Conference Paper

Growth and Segregation of Intermenallic Phases in Zirconium Alloys

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Abstract

Relations between the processes of growth of intermetallic inclusions and their surface segregation in binary and ternary alloys of zirconium are presented. An increased surface concentration of iron atoms was observed, and is associated with intermetallic inclusion growth with increased annealing temperature of the deformed alloys. Modelling the asymmetric growth of these intermetallic inclusions, leading to their migration, have enabled the determination of the diffusion coefficient of iron in these intermetallics.

Keywords: Zirconium alloys, Iron state, Mössbauer effect

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1. INTRODUCTION

Zirconium alloys and their formation processes have been widely investigated using various methods [1–8]. When developing heat-resistant zirconium alloys, it is necessary to take into account both microstructural heterogeneity and dispersion strengthening phases. The main problem of zirconium alloys are radiation growth and radiation creep, due to the anisotropy of α-zirconium. A related issue is the study of the processes of intermetallic phase formation in zirconium alloys of complex composition. Previously discovered surface segregation of intermetallic inclusions in alloys [9] elucidates the role of elemental segregation, its mechanisms, and methods of increasing the radiation and corrosion resistance of zirconium alloys under irradiation at the microscopic level. Therefore, studying radiation-induced changes of the microstructure of zirconium alloys and methods of modifying subsurface layers are critical for improving corrosion and radiation resistance, as well as predicting material property changes under irradiation and corrosion. The aim of this work is to research the combined processes of growth and surface segregation of intermetallic particles in binary and ternary zirconium-based alloys.

2. MATERIALS AND EXPERIMENTAL METHODS

The following alloys were investigated and prepared as described in reference [10]: Zr-1.03Fe; Zr-0.51Fe; Zr-0.51Fe-M (M = Nb, Sn, Ta, Cr), with all fractions given in atomic percent. Cold worked foils of each alloy were annealed in a vacuum furnace at a pressure of $1.3 \cdot 10^{-4}$ Pa at 770–1070K for one hour. Mössbauer spectroscopy of the ^{57}Fe nuclei was conducted in the backscattering geometry by the measurement of internal conversion electrons (CEMS). Surface X-ray spectral analysis was carried out using a Camebax MBX 268 spectrometer. X-ray diffraction was performed using a DRON-3.0 diffractometer with a Cu-K_{α} radiation source in transmission mode. An EM-200 electron microscope and JEOL JSM-840 scanning electron microscope were used to investigate the surface condition of each alloy.

3. RESULTS AND DISCUSSION

Mössbauer spectroscopy results of the as-deformed alloy Zr-1.03Fe are given in in Fig. 1, showing a dependence of the scattering effect relations (Fig. 1a) and quadrupole splitting (Fig. 1b) on the annealing temperature. The sharp increase of the effect of scattering ε_{T-} above an annealing temperature of 670K was observed with a corresponding increase in quadrupole splitting. The values of the isomer shift remained unchanged. This indicates a change in crystal symmetry, corresponding to the formation of Zr_3Fe by segregation in surface layers up to 3000Å deep.

Calculation of the segregation coefficient χ was performed according to the formula $\chi = (y/1 - y)/(x/1 - x)$, where x is volume concentration of the ^{57}Fe isotope and y is the surface concentration of ^{57}Fe impurities in the measured phase [11]. Calculation of the iron concentration was performed according to the formula: $C_{Fe} = C_{orig.} \cdot \chi$, where the value of the $C_{orig.}$ is the surface impurity concentration of ^{57}Fe in the intermetallic phases within 3000Å of the surface.

Fig. 2 illustrates the dependencies of the iron surface concentration and the size of the inclusions on the annealing temperature. Electron microscopy showed abnormal grain and sub-grain growth in the zirconium matrix above 720K. The average size of the included precipitates (inclusions) deformed alloys increased by 3-4 times from 100–200Å to 300-800 Å, and the average distance between inclusions increased 3–5 times from original values of 300–400 Å. The observed increases depend on the alloy composition. The increase of iron surface concentration in the form of intermetallic

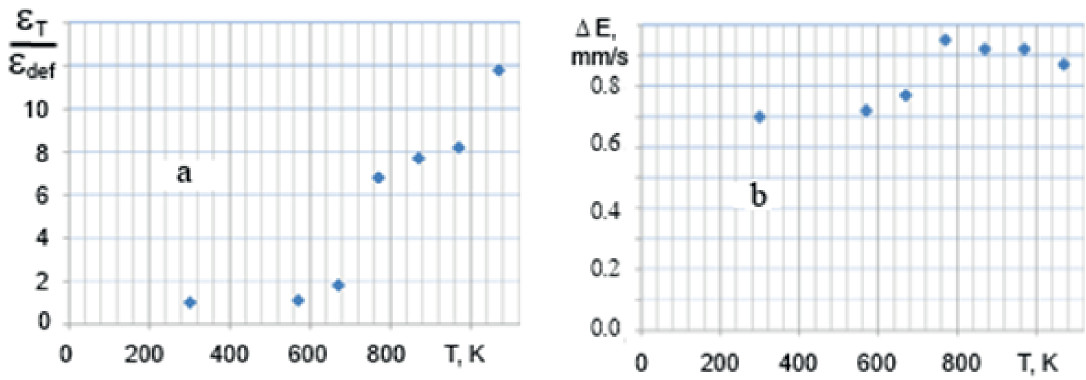

Figure 1: The dependence of the effect of scattering (a) and quadrupole splitting ΔE_Q (b) on the annealing temperature of Zr-1.03Fe. ϵ_T- represents the scattering effect of the annealed specimen, ϵ_{def}- represents the scattering effect of the deformed specimen, and ΔE-represents measured quadrupole splitting.

particles correlates with the increasing inclusion size and increased annealing temperature. It is seen that a significant increase in the degree of enrichment takes place starting from annealing temperatures of 900K, while inclusion size increases starting from 45 nm.

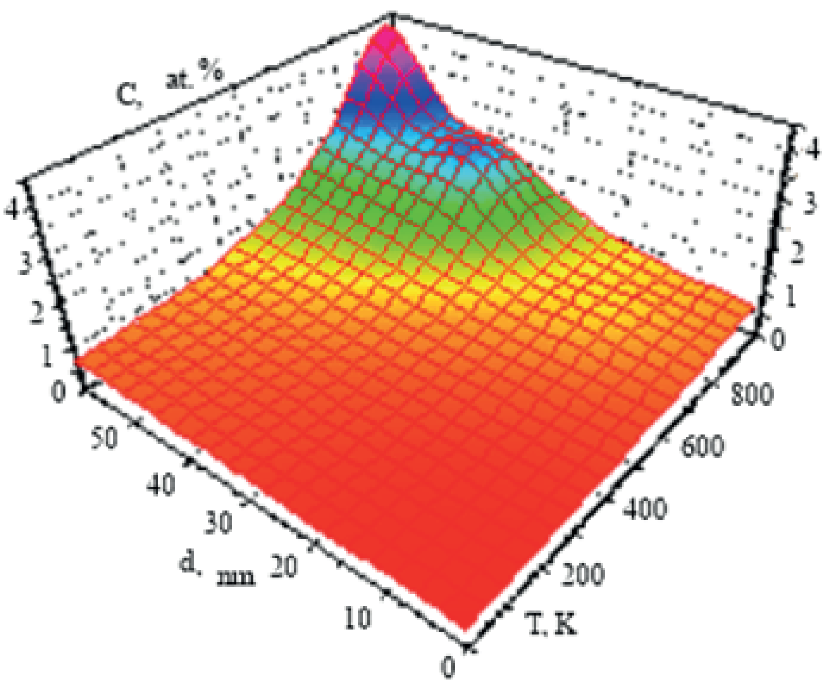

Figure 2: Dependence of iron surface concentration on the size of the inclusions and the annealing temperature of the alloy Zr-Fe-Nb in the extended temperature range of annealing.

The process of segregation of iron-containing intermetallic inclusions in the surface layer is illustrated by the data in Fig. 3. These data were obtained by electron probe analysis from the center of the inclusion. According to Fig 3 the concentration of Zr decreases, and the concentration of Fe increases as a function of depth. The main idea in the combined process of growth and segregation is that the growth of inclusions of intermetallic phases is accompanied by the migration of inclusions as a whole.

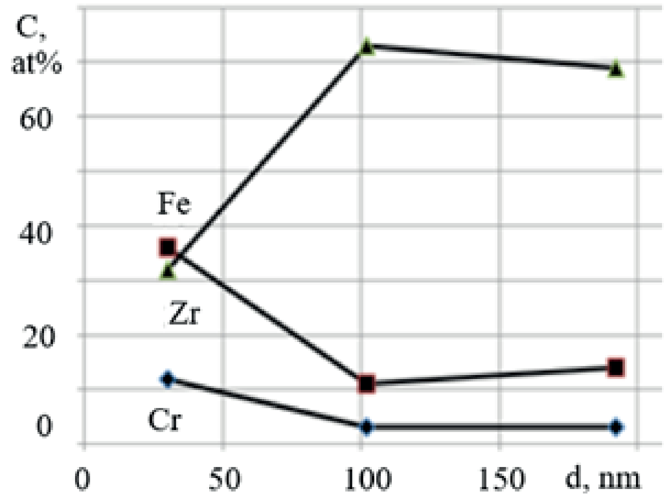

Figure 3: Selective depth data analysis the probe beam for different areas of the sample surface.

A model of joint processes of diffusion, growth, and migration of intermetallic compounds, leading to the segregation of intermetallic phases, was proposed in reference [11]. With the growth of inclusions of intermetallic phases in the Zr-Zr_3Fe system, where the components of Zr and Fe are almost mutually insoluble, the atoms of the components within the inclusion of intermetallic phases diffuse via high-mobiligy sub-lattice positions, determined by the diffusion coefficients $D_{Zr}{}^{i}$ and $D_{Fe}{}^{i}$. When Zr_3Fe intermetallic phases exist, there exist directed streams of Zr and Fe atoms through these sub-lattice positions. The main finding in the combined process of growth and segregation is that the growth of inclusions of intermetallic phases is accompanied by the inclusion of migration as a whole. This means that the growth of a separate inclusion of an intermetallic phase occurs asymmetrically. Therefore, the number of atomic planes of Zr and Fe varies during intermetallic inclusion growth. As mentioned above, the dislocation density is greatest in thin surface layer - this is the cause of the movement of the intermetallic particles to the surface with the simultaneous growth of intermetallic inclusions.

Assuming that the diffusion coefficient in the volume of intermetallic particles is independent of concentration, the speed of displacement of the boundary matrix-inclusion Zr-Zr_xFe_y can be written as follows: $V_{Fe} = -I_{Fe}W_{Fe} = D_{Fe}\frac{\partial C_{Fe}}{\partial x}$ [12]. The movement of the intermetallic particles can occur at a speed greater than the speed of the border. To determine $D_A{}^{i}$ and $D_B{}^{i}$, one must use the desired values of$\partial C_A^i/\partial x$ and $\partial C_B^i/\partial x$.

The data in Fig. 3 can be used to estimate these parameters and to determine the diffusion coefficient of iron in migrating and growing intermetallic particles. In Fig. 3 it is shown that the iron concentration increases when the concentration of zirconium decreases. This is due to the partial substitution of the surface layer of the zirconium matrix by inclusions.

As a result of simple calculations one arrives at the value of the diffusion coefficient of iron atoms in intermetallic inclusions as $D_{Fe} = 3.5 \cdot 10^{-3}$ cm^2/s, noticeably lower than the diffusion coefficient of Fe atoms in the alpha- zirconium of $2.5 \cdot 10^{-2}$ cm^2/s [12]. Taking into account the structure of the Zr_3Fe phases and Zr_2Fe, we can assume that the diffusion of iron atoms occurs in the [100] and [001] directions, respectively. Perhaps the inclusion of intermetallic phases are oriented in these directions, and the process of segregation of intermetallic inclusions in subsurface layers during the annealing of deformed alloys is reversible.

4. CONCLUSIONS

It is found that the increase in the surface atomic concentration of iron is associated with increase in the size of intermetallic inclusions with increasing annealing temperature in zirconium alloys. Increased enrichment begins at annealing temperatures of 900K and inclusions at least 45 nm in size. In the framework of a simple model of asymmetric growth of intermetallic inclusions, leading to their migration and interaction with grain boundaries, the diffusion coefficient of iron atoms in intermetallic inclusion has been determined to be $D_{Fe} = 3.5 \cdot 10^{-3}$ cm^2/s.

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