THE FEATURES OF FORMATION OF THE SURFACE GRADIENT LAYERS IN ZIRCONIUM

V.G. Kirichenko, O.O. Yampolskyi
V.N. Karazin Kharkiv National University, Kharkov, Ukraine
E-mail: yadipl@mail.ru; tel. +38(057)335-37-55

It was found that increasing the surface concentration of iron atoms in zirconium alloys in the surface layer thickness up to 0.3 μm results to the formation of gradient structures. This process can help to optimize the physical and mechanical characteristics of the alloys due to intermetallic compounds enriched surface layer.

PACS: 61.80.Ba

Recently, much attention is paid to research and development of functional gradient materials with high technological and operational characteristics that require new methods of formation of gradient structures [1–3]. Combining layers with different properties is the basic idea of creating gradient materials. The main idea of creating gradient materials consists in combining the layers with different properties. Thus, the basis of modifying is the doping of the surface layer of zirconium alloys by atoms of a multilayer film (Al + Fe + Mo + Y), total film thickness of 120 nm by irradiation with Ar + ions with an energy of 10 keV [2]. This process leads to formation of two-layer oxide film with slow growth speed in the second stage on modified zirconium alloys that have gradient distribution of alloying elements in the oxidation zone. Creating the gradient structure at intensive plastic deformation of the surface alloys of titanium and iron is shown in [3]. Simultaneous superposition of several schemes of deformation significantly increases the hardness of the surface layers. These effects of surface hardening with complex schemes is explained by features of structure formation of nano-grain strain deformation origin.

Besides, optimization of the physical and mechanical properties of metallic materials is possible if nanoparticles are introduced into the surface layers. Consequently the gradient structure are formed and characterized by changing the concentration of elements and impurities, defects and phase composition by layer depth [4].

Exploitable and characteristics of materials, nuclear and radiation technologies such as zirconium alloys are determined by phase changes and segregation processes of one of the components of the alloy on the surface in areas of stress concentration during irradiation. Zirconium alloys and processes of its formation are widely studied with various methods.

In this work we research zirconium alloys for creation a gradient structures through targeted selection of the type of heat treatment of the deformed alloys.

METHODS OF EXPERIMENTAL RESEARCH

The alloys: Zr-1.03 at.% Fe; Zr-0.51 at.% Fe-M (M = Nb, Ta) were manufactured for researching. Methods of preparation is described in [5]. Mossbauer spectroscopy of ^{57}Fe nuclei in backscattering geometry with the registration of the internal conversion electrons was used. X-ray spectral analysis of the surface of the annealed samples of zirconium alloys was produced by the spectrometer “Camebax MBX 268”. X-ray analysis of alloys was produced by DRON-3.0 in Cu-k_α-radiation. Surface analysis was produced by the scanning electron microscope JEOL JSM-840 and “Quanta 3D”.

RESULTS AND DISCUSSION

Fig. 1 shows MSCE scattering spectras of the surface of the Zr-1.03 at.% Fe alloy in a deformed state and after annealing at 970 K for 5 h. Parameters phase spectra that are

$$\chi = (y/1-y) \,/\, (x/ 1-x), \qquad (1)$$

where x – the volume concentration of the isotope ^{57}Fe; y – the surface concentration of ^{57}Fe.

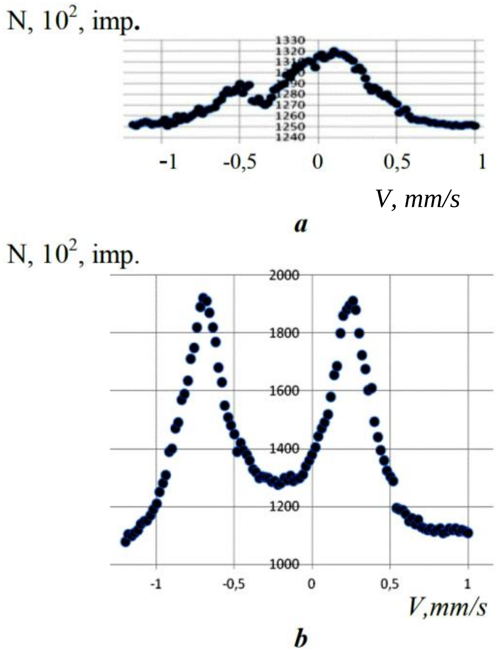

Fig. 1. MSCE spectra: deformed alloy Zr-1.03 at.% Fe (a), Zr-1.03 at.% Fe alloy annealed at 970 K, 5 h (b)

The calculation of the concentration C_{Fe} is defined by

$$C_{Fe} = C_{исх} \cdot \chi , \qquad (2)$$

ISSN 1562-6016. PAST. 2017. №2(108), p. 114-116.

where the value $C_{исх}$ is the surface concentration of impurities ^{57}Fe in the composition of the original intermetallic phase in the layer to 3000 Å. Increasing the intensity of the spectra complies to increasing in concentration corresponds to 11% compared with the initial concentration of 1.03 at.% Fe.

Experimental data are presented as constructed in this work the three-dimensional diagrams in the coordinates C-T-t to describe the surface segregation of intermetallic phases inclusions, where C – concentration ^{57}Fe atoms composed of intermetallic phase; T – the annealing temperature; t – annealing time (Fig. 2).

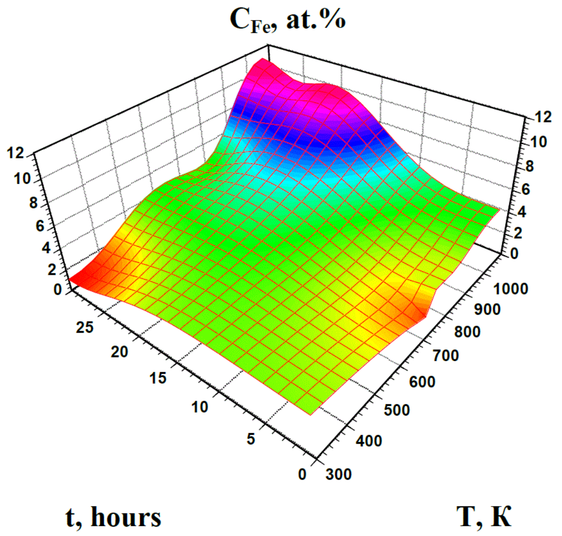

Fig. 2. The diagram in C-T-t coordinates for the alloy Zr-1.03 at.% Fe

It is seen from the diagram that the heat treatment conditions allow to reach the concentration of iron atoms in the composition of the intermetallic phases in the surface layer of 2 to 11 at.% compared with the initial state of a deformed alloy. Previously, [6], it was found that the increase in the surface concentration of iron atoms in zirconium alloys in a layer thickness of 0.3 μm associated with increasing the size of inclusions at growth temperature annealing alloys. X-ray spectral analysis confirms the right segregation of phases on the surface of alloys.

In cold plastic deformation – created the fine structure of the alloy through which facilitated migration of intermetallic phases in the surface layer during subsequent annealing, and actually creates a gradient in the layer surface structure to a depth of 0.3 μm. Processing the alloys at these stages of thermomechanical processing. Parameters (the degree of deformation of up to 98%, annealing at 770…1070 K for 1…20 h) using the selected data set concentration increment depending on temperature ΔC/ΔT and time ΔC/Δt.

From the diagram in Fig. 2 shows that an increase in iron concentration in the composition of intermetallic phases increases with increasing temperature and annealing time (about 10 times at the annealing temperature 1070 K). Almost all iron atoms at a content of 1.03 at.% are part of Zr_3Fe intermetallic phase with a small addition of β-Zr_4Fe, as the corrected value solubility limit in zirconium iron less than 0.02 at.% at 970 K [6].

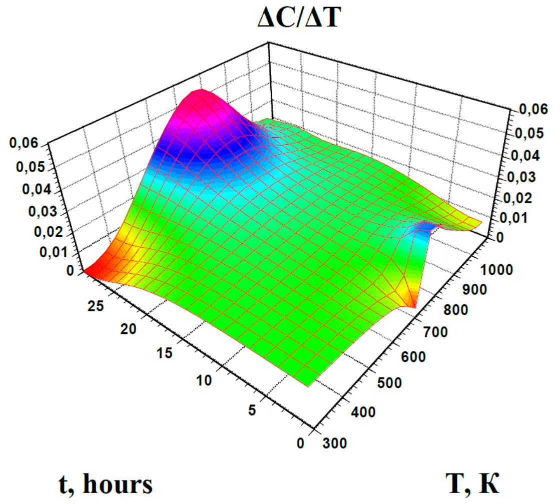

Fig. 3. Diagramma in coordinates ΔC/ΔT-T-t alloy Zr-1.03 at.% Fe

Almost all iron atoms at a content of 1.03 at.% are part of Zr_3Fe intermetallic phase with a small addition of β-Zr_4Fe, as the corrected value solubility limit in zirconium iron less than 0.02 at.% at 970 K [6].

For more information about the growth of the intermetallic concentration in the surface layer to a depth of 0.3 μm can be obtained from the analysis of the diagrams shown in Figs. 3 and 4. Fig. 3 shows the increase in iron concentration, i. e. content intermetallic phase with respect to temperature increase, depending on the temperature and time of annealing deformed alloys.

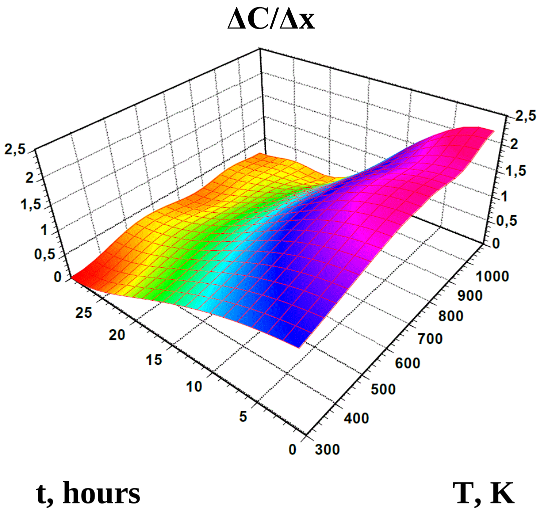

Fig. 4. Diagramma in coordinates ΔC/Δx-T-t alloy Zr-1.03 at.% Fe

We see the greatest value in the annealing temperature range 700…800 K concentration ratio of growth to the increase ΔC/ΔT reaches to the subsequent stabilization of the growth values. The data in Fig. 4 increase in concentration relative growth annealing time ΔC/Δt generally confirm these findings, emphasizing that the greatest increase in iron concentration and consequently intermetallic phases in the surface layer accounts for annealing times of up to 5 h, followed by concentration of growth stabilization until the annealing time of 30 h. Thus, in this case the surface layer gradient is generated most intensively in the annealing temperature range 700…800 K and the annealing time up to 5 h.

It should be emphasized that the driving force of the process of segregation of intermetallic inclusions in the surface layer is to return the stored plastic strain energy [7]. It was noted that the maximum allocation of the stored strain energy with increasing annealing temperature towards lower annealing times than in good agreement with the data shown in Fig. 4.

CONCLUSIONS

It is shown that zirconium-based alloys with dopants having limited solubility in zirconia, may form near the surface gradient structures. In the case of the alloy Zr-1.03 at.% Fe gradient barrier layer most intensively generated in the temperature range 700…800 K and the annealing time up to 5 hours.

REFERENCES

1. K.S. Na, J.H. Kim. Optimization of volume fractions for functionally graded panels considering stress and critical temperature // *Composite structures.* 2009, v. 89(4), p. 509-516.

2. Б.А. Калин, Н.В. Волков, В.Л. Якушин. Радиационно-пучковое воздействие – метод создания градиентного структурно-фазового состояния в материалах атомной техники // *Вопросы атомной науки и техники. Серия «Физика радиационных повреждений и радиационное материаловедение» (90).* 2007, №2, с. 164-171.

3. Н.И. Даниленко, Ю.Н. Подрезов, С.А. Фирстов, С.Е. Шейкин. Создание градиентной структуры при поверхностной интенсивной пластической деформации // *Технологические системы.* 2014, №1 (66), с. 31-38.

4. И.А. Курзина. *Градиентные поверхностные слои на основе наноразмерных металлических частиц: синтез, структура, свойства:* Автор. … докт. физ.-мат. наук. Барнаул, 2011, 42 с.

5. В.Г. Кириченко, Н.А. Азаренков. *Ядерно-физическое металловедение сплавов циркония.* Харьков: ХНУ им. В.Н. Каразина, 2012, 336 с.

6. V.P. Filippov, V.G. Kirichenko, V.A. Salomasov, A.M. Khazanov. Phase transformations in intermetallic phases in zirconium alloys // *HYPERFINE INTERACTIONS,* 2016. DOI: HYPE-D-16-00049R2.

7. Р. Хоникомб. *Пластическая деформация металлов.* М.: «Мир», 1972, 408 с.

Article received 30.12.2016

ОСОБЕННОСТИ ФОРМИРОВАНИЯ ПОВЕРХНОСТНЫХ ГРАДИЕНТНЫХ СЛОЕВ В ЦИРКОНИЕВЫХ СПЛАВАХ

В.Г. Кириченко, А.А. Ямпольский

Установлено, что увеличение поверхностной концентрации атомов железа в сплавах циркония в поверхностном слое толщиной до 0,3 мкм приводит к формированию градиентных структур. Этот процесс, в свою очередь, может способствовать оптимизации физико-механических характеристик сплавов в результате обогащенного интерметаллида поверхностного слоя.

ОСОБЛИВОСТІ ФОРМУВАННЯ ПОВЕРХНЕВИХ ГРАДІЄНТНИХ ШАРІВ У ЦИРКОНІЄВИХ СПЛАВАХ

В.Г. Кіріченко, О.О. Ямпольський

Виявлено, що збільшення поверхневої концентрації атомів заліза в сплавах цирконію в поверхневому шарі товщиною до 0,3 мкм призводить до формування градієнтних структур. Цей процес, в свою чергу, може сприяти оптимізації фізико-механічних характеристик сплавів за рахунок збагаченого інтерметаліда поверхневого шару.