26565/2312-4334-2017-3-06

PACS: 61.80.Ba

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

V.G. Kirichenko, V.A. Kobylnik, T.A. Kovalenko, O.A. Usatova
V. N. Karazin Kharkiv National University
4. Svobody Sq., 61022, Kharkiv, Ukraine
E-mail: val.kir.248@gmail.com
Received April 25, 2017

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 ^{57}Fe 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 inclusions of intermetallic phases and phase modification in the surface layer.
KEY WORDS: zirconium, alloys, phases, segregation, ion, irradiation

ФОРМУВАННЯ ПОВЕРХНЕВИХ ШАРІВ В Zr-Fe СПЛАВАХ ПРИ ІОННОМУ ОПРОМІНЮВАННІ

В.Г. Кіріченко, В.А. Кобильник, Т.О. Коваленко, О.О. Усатова
Харківський національний університет імені В.Н. Каразіна
61022, Харків, м. Свободи, 4

У роботі проведено дослідження фазових перетворень в інтерметалічних фазах, які виділяються у вигляді дрібнодисперсних включень в бінарних сплавах на основі цирконію після іонного опромінення і подальшого ізотермічного відпалу. Використовували мессбауерівську спектроскопію на ядрах ^{57}Fe в геометрії зворотного розсіювання з реєстрацією електронів внутрішньої конверсії, рентгеноспектральний аналіз, рентгеноструктурний аналіз і електронну мікроскопію. В результаті виявлена сегрегація і фазовий склад интерметаллических фаз в поверхневому шарі змінюється при іонному опроміненні. Подальший ізотермічний відпал після опромінення призводить до зміни концентрації включень интерметаллических фаз і модифікації фаз в поверхневому шарі.
КЛЮЧОВІ СЛОВА: цирконій, сплави, фази, зріст, сегрегація, іон, опромінення

ФОРМИРОВАНИЕ ПОВЕРХНОСТНЫХ СЛОЕВ В Zr-Fe СПЛАВАХ ПРИ ИОННОМ ОБЛУЧЕНИИ

В.Г. Кириченко, В.А. Кобыльник, Т.А. Коваленко, О.А. Усатова
Харьковский национальный университет имени В.Н. Каразина
61022, г. Харьков, пл. Свободы, 4

В работе проведено исследование фазовых превращений в интерметаллических фазах , которые выделяются в виде мелкодисперсных включений в бинарных сплавах на основе циркония после ионного облучения и последующего изотермического отжига. Использовали мессбауэровскую спектроскопию на ядрах ^{57}Fe в геометрии обратного рассеяния с регистрацией электронов внутренней конверсии, рентгеноспектральный анализ, рентгеноструктурный анализ и электронную микроскопию. В результате обнаруженная сегрегация и фазовый состав интерметаллических фаз в поверхностном слое изменяется при ионном облучении. Последующий изотермический отжиг после облучения приводит к изменению концентрации включений интерметаллических фаз и модификации фаз в поверхностном слое.
КЛЮЧЕВЫЕ СЛОВА: цирконий, сплавы, сегрегация, ион, облучение

Zirconium alloys such as E-110M, E-125, E-635, Zry-2, Zry-4, M5, ZIRLO have been widely used in nuclear power engineering [1]. The basic problems in the operation of zirconium alloys under irradiation are due to the presence of radiation growth and radiation creep due to anisotropy of α - zirconium. Used zirconium alloys differ with radiation growth, radiation creep, corrosion resistance, high temperature strength [2]. The experimental results on the formation of gradient corrosion-resistant structural-phase states in materials and fuel claddings of thermal reactors have been considered and summarized [3]. The action by high-temperature pulsed plasma flows is effective for changing the surface layer of materials. For example, as applied to E110 and E635 zirconium alloys, new structural-phase states formed by the method of “ion mixing” [3].

Such effects are associated with recently discovered gradient materials with high technological properties [4]. Optimization of gradient materials is realized by introducing nanoparticles into the surface layers. In [5] it is found that an increase in the surface concentration of iron atoms in zirconium alloys in a layer up to 0.3 μm thick is associated with an increase in the size of inclusions with an increase in the annealing temperature of the deformed alloys. The amorphization alloys based on zirconium under ion irradiation was observed [6]. The formation of amorphous intermetallic phases on the surface of zirconium alloys after ion irradiation can be attributed to the viscosity of zircaloys and the influence of the viscosity of the metallic matrix on the crystallization of amorphous phases during annealing after irradiation [6].

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 α-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_4Fe, Zr_3Fe, Zr_2Fe, $ZrFe_2$ and $ZrFe_3$ [9].The equilibrium Zr-Fe phase diagram is shown in Fig. 1 [10].

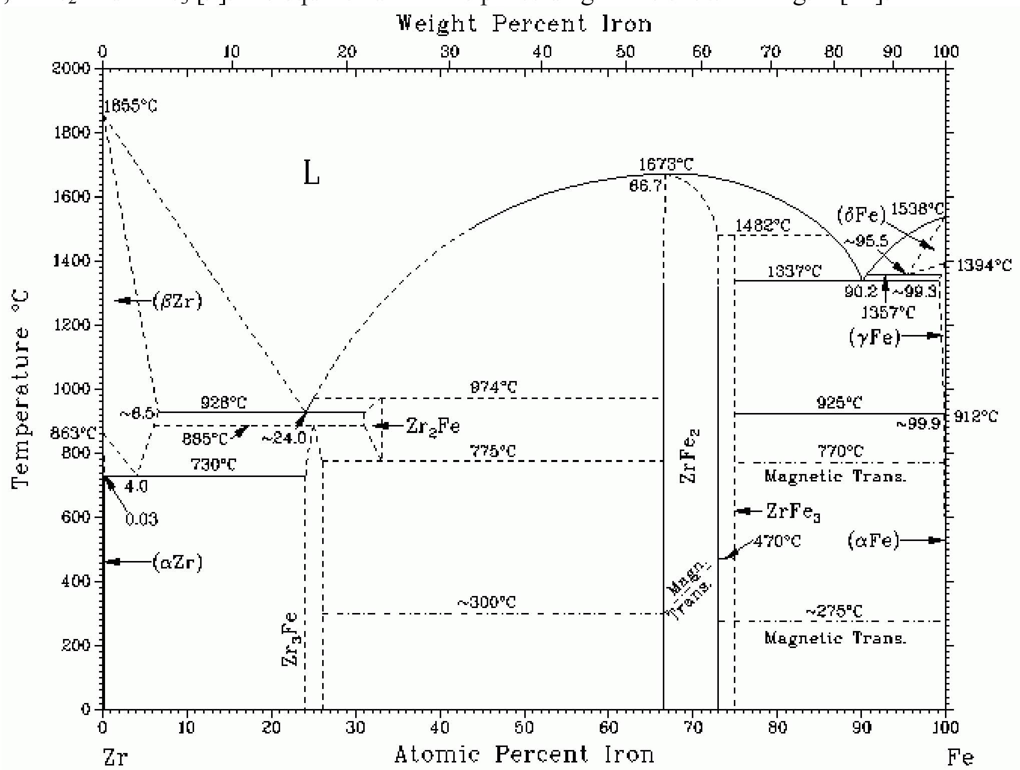

Fig. 1. The equilibrium Zr-Fe phase diagram

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

Table

The Mossbauer parameters of the phases in the binary system Zr-Fe

Phase	Isomer shift, δ, mm/s	Quadruple splitting, Δ, mm/s	Composition, at. % Fe	Crystal structure
$ZrFe_2$	- 0.22(1)	0.46(1)	67	C15 type
Zr_2Fe	- 0.31(1)	0.75(1)	33	$CuAl_2$ type
Zr_2Fe	- 0.12(1)	0.30(1)	33	Ti_2Ni type
Zr_3Fe	- 0.33(1)	0.91(1)	25	Re_3B type
α-Zr_4Fe	- 0.34(1)	0.85(1)	20	hexagonal structure
β-Zr_4Fe	- 0.3(1)	0.75(1)	20	orthorhombic structure
ZrFe (solid solution)	0.04(1)	-	0.02	α-phase

CEMS scattering spectrum of the surface of the Zr-1.03 aт % 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_3Fe.

According to experimental data the stable phase Zr_3Fe is formed after high temperature annealing (1100-1200 K) and has the orthorhombic Re_3B type structure with *a*=3.326 Å, *b*=10.988 Å, *c*=8.807 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.

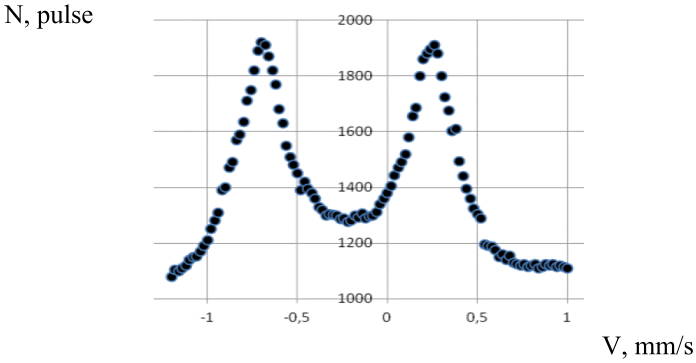

Fig. 2. CEMS scattering spectrum of the surface of the Zr-1,03 aт% Fe alloy after annealing at 970 K for 5 h

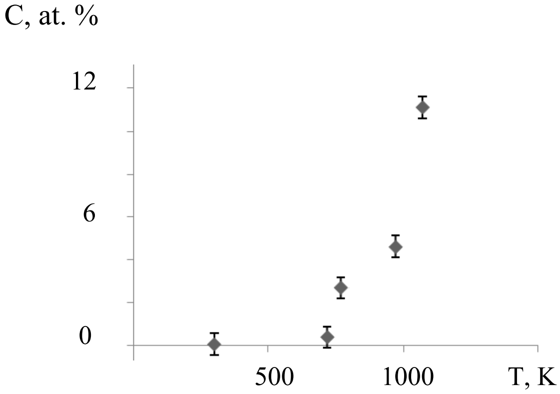

Fig. 3`. Dependence of iron concentrations in the surface layer Depth 300 nm of the alloy from the thermal annealing temperature of the deformed layer Zr-1.03 at.% Fe

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.

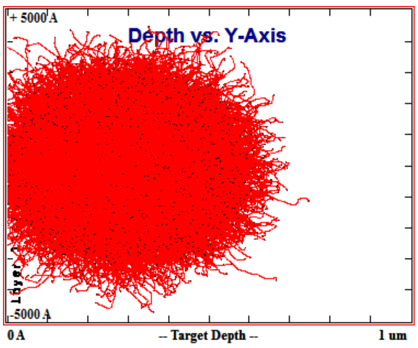

Fig. 4. Damage cascade with energy of 600 keV ions

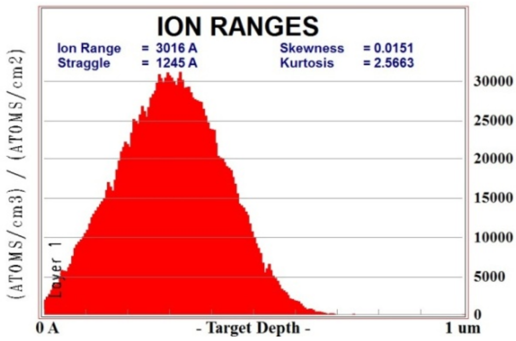

Fig. 5. Ion distribution under energy of 600 keV ions

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 ΔC 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.

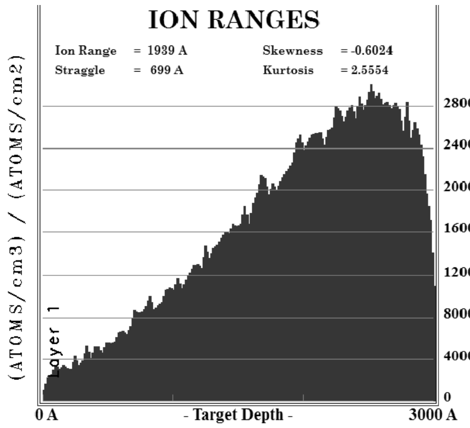

Fig. 6. Distribution of iron ions in the zirconium-iron alloy layer with a layer depth of 300 nm

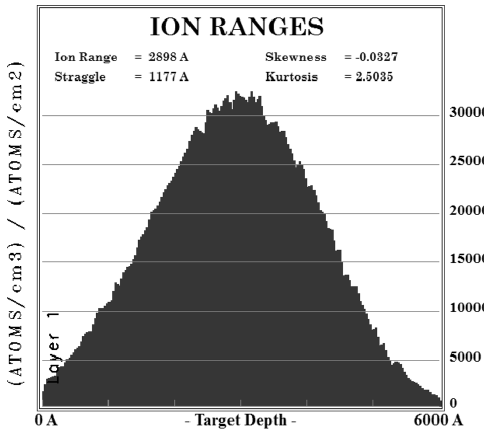

Fig. 7. Distribution of iron ions in the zirconium-iron alloy layer with a layer depth of 600 nm

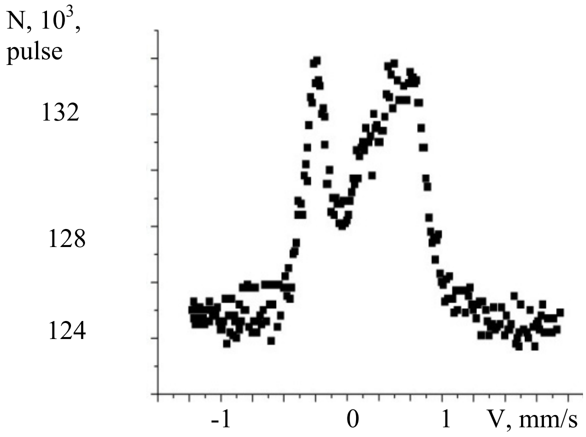

Fig. 8. CEMS spectrum of surface of Zr-1.03 at% Fe alloy after iron ion irradiation with an energy of 600 keV and after annealing at 970 K for 5 h

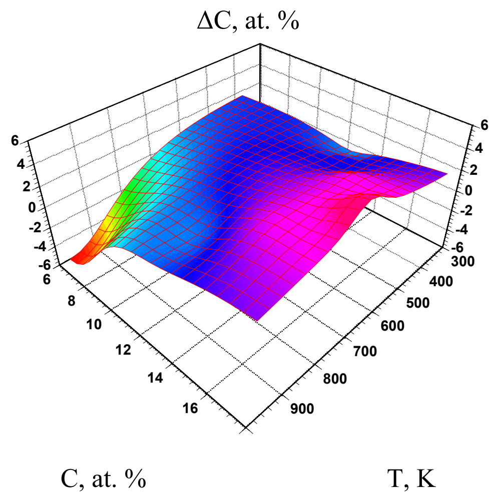

Fig. 9. The dependence of the concentration change in the 300 nm layer on the iron content in the layer and the additional annealing temperature after irradiationture

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.

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^{4+} ions with energy 600 keV of surface enriched layer leads to transformation of crystalline Zr_3Fe 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

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