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Phase transformations in intermetallic phases in zirconium alloys

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Abstract Phase change was analyzed in intermetallic compounds of zirconium alloys (Zr – 1.03 at.% Fe; Zr – 0.51 at.% Fe; Zr – 0.51 at.% Fe – M (M = Nb, Sn). Mössbauer spectroscopy on ^{57}Fe nuclei in backscattering geometry with the registration of the internal conversion electrons and XRD were used. Four types of iron bearing intermetallic compounds with Nb were detected. A relationship was found between the growth process of intermetallic inclusions and segregation of these phases. The growth kinetics of inclusions possibly is not controlled by bulk diffusion, and a lower value of the iron atom's activation energy of migration can be attributed to the existence of enhanced diffusion paths and interface boundaries.

Keywords Zirconium · Alloys · Phases · Growth · Segregation

1 Introduction

Functional properties and surface characteristics of zirconium alloys in areas of stress concentration are significantly impacted by phase transformation and segregation processes,

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which take place when alloy component concentration distribution deviates from equilibrium. The main goal is to study the structural phase composition, microstructure evolution mechanisms and redistribution of alloying elements under thermal activation and radiation induced phase transformations. Therefore, as a whole the radiation and corrosion resistance of the Zr alloys is determined not only by the phase composition, intermetallic compound distribution dispersity and uniformity on the surface of the particle but also by the microstructure of the metal matrix. The reverse processes and recrystallization of complex doped alloys based on zirconium are studied insufficiently yet. So it is important to determine the recrystallization temperature and temperature interval of relative stability of the iron-doped alloys with deformed structure based on α-Zr. The goal of this work is investigation of phase transformation effects in intermetallic phases of zirconium alloys Zr – Fe – M (M = Nb, Sn).

2 Experimental

Alloys of the following composition were studied: Zr – 1.03 at.% Fe; Zr – 0.51 at.% Fe ; Zr – 0.51 at.% Fe – M where M = Nb, Sn. Methods of their preparation were described in [1, 2]. Mössbauer Spectroscopy was used with registration of internal conversion electrons (CEMS). X-ray spectral analysis of the surface of annealed zirconium alloy samples was performed with the help of "Camebax MBX" spectrometer. X-ray diffraction study of the alloys was performed using the DRON-3.0 diffractometer Cu-Kα radiation. XRD analysis showed that at all stages of thermo mechanical treatment (TMT) zirconium alloys are composed of only the alpha-Zr phase.

Surface analysis of samples was performed using scanning electron microscopes JEOL JSM-840 and "Quanta 3D".

3 Results and discussion

Mössbauer spectra of binary alloys have a shape of quadrupole pair of lines [1, 2]. The parameters of spectra are given in Table 1. The values of isomer shifts (IS) and quadrupole splitting (QS) of investigated binary alloys match results reported in [1, 3, 4], which indicates that there are no peculiarities in formation of intermetallic compounds. Analysis of data in Table 1 for ternary alloy Zr-Fe-Sn confirms the existence of intermetallic compound Zr_2Fe with QS=0.56 mm/s (matches known data). This proves absence of Sn influence on iron state in intermetallic precipitates. Influence of another elements such as Nb is shown using an example of alloys Zr-0.51at.%Fe-Nb(0.5 ;1.0; 2.5 %) (Table 1). CEMS spectra of the alloy Zr-0.51 at. %Fe-0.5 at. %Nb after annealing at T=770 K (1) and T=970 K (2) are shown in Figs. 1 and 2. Spectra were obtained at room temperature. Spectra can be interpreted as a superposition of quadrupole doublets corresponding to paramagnetic phases. In the ternary alloys Zr-0.51 at.% Fe – M with M=Nb, Sn, and quaternary alloy with addition of Nb, Sn, the iron CEMS spectra were fitted as superposition of four doublets. The results of fitting are given in Table 1. Doublets with a larger value of quadrupole splitting were related to the phases $(Zr_{1-x}, Nb_x)_2Fe$ (phase 1), while doublets with smaller values were attributed to the phase $(Zr_{1-x}, Nb_x)Fe_2$ (phase 2).

The comparison of spectral parameters of ternary and quaternary alloys in group 2 (Table 1) allows to conclude that adding of Sn in Nb containing alloy doesn't influence on iron state in the intermetallic compounds formed in this alloy. The following are the

Table 1 Mössbauer parameters of the main phases in the systems Zr-Fe, Zr-Fe-Nb and Zr-Fe-Sn-Nb (annealing temperature T=770 K)

The group of alloys	Alloy	Phase	IS, mm/s	QS, mm/s
Group 1				
Binary alloy zirconium-iron	Zr-0.51 at.% Fe			
	Zr-1.03at.% Fe	Zr_3Fe	- 0.33(1)	0.97(1)
		Zr_2Fe(type uAl_2)	- 0.31(1)	0.56(1)
Ternary alloy	Zr-Fe-Sn	Zr_3Fe	-0.35(1)	0.85(1)
		Zr_2Fe(type uAl_2)	-0.15(1)	0.56(1)
Group2				
Ternary alloy Zr-Fe-4d M	Zr-0.51at.%Fe-Nb(0.5;1.0;2.5 %) Zr-Fe-Nb	$(Zr_{1-x}, Nb_x)_2Fe$	-0.30(1)	0.61(1)
		$(Zr_{1-x}, Nb_x)Fe_2$	-0.19(1)	-0.27(1)
		$(Zr_{1-x}, Nb_x)_2Fe$	0.27(1)	0.55(1)
		$(Zr_{1-x}, Nb_x)Fe_2$	-0.16(1)	0.28(1)
Quaternary alloy	Zr-0.51at.%Fe-Nb(0.5;1.0;2.5 %) Zr-Fe-Nb	$(Zr_{1-x}, Nb_x)_2Fe$	-0.30(1)	0.61(1)
		$(Zr_{1-x}, Nb_x)Fe_2$	-0.19(1)	-0.27(1)
		$(Zr_{1-x}, Nb_x)_2Fe$	0.27(1)	0.55(1)
		$(Zr_{1-x}, Nb_x)Fe_2$	-0.16(1)	0.28(1)

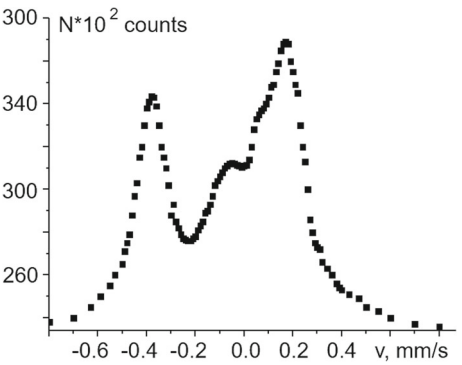

Fig. 1 CEMS spectra of Zr-0.51 at. % Fe -0.5 at. % Nb after annealing at T=770 K

results of the study of phase transformation processes, segregation of intermetallic phase inclusions, and growth of inclusions.

During the phase transformation 1→2 the iron containing intermetallic inclusions begin to develop rapidly at temperatures T>670K in Zr- Fe alloy doped by Nb. Xray spectral data show increase of the amount of iron in the surface layer (Fig. 3). Intermetallic particles up to 10 μm are visible on the surface (Fig. 3). They did not exist before annealing, which allows to conclude that iron concentration on the surface of the alloy increases during annealing process. This phenomenon was also reported in [2]. Iron concentration in the particle is inhomogeneous as shown by the chart in white on top of the micrograph.

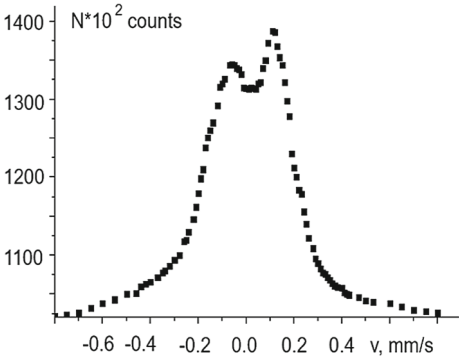

Fig. 2 CEMS spectra of Zr-0.51 at. % Fe-0.5 at. % Nb after annealing at T=970 K

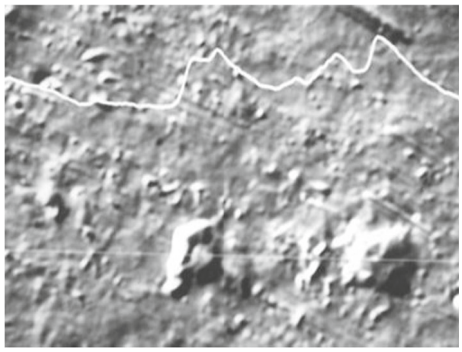

Fig. 3 Micrograph of the surface sample of alloy zirconium - iron after annealing in vacuum at T=870 K for 5 hours. Iron distribution along the scanning line is shown in white 800^{x}

The change in the Mössbauer spectral parameters is attributed to the influence of the third element in the local environment of iron atoms in ternary and quaternary zirconium alloys and correlates with specifics of crystallization process (Table 1).

In the ternary alloys with Nb and quaternary alloy with addition of Nb, Sn, iron doublets with a larger value of quadrupole splitting were related to the phases $(Zr_{1-x}, M_x)_2Fe$ (phase 1), while doublets with smaller values of the quadrupole splitting were attributed to the $(Zr_{1-x}, M_x)Fe_2$ phase. The drop of intensity of the doublet 1 and simultaneous increase of intensity of the doublet 2 evidently indicates a phase transformation $1 \rightarrow 2$, which takes place during annealing (Figs. 1 and 2).

The Mössbauer parameters of the four doublets belonging to the ternary and quaternary alloys are exactly the same. This also proves absence of Sn influence on iron state in intermetallic precipitates.

The phase Zr_2Fe is formed in alloys Zr-Fe-Nb containing up to 15 wt% of (Nb+Fe) in the temperature interval 873-1373K [5]. In our case, the alloy phases $(Zr_{1-x}, Nb_x)_2Fe$ (phase 1) and $(Zr_{1-x}, Nb_x)Fe_2$ (phase 2) are present as inclusions in the α-region. Zr lattice parameter ratio c/a dependence on annealing temperature is shown in Fig. 4. The increase in c/a with increasing of annealing temperature and transition of iron atoms from phase $(Zr_{1-X}, Nb_X)_2Fe$ to $(Zr_{1-X}, Nb_X)Fe_2$ during the crystal growth might be related to the preferred orientation of the growing phase along c axis.

The elastic energy increases as $(V)^2$ following the particle size growth. However, in this process the discharge area and hence the surface energy are reduced [6]. Therefore, one

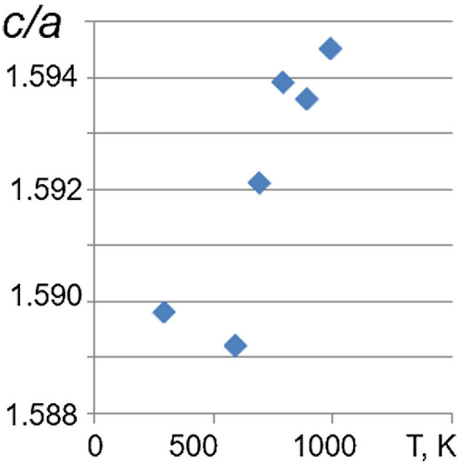

Fig. 4 The dependence of c/a on annealing temperature of the alloy Zr-Fe-Nb

should consider some factors such as specific volume (plays an active role), diffusion mobility of phase boundaries. In addition, one should consider the availability of substructure modification [6], accelerating the growth process. The conditions of stability of a disperse system are lower values of interphase boundary energy, precipitates solubility. A stable distribution of nucleation and sustainable particle growth can take place in alloys with noticeable elastic mismatch of the lattices, although the reasons for this are not yet clear [4, 6].

The mechanisms of particle growth through phase transformation and recrystallization are interrelated. The Iron atoms do not penetrate the Zirconia matrix, because their solubility at 600 °C does not exceed 0.02 %. In our case we have two types of phases, so iron atoms move from one phase to another on short routes of diffusion.

This is confirmed by the measurement of the effective activation energy of migration of iron atoms from phase 1 into phase 2. Experimental data were processed using Austin-Rickets equation [2] $^{E}/_{(1-\gamma)} = (At)^n$, where γ –the proportion of the total number of Iron atoms located in the phase 1; A–temperature-dependent constant; t– the time of annealing. The value of n was equal to 0.3 at T=770 K and 0.44 at T=970 K, which is close to the theoretical value of n=1/3 predicted for diffusional growth of particles [2]. In this paper the fraction of the total number of iron atoms located in the phase (γ) was estimated using the area of spectral lines measured at different temperatures. Activation energy was determined using the value of constant A.

According to X-ray spectral data the amount of iron in the surface layer increases in the same temperature interval in which recrystallization of zirconium matrix and phase transformation 1→2 takes place (Fig. 3). This means that particle growth is not limited by the mobility of interphase boundaries. So the initial growth of precipitates from supersaturated solid solution must also take place by diffusion mechanism and should not depend on the mobility of the boundaries.

In our case this condition is not satisfied. The average value of activation energy for all alloys is obtained from the slope of the Arrhenius plot assuming exponential dependence A∼ exp(-E/kT) (E= (1.5±0.2) eV). Notably it is less than the activation energy of 2.06 eV for impurity diffusion of Fe in alpha-Zr via interstitial mechanism [2]. A lower value of the activation energy E in the present case may be explained by the presence of interstitial paths of accelerated diffusion due to intergranular and interface boundaries.

4 Conclusions

1. The phase transformation was investigated in binary, ternary and quaternary iron bearing alloys based on zirconium during the annealing process.
2. It is shown that in the binary alloys with iron the intermetallic Zr_3Fe particles are formed, tin addition does not affect the state of iron in the intermetallic particles.
3. Adding of niobium results in formation of intermetallic compounds like $(Zr_{1-x}, Nb_x)_2Fe$ and $(Zr_{1-x}, Nb_x)Fe_2$, whose Mössbauer spectra parameters indicate the formation of four types of intermetallic compounds - two with large QS (0.55 and 0.61 mm/s) and two with small QS(0.27(1) mm/s).
3. It was found that:
   transformation of $((Zr_{1-x}, Nb_x)_2Fe$ phase (large quadrupole splitting) into (Zr_{1-x}, Nb_x) Fe_2 phase (small quadrupole splitting) takes place during annealing.
4. The activation energy of migration of Iron atoms in the process of particle growth is determined to be 1.5 eV.
5. It has been shown that the kinetics of particle growth is associated with migration between the grain and interphase boundaries in the matrix of zirconium alloys during annealing.

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