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Interdiffusion in the U–Zr system at δ-phase compositions

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Abstract

Interdiffusion measurements in the δ-UZr_2 phase of the U–Zr binary system were conducted in the temperature range 773–873 K and at composition intervals of ~7 at% by means of an electron-probe micro-analyzer (EPMA), and compared with those for (γU,βZr) solid solutions obtained at higher temperatures of 923–1023 K. The interdiffusion coefficients of the δ-UZr_2 phase, which were determined by the Boltzmann–Matano method from concentration gradients, were found to be smaller than those extrapolated from the (γU,βZr) solid solutions. © 1998 Elsevier Science S.A.

Keywords: Delta phase; EPMA; Interdiffusion; Omega structure; Uranium alloy

1. Introduction

The structure and phase stability of δ-UZr_2 in the U–Zr binary system [1] are of theoretical interest, since δ-UZr_2 possesses a modified C32 AlB_2-type crystal structure like the so-called ω-phase, which is a metastable phase of Zr-based alloys [2]. The ω-phase is one of the most extensively studied metastable phases, since its existence in the alloys has various implications for their physical properties. The lattice stability and crystal structure of δ-UZr_2 have been studied by X-ray, neutron diffraction and thermal analysis [3,4].

There has been renewed interest in zirconium-based actinide alloys such as U–Zr and U–Pu–Zr as nuclear fuels for fast reactors. Thus, diffusion data and the thermodynamic properties of the alloys are very important for understanding the phenomena occurring under irradiation. The interdiffusion behavior in homogeneous cubic (γU,βZr) phases of U–Zr alloys was investigated systematically by Adda et al. [5,6] and Ogata et al. [7]. Two clearly expressed minima of the interdiffusion coefficients were observed at compositions of N_{Zr}~0.7 above 1223 K and N_{Zr}~0.3 and ~0.7 below 1223K, respectively. The compositions of the minima correspond to those of the δ-phase and the immiscibility gap designated $\gamma_1+\gamma_2$ at lower temperatures in the U–Zr system. Ogata et al. [7] demonstrated that the interdiffusion coefficients of (γU,βZr) solid solutions in the U–Zr system are closely related to the thermodynamic properties. However, no diffusion data for the δ-phase are available, since the diffusivity is very small and the phase stability is significantly affected by impurities such as oxygen and nitrogen.

In this study, the interdiffusion coefficients of the δ-phase in the U–Zr system were measured by an X-ray microspectral analysis using an electron-probe micro-analyzer and compared with those for (γU,βZr) solid solutions.

2. Experimental

2.1. Samples and measurements

U–Zr alloys with compositions 68, 75 and 78 at% Zr, which are within the homogeneity range of the δ-phase at 773–873 K [3], were prepared by arc-melting mixtures of pure uranium and zirconium metals in an argon atmosphere. The arc-melting was repeated several times to ensure complete homogeneity of the alloy buttons. The arc-melted buttons were wrapped in tantalum foil, sealed in evacuated and He-filled quartz ampoules and annealed for 72 h at 1123 K. The annealed alloy buttons were then cut into rectangular pieces of size ~4 mm×~4 mm×~2 mm and their surfaces polished with diamond paste.

A semi-infinite-type diffusion couple was set in a special stainless steel holder and pressed by screws. Details of the holder structure are described elsewhere [7]. Compatibility between the diffusion couple and the holder during anneal-

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ing was ensured with tantalum or tungsten foils, where a Kirkendall marker was not used. The holder containing the diffusion couple was sealed in an evacuated and He-filled quartz ampoule and diffusion-annealed at temperatures controlled within ±1 K in the range 773–1073 K for 249–7480 days. The conditions for the diffusion anneal are summarized in Table 1. After diffusion annealing the quartz ampoule was quenched in water. The diffusion couple was cut parallel to the diffusion direction and polished with diamond paste.

Contamination of the U–Zr alloys by oxygen and nitrogen during annealing was examined using a hot extraction method, where oxygen and nitrogen contents were analyzed simultaneously by IR and thermal conductivity cells, respectively. The oxygen contents of the U–Zr alloys of 68–78 at% Zr were ~62 and ~113 ppm by weight before and after diffusion annealing, respectively, and the nitrogen contents were ~12 and ~32 ppm by weight, respectively, indicating slight contamination by oxygen and nitrogen during the heat treatments.

The elemental distribution across the diffusion zone parallel to the diffusion direction was measured using an electron-probe micro-analyzer (Shimazu Co., EPM-810Q) in the wavelength dispersive mode. The probe was operated at 25 kV accelerating voltage and 5 nA absorbed beam current. The intensity profiles for the characteristic X-rays of U Mα and Zr Lα were obtained by scanning the diffusion couple with steps of 1 μm for analyzing the δ-phase below 873 K and 3–5 μm for the (γU,βZr) phase above 873 K at several locations. The calibration curve method was used to convert the X-ray intensities into U and Zr concentrations. The calibration curves for uranium and zirconium were prepared using several standard U–Zr alloys. The sensitivity in the concentrations of uranium and zirconium was about 10^{-3} wt%.

The concentration–penetration profiles were analyzed using the Boltzmann–Matano method [8] to obtain the diffusion coefficients. The interdiffusion coefficient $\tilde{D}(C)$ is obtained from

$$\tilde{D}(C^*) = -\frac{1}{2t}\int_{C_0}^{C^*} x\,\mathrm{d}C \Bigg/ \left(\frac{\mathrm{d}C}{\mathrm{d}x}\right)_{C=C^*} \tag{1}$$

where $\tilde{D}(C^*)$ is the interdiffusion coefficient at composition C^*, t is the time of diffusion anneal (s), and C_0 and C_1 are the concentrations at the two ends of the diffusion zone. The origin of the abscissa x, which is denoted as the Matano interface, is defined by the condition

$$\int_{C_0}^{C_1} x\,\mathrm{d}C = 0 \tag{2}$$

The integration in Eqs. (1) and (2) was performed numerically using the trapezoidal method [7].

3. Results and discussion

The back-scattered electron image of the diffusion zone of the diffusion couple between U–68 at% Zr and U–75 at% Zr alloys, which were diffusion-annealed for 7480 h at 823 K, is shown in Fig. 1a. Both the initial and shifted interfaces are not visible, because of the very close composition interval of 7 at% Zr and the absence of a kirkendall marker. In the Zr-rich phase of the U–75 at% Zr alloy, a few fine inclusions were observed. From the EPMA analysis, they were estimated to be a zirconium-rich phase, probably a Zr–O phase, or oxygen-stabilized α-Zr. It is well known that the α-Zr phase is stabilized significantly by oxygen, which is soluble up to about 25 at% corresponding to Zr_3O. As shown in Table 1, the diffusion anneals in the δ-phase were performed at five temperatures between 773 and 873 K, but, unfortunately, only the data at 823 and 853 K were effective for measuring the concentration–penetration profiles. In the case of the diffusion couples annealed at 773 and 793 K, as shown in Fig. 1b, a two-phase precipitate, which was estimated to be composed of metallic U (white phase) and Zr (gray phase), was observed along the initial interface of the diffusion couple and grain boundaries, and the widths of the diffusion zones across the precipitates were about 10 μm, insufficient to obtain accurate profiles, because of the finite sizes of the electron beam and the excited volume. On the other hand, at 873 K, the U-rich alloy

Table 1
Conditions for the diffusion annealings

Diffusion couple	Phase[a]	Annealing temperature (K)	Annealing time (h)
U–68Zr/U–78Zr	(γU,βZr)	1023	249
U–68Zr/U–78Zr	(γU,βZr)	973	1040
U–68Zr/U–75Zr	(γU,βZr)	923	1191
U–67Zr/U–75Zr	δ	873	2400 (1800)
U–67Zr/U–75Zr	δ	853	2090
U–68Zr/U–75Zr	δ	823	7480
U–68Zr/U–75Zr	δ	793	2400
U–68Zr/U–75Zr	δ	773	2400

[a] Expected phase from the U–Zr phase diagram [1].

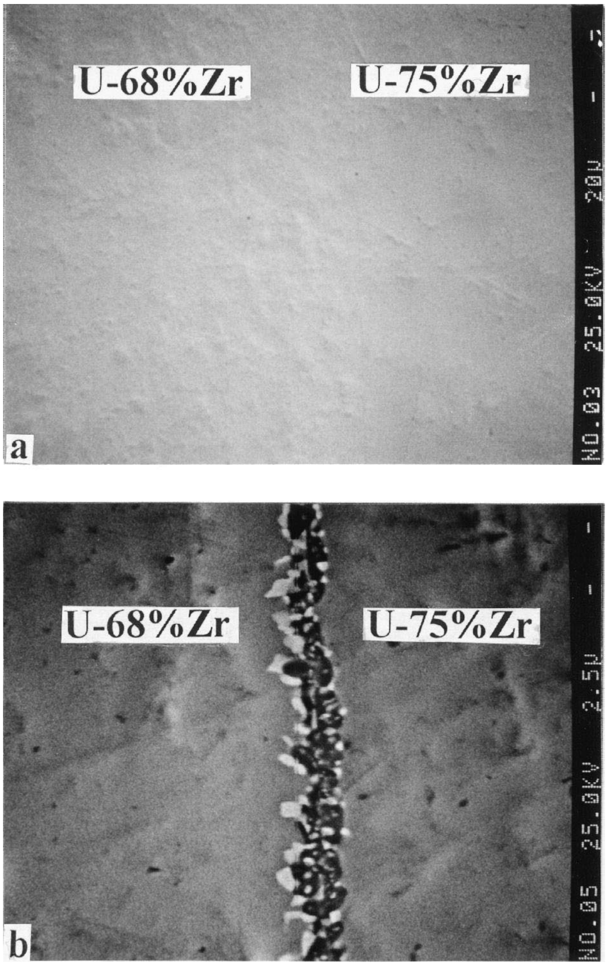

Fig. 1. Back-scattered electron images of the diffusion zone in the U–68Zr/U–75Zr couple (a) annealed at 823 K, and (b) annealed at 793 K, showing a two-phase precipitate at the interface.

(68 at% Zr) in the diffusion couple changed to two phases after annealing, probably due to the phase relation around this region in the U–Zr system [1,3]. This phenomenon may be influenced by impurities or the high pressure applied during preparation of the diffusion couple. For the diffusion couple between pure U and Zr annealed at 873 K [9], the phase produced near the interface was not the δ-UZr_2 phase, but ω-Zr containing a few percent of U.

Fig. 2 shows the concentration–penetration profiles over the entire diffusion zone of the same diffusion couple as Fig. 1a. The width of the diffusion zone is easily found to be about 70 µm across the Matano interface. For the annealings of the bcc (γU,βZr) solid solutions, the widths attained 400–500 µm, as shown in Fig. 3. The interdiffusion coefficients $\tilde{D}$ were evaluated from the concentration–penetration profiles for various temperatures using the Boltzmann–Matano method. Fig. 4 shows the dependence of $\tilde{D}$ on alloy composition and temperature. No strong composition dependence of $\tilde{D}$ in (γU,βZr) solutions above 923 K and in the δ-phase below 853 K were observed in the range 68–75 at% Zr. However, $\tilde{D}$ in the δ-phase tends to increase slightly with increasing Zr concentration. It was also found that $\tilde{D}$ decreases significantly from the (γU,βZr) solid solution to the δ-phase.

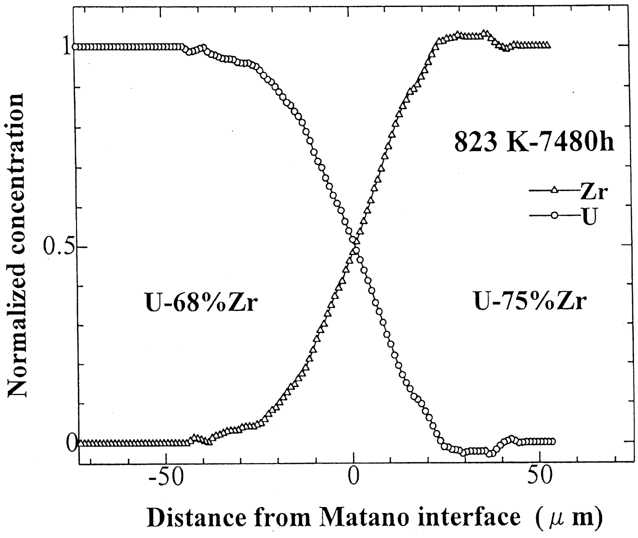

Fig. 2. Concentration–penetration profiles for the U–68Zr/U–75Zr couple annealed at 823 K.

The temperature dependence of the average interdiffusion coefficients in the composition range 71–73 at% Zr is shown in Fig. 5 and Table 2, which includes $\tilde{D}$ in (γU,βZr) above 973 K obtained by Ogata et al. [7]. The temperature dependence of the present $\tilde{D}$ is in good agreement with that of the previously reported $\tilde{D}$, and the Arrhenius relationship thus established from these plots can be represented by the following expression:

$$\tilde{D}\ (\mathrm{m^2\ s^{-1}}) = 7.56\times10^{-9}\exp(-129.0/RT) \qquad (3)$$

where R is expressed in kJ $\mathrm{mol^{-1}}$. The frequency factor

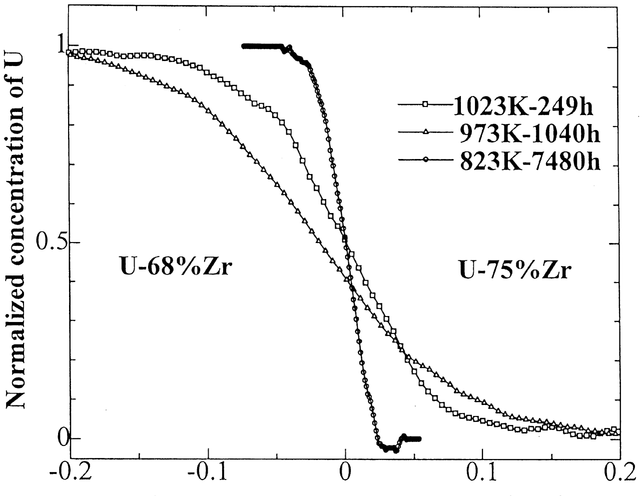

Fig. 3. Concentration–penetration profiles for the U–68Zr/U–75Zr couples annealed at 823, 973 and 1023 K.

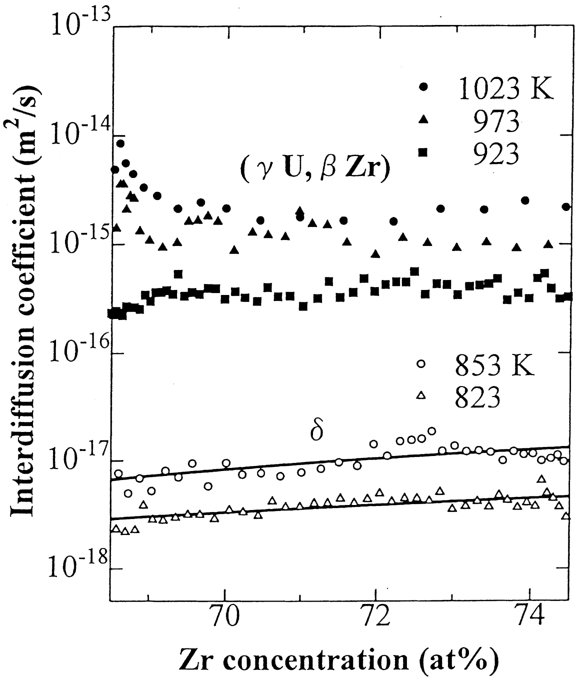

Fig. 4. Composition dependence of the interdiffusion coefficients for U–Zr alloys in the δ-phase and (γU,βZr) solid solutions.

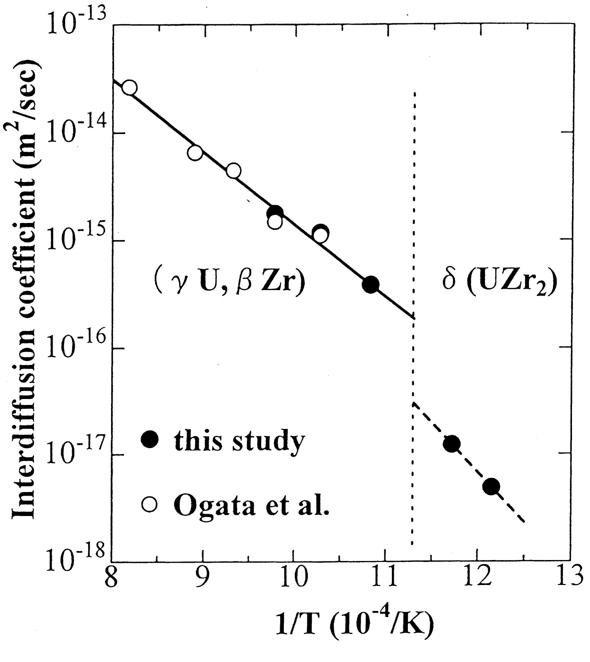

Fig. 5. Arrhenius plot of the interdiffusion coefficients.

and the activation energy are also in good agreement with those reported at 70 at% Zr by Adda et al. [5], $5.5\times 10^{-9}\ m^2\,s^{-1}$ and $124\ kJ\,mol^{-1}$.

The interdiffusion coefficients for the δ-phase were found to be significantly smaller than those extrapolated from the (γU,βZr) solid solutions to the δ-phase. The $\tilde{D}$ values for the δ-phase were very similar to the self-diffusion coefficients for α-U [10], which was expressed by $2\times 10^{-7}\exp(-167/RT)\ m^2\,s^{-1}$. Adda et al. [5] reported the diffusion reaction for a U and Zr couple at temperatures of 823 and 873 K and the formation of the reaction zones was very slow compared with that above 923 K. From their photographs of the reaction zones, the rate constant ($k=x/t^{1/2}$) for the growth of the phase formed at the interface was determined to be ~0.34 and ~1.35 $\mu m\,h^{-1/2}$ for 823 and 873 K, respectively. Mash et al. [11] also reported a similar study in the temperature range 573–1323 K with a significant decrease in the penetration rate of U into Zr below 873 K. The rate constants ranged from 0.17 to 0.67 $\mu m\,h^{-1/2}$ at temperatures of 573–873 K. The phase formed at the interface of the U/Zr couples at these temperatures can be expected to be the δ-phase for the U–Zr system [1,3], and the growth rate or the penetration rate is proportional to $\tilde{D}^{1/2}$. The apparent interdiffusion coefficients can be calculated from the relation $x=\sqrt{2\tilde{D}t}$. Thus the apparent $\tilde{D}$ values were estimated to be ~1.6×10^{-17} and ~$2.5\times 10^{-16}\ m^2\,s^{-1}$ for 823 and 873 K, respectively [5], and 4×10^{-18}–$6.2\times 10^{-17}\ m^2\,s^{-1}$ for 573–873 K [11]. The $\tilde{D}$ values of the δ-phase are significantly larger than those found in this work, as shown in Fig. 5.

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Table 2
Average interdiffusion coefficients at the δ composition in U–Zr alloys

Temperature (K)	Phase	This study ($m^2\,s^{-1}$, $\times 10^{17}$)	Ogata et al. ($m^2\,s^{-1}$, $\times 10^{17}$)
823	δ	0.49±0.10	
853	δ	1.22±0.29	
923	(γU,βZr)	38.3±7.2	
973	(γU,βZr)	117±28	110
1023	(γU,βZr)	177±22	148

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