Journal of Alloys and Compounds, 213/214 (1994) 366–368
JALCOM 4088

Reactions between U–Zr alloys and nitrogen

Mitsuo Akabori, Akinori Itoh, Toru Ogawa and Mitsuhiro Ugajin
Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken 319-11 (Japan)

Abstract

The reactions of U–Zr alloys with nitrogen were studied at temperatures ranging from 873 to 1273 K. Electron probe microanalysis, wide angle and microbeam X-ray diffraction techniques were applied for the identification of reaction products. Adherent multi-layered scales were formed during the anneals under nitrogen pressures of 0.19 and 20 kPa. They were mainly composed of U_2N_3, ZrN and α-Zr(N). The scale thickness and morphology depended on the alloy compositions and temperatures.

1. Introduction

The U–Zr binary alloy is an important subsystem of the promising U–Pu–Zr alloy nuclear fuels. The phase behaviour and migration of the component elements in the alloy are of particular importance, since they affect the fuel performance in terms of component redistribution, fuel melting, fuel–cladding compatibility and so on. The phase behaviour will be significantly influenced by impurities and these effects have been discussed in a review of the U–Zr system [1]. In particular, the δ phase region of the U–Zr alloy is significantly narrowed by impurity oxygen [2]. Recently, the formation of a Zr-rich thin layer at the interface between U–Pu–Zr fuels and HT-9 cladding has been observed [3]. The Zr-rich layer contained nitrogen up to the solubility limit (about 25 wt.%) in the α-Zr phase. This formation is considered to be due to impurity nitrogen in the alloy fuels. The purpose of the present study is to obtain a basic understanding of the reaction of U–Zr alloys with impurity nitrogen and the behaviour of the U–Zr–N system.

2. Experimental details

U–18,50,67at.%Zr alloys were prepared by arc melting together pure uranium and zirconium metals. Details of the preparation method have been described elsewhere [4]. After homogenization at 1123 K for 72 h the alloys were cut into cuboids of size (1–2) mm × (1–3) mm × 1 mm, then all surfaces of the specimens were metallographically polished with diamond pastes. Two nitrogen pressures of about 20 and 0.19 kPa were selected for the nitriding reaction. In 0.19 kPa nitrogen, for example, U_2N_3 should decompose at temperatures above about 1173 K to form UN. In 20 kPa nitrogen U_2N_3 becomes stable at all reaction temperatures. The alloy specimens were sealed in quartz ampoules which had been evacuated and then filled with high purity nitrogen gas. In the case of low nitrogen pressure (0.19 kPa) a quartz ampoule joined with an approximately 1 l Pyrex flask was used in order to minimize the nitrogen pressure decrease during the reaction. Reaction experiments were performed at temperatures of 873–1273 K for 15–1000 h. After annealing, the alloys were examined by electron probe microanalysis (EPMA) and microbeam (about 100 μm diameter) X-ray diffraction techniques. The alloys were analysed by point-to-point counting techniques for concentration profile and phase identification, where the acceleration voltages were 15 and 25 kV for nitrogen and alloy elements respectively and the beam size was about 1 μm diameter. The X-ray intensities were converted into compositions with pure elements and ZrN standards, where the calibration curve method was used for composition analysis of U and Zr [4].

3. Results

The cross-section of the alloys showed adherent multilayer structures. Phases formed at various temperatures and compositions are summarized in Table 1. The layer formation can be mainly divided into two categories.

(1) $T \geqslant 1073$ K: U_2N_3/ZrN(U)/α-Zr(N)/matrix alloy.

(2) $T \leqslant 973$ K: U_2N_3/ZrN(U)/α-Zr(N)/U(Zr)/matrix alloy.

0925-8388/94/$07.00 © 1994 Elsevier Science S.A. All rights reserved
SSDI 0925-8388(94)04088-L

TABLE 1. Reaction layers on the U–Zr alloys in approximately 20 kPa nitrogen

Temperature (K)	U–18at.%Zr	U–50at.%Zr	U–67at.%Zr
1273	A	A	A
1173	A	A	A
1073	A	A	A
973	B′	B	A
873	B′	B	B

A, U_2N_3/ZrN(U)/α-Zr(N)/matrix alloy; B, U_2N_3/ZrN(U)/α-Zr(N)/U(Zr)/matrix alloy; B′, (U_2N_3 + ZrN)/(α-Zr + U)/matrix alloy, where the U_2N_3 + ZrN layer tended to pulverize.

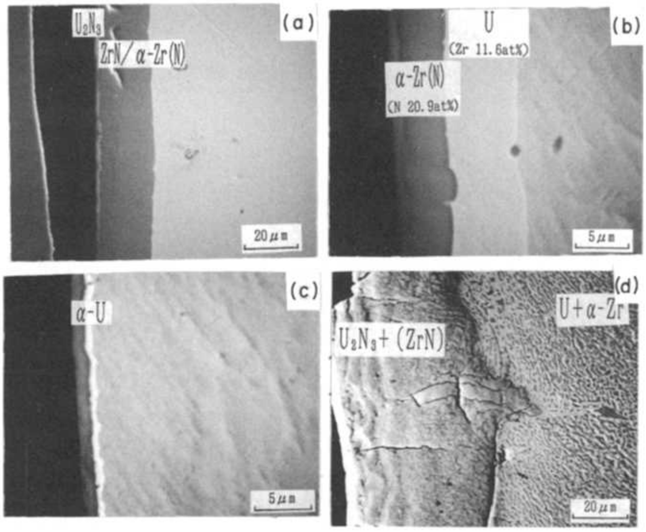

Fig. 1. EPMA micrographs of cross-sections of the U–Zr alloys reacted in 20 kPa nitrogen: (a) U–18at.%Zr at 1273 K for 72 h; (b) U–50at.%Zr at 973 K for 1000 h; (c) U–67at.%Zr at 873 K for 1000 h; (d) U–18at.%Zr at 973 K for 15 h.

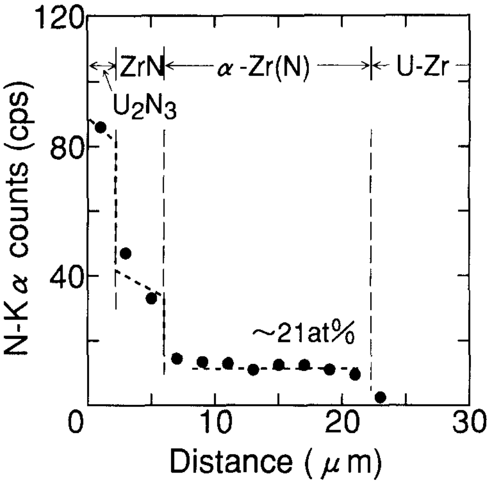

Fig. 2. Profile of N Kα counts through the reaction layers formed over the U–18at.%Zr alloy reacted in 20 kPa nitrogen at 1273 K for 72 h.

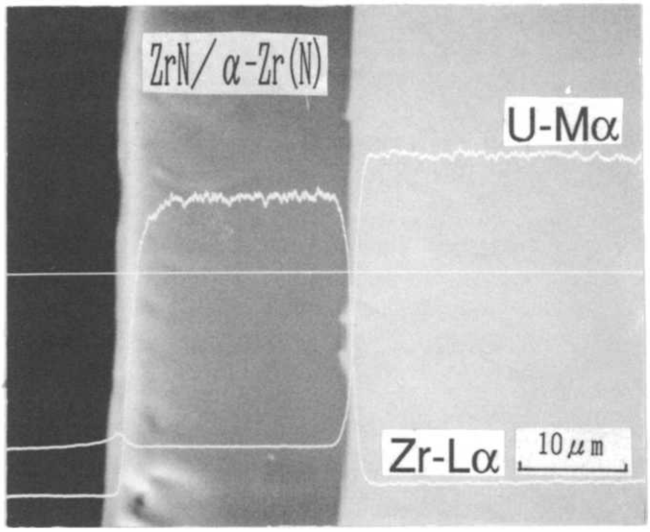

Fig. 3. EPMA micrograph of a cross-section of the U–18at.%Zr alloy reacted in 0.19 kPa nitrogen at 1273 K for 72 h. Lines in the figure are X-ray line analysis indicating the distribution of U and Zr in the reaction layer.

Typical EPMA photographs are shown in Fig. 1. From the observation of the cross-sections the formation of a continuous U_2N_3 layer at the surface seemed to be suppressed in the alloys with high Zr contents and only islands of U_2N_3 phase were observed on the surface of the Zr-rich alloys. Figure 2 shows the results of point analysis of the nitrogen concentration on the cross-section of the U–18at.%Zr alloy at 1273 K. The nitrogen content in the α-Zr layer was about 21 at.%, which is comparable with the solubility limit of nitrogen (about 22 at.%). Those in the U–Zr matrix alloys were less than the detection limit (0.5 wt.%), suggesting that the solubility of nitrogen in the U–Zr alloy phases is very small and their phase stabilities are significantly reduced by impurity nitrogen. The EPMA also showed that the U contents in the ZrN and α-Zr layers were approximately equal (about 0.1 at.%). The major difference between the categories (1) and (2) is the presence of U-rich alloy layers at the α-Zr(N)–matrix alloy interface. The layer formed on the U–50at.%Zr alloy at 973 K, as shown in Fig. 1(b), contained Zr up to 11.6 at.%. From the U–Zr phase diagram [1] the U-rich alloy layer is considered to be the b.c.c. γ phase at that temperature. Also, the layer formed at 873 K, as shown in Fig. 1(c), was presumed to be α-U containing a little Zr.

On the other hand, in the case of U–18at.%Zr alloys at lower temperatures (873 and 973 K) the formation of uniform reaction layers was not observed, as shown in Fig. 1(d). The products formed near the surface were a mixture of U_2N_3 and ZrN, while the interior consisted of a U-rich phase and α-Zr. The nitride region was significantly cracked and tended to pulverize as the reaction proceeded. The nitride region could not maintain the adherent layer structure in the process of the nitriding reaction.

From the reaction experiments under low pressure at 1273 K, as shown in Fig. 3, the formation of the reaction layers is of the same type as for category (1) and the layer sequence is U-rich nitride/ZrN(U)/α-Zr(N)/matrix alloy. However, the very thin U-rich segregation on the surface of the ZrN(U) layer could not be identified. The U-rich phase is considered to be a mononitride, because U_2N_3 decomposes at 1273 K under such a low nitrogen pressure [5].

The formation of the reaction layers is influenced by the diffusion coefficients of the alloy components and nitrogen through both the reaction layers and the matrix alloy and by the affinities of the alloy elements for nitrogen. A thermodynamic analysis is presented in ref. 6. The diffusion coefficients of nitrogen through the reaction layers are much faster than those of U and Zr. However, the diffusion data of U and Zr in the U–Zr alloys are insufficient for a more detailed analysis.

References

1 R.I. Sheldon and D.E. Peterson, in T.B. Massalski, H. Okamoto, P.R. Subramanian and L. Kacprzak (eds), *Binary Alloy Phase Diagrams,* Vol. 3, American Society for Metals, Metals Park, OH, 1990, pp. 3520–3523.

2 F.A. Rough, A.E. Austin, A.A. Bauer and J.R. Doig, *Battelle Memorial Institute Rep., BMI-1092,* 1956.

3 G.L. Hofman, A.G. Hins, D.L. Porter, L. Leibowitz and E.L. Wood, *Argonne National Laboratory Rep. Conf-860931-6,* 1986.

4 M. Akabori, A. Itoh, T. Ogawa, F. Kobayashi and Y. Suzuki, *J. Nucl. Mater., 188* (1992) 249.

5 H. Tagawa, *J. Nucl. Mater., 51* (1974) 78.

6 T. Ogawa and M. Akabori, *J. Alloys Comp., 213/214* (1994) 173.