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Letter to the Editors

Formation of nitrides at the surface of U–Zr alloys

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Abstract

The phase behavior of ternary system U–Zr–N was investigated by surface analysis of U–Zr alloys reacted with nitrogen gas by Auger electron spectroscopy (AES) and electron-probe microanalysis (EPMA). U–18, –50 and –67 at.% Zr alloys were reacted with nitrogen at 0.19 kPa and 1273 K, and the reaction layers were analyzed. The reaction layers formed at the alloy surfaces were (U,Zr)N/ZrN/αZr/alloy matrix. The compositions of the (U,Zr)N mononitride phases changed from those of the matrix alloys to ZrN continuously. The thicknesses of the (U,Zr)N layers were below about 0.2 μm and were larger for U-rich alloy. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The U–Zr binary system is one of the most extensively investigated alloy systems of uranium and the detailed knowledge would be very useful to evaluate the promising U–Pu–Zr alloy fuels for the fast reactor. The phase behavior and migration of the component elements in the alloys 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 behavior is significantly influenced by impurities such as oxygen, nitrogen, etc. In U–Pu–Zr fuels [1], a zirconium–nitrogen layer of a few μm in thickness containing up to 20 at.% nitrogen has been observed at the inner surface of the claddings, which retards molten phase formation at the fuel–cladding interface. The formation of the Zr-rich layer seemed to be related to the availability of impurity nitrogen. The deposition of similar Zr-rich rind layers was also observed between U–10Zr fuels and claddings in the irradiated U–Zr fuels [2]. The Zr-rich rind was formed during the initial injection casting of the U–Zr fuel. More recently, U–Pu–Zr alloy fuels with a barrier of ZrN or αZr have been proposed in order to retard the interdiffusion of fuel and cladding components at the fuel/cladding interface and the formation of molten phase (U–Pu–Fe, etc.) [3].

In our previous works [4,5], the phase behavior of the ternary system U–Zr–N has been studied. The experimental result indicated that adherent multi-layered structure was formed at the surface of U–Zr alloys, which were annealed at 873–1273 K under nitrogen pressures of 0.19 and 20 kPa. From electron-probe microanalysis (EPMA), the general layer structure under high nitrogen pressure was found to be

$$U_2N_3/ZrN/\alpha Zr(N)/\text{matrix alloy},$$

where αZr(N) means nitrogen-containing h.c.p. αZr. On the other hand, under low nitrogen pressure, a very thin U-rich scale over the ZrN layer was observed, but the composition of this U-rich phase could not be determined from the EPMA, because the thickness was nearly equal to or below the resolution of the electron probe (~1 μm). Thermodynamic analysis by Ogawa et al. [5] predicted that stable phases change with nitrogen pressure. At a low nitrogen pressure U_2N_3 is replaced by UN or (U,Zr)N. In this study, the U-rich phase formed over the ZrN layer under low nitrogen pressure was investigated by means of Auger electron spectroscopy (AES) to determine the phase structure.

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2. Experimental

2.1. Sample preparation and heat treatment

Uranium–zirconium alloys containing 18, 50 and 67 at.% Zr were prepared by arc-melting of 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 pieces of about $1.5 \times 3 \times 1$ mm^3, and then all faces of the specimens were metallographically polished with diamond pastes. The alloy sample sealed in a quartz ampoule was joined to a 2 l Pyrex flask filled with purified nitrogen gas. The reaction temperature and time were 1273 K and 72 h, respectively. After heating, the samples were quenched in water.

2.2. Sample analysis

After annealing, the samples were analyzed by means of EPMA, X-ray diffraction and AES. X-ray diffraction analysis of the alloy surfaces was done by means of an X-ray diffractometer equipped with a position sensitive detector covering 120° in 2θ. The EPMA measurements were performed with the Shimazu 810Q type analyzer. The alloys were analyzed by point-to-point counting technique for concentration profiles and phase identification. The acceleration voltages were 15 and 25 kV for nitrogen and alloy elements, respectively, and the beam size was about 1 μm in diameter. The characteristic X-ray intensities were converted into compositions with pure metals, UN and ZrN standards. The detection limits of the EPMA analysis are about 0.1, 0.1 and 0.5 wt% for U, Zr and N, respectively.

The AES measurements were performed with an analyzer, type ANELVA EMAS-II. Beam diameter was about 1 μm, and a primary beam current was 0.3 μA at a primary beam energy of 10 keV. Before the surface analysis was carried out, the sample surface was sputtered by Ar^+ ion. In this way surface contamination was avoided and a fresh surface having the bulk composition was obtained. Alternate sputtering and Auger analysis were carried out during depth analysis. The argon ion beam used for the sputtering experiments had an energy of 2 keV. By performing the identical sputtering, the sputtering rate was measured to be ~3.6 nm/min with SiO_2 sample.

The AES spectra were examined in a semi-quantitative way using the equation of Palmberg et al. [6],

$$C_x = [I_x/S_x] \Big/ \int [I_\alpha/S_\alpha], \qquad (1)$$

where C is the concentration (in at.%), I is the peak intensity and S is the relative elemental sensitivity factor for the Auger line used. The uranium and zirconium sensitivity factors were obtained from the spectra of UN and ZrN standards. The uranium NOO (74 eV), the zirconium MNN (147 eV) and the nitrogen KLL (380 eV) Auger peaks were used. The uranium NOO (275 eV) signal was not used, because a small amount of carbon contamination was always present in the apparatus and the carbon KLL peak has a kinetic energy of 270 eV.

3. Results and discussion

Fig. 1 shows EPMA micrographs of cross-sections of the U–18, –50 and –67 at.% Zr alloys reacted in 0.19 kPa nitrogen at 1273 K for 72 h. From the line analysis by EPMA, the formation of U-rich layer on the alloy surface was observed. With increasing uranium concentration in the alloys, the formation of the U-rich layer became more marked. Fig. 2 shows the profile of N–Kα counts through the reaction layers formed over the U–18 at.% Zr alloy. The layer sequence was found to be

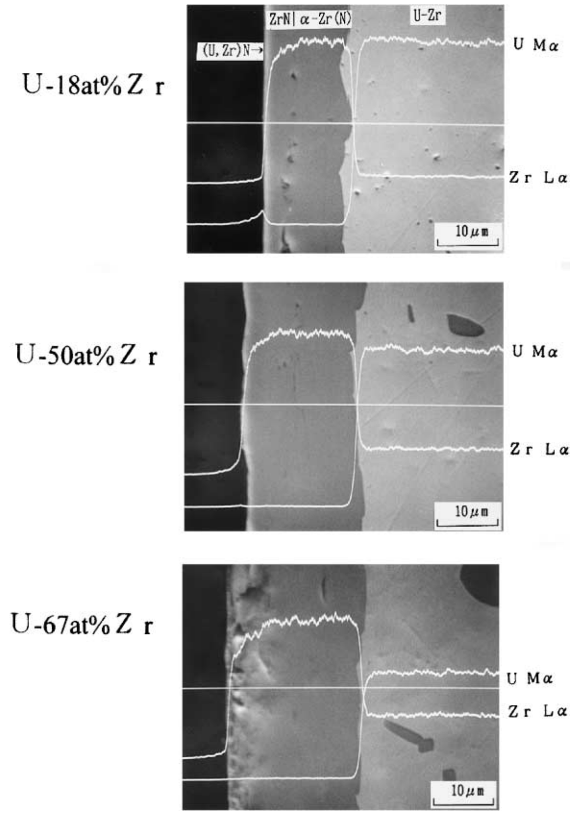

Fig. 1. EPMA micrographs of cross-sections of the U–Zr alloys reacted at 1273 K in 19 kPa N_2: (a) U–18 at.% Zr; (b) U–50 at.% Zr; (c) U–67 at.% Zr alloys. Lines in the figures are X-ray line analysis indicating the distribution of U and Zr in the reaction layers.

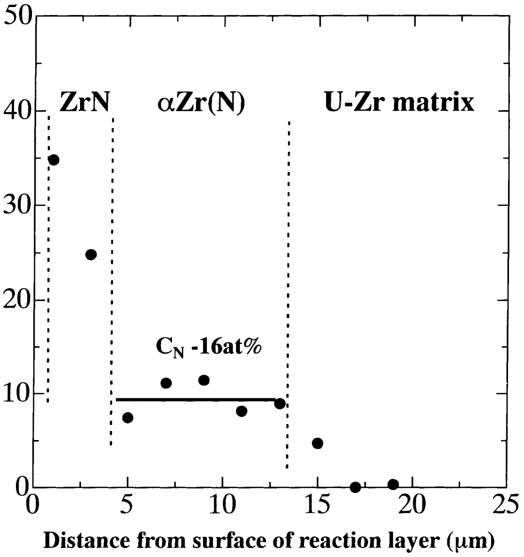

Fig. 2. Profile of N–Kα counts through the reaction layers formed over the U–18 at.% Zr alloy.

U-rich phase/ZrN/αZr(N)/U–Zr alloy matrix.

From the zirconium profiles in Fig. 1 and the nitrogen profile in Fig. 2, depth dependencies of the ZrN compositions were observed. ZrN is the only intermediate phase in Zr–N system and has non-stoichiometric composition $Zr_{1-x}N$. The nitrogen contents decrease continuously with increasing depth. The nitrogen content in the αZr(N) phase is approximately constant over the layer and about 16 at.% which is significantly low, compared with 21 at.% observed at the high nitrogen pressures [4] as well as with the solubility limit of nitrogen in hcp αZr (about 24 at.%). This suggests that the U-rich phase over the ZrN acts as diffusion barriers to nitrogen. On the other hand, the nitrogen contents in the U–Zr matrix were below the detection limit of EPMA (0.5 wt%), suggesting the phase instability of U–Zr alloys with increase of nitrogen content. The EPMA results also indicated that the U contents in the ZrN and αZr(N) layers were very low and below about 0.1 wt%. The negligible solubility of U in ZrN or αZr(N) layer suggests an effective barrier of ZrN or αZr layer on interdiffusion of metallic elements.

The X-ray diffraction analysis was applied to both the non-treated and Ar^+ sputtered surfaces of the U–18 at.% Zr alloy. The X-ray diffraction patterns indicated that almost all peaks observed were those of ZrN: only faint peaks arising from trace quantities of UN or (U,Zr)N were observed. Also, the intensities of UN were stronger for the non-sputtered surface than for the Ar^+ sputtered. This result suggested that a uranium mononitride phase, probably UN or (U,Zr)N, is formed over the ZrN layer.

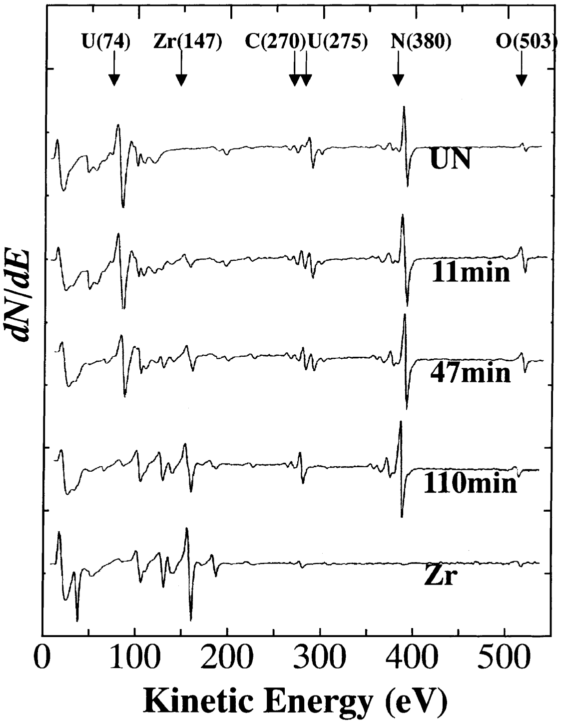

Fig. 3. Auger electron spectra of Ar^+ ion sputtered U–18 at.% Zr, UN and Zr surfaces.

Fig. 3 shows Auger electron spectra of the surfaces of U–18 at.% Zr alloy sputtered by Ar^+ ions, including those of UN and Zr standards. The intensity of U (74 eV) peak decreased with sputtering time. The formation of U-rich phase at the surface is also indicated by an increase of the zirconium signal as function of the Ar^+ ion sputtering time. Therefore, it can be concluded that the uranium segregation occurs at the alloy surface, and that the uranium concentration is very small after 110 min sputtering. On the other hand, the intensities of carbon and oxygen signals were constant after 11 min sputtering, suggesting that carbon and oxygen are background or original impurities in the alloy.

Depth profiles of U, Zr and N in the U–18, –50 and –67 at.% alloys are shown in Fig. 4. The intensities of nitrogen signals were constant through the surface scales formed over the ZrN layers and were about 50 at.%. The results suggested that the U-rich layers formed over the ZrN layers were mononitride phases and contained both uranium and zirconium. Also, it can be seen that there are depth dependencies of uranium and zirconium concentrations in the (U,Zr)N mononitride phases. The concentrations of uranium within the (U,Z)N layers decrease gradually and those of zirconium increase. Furthermore, no composition gaps within the (U,Zr)N layers were observed, suggesting that the (U,Zr)N layers are continuous solid-solutions between UN and ZrN.

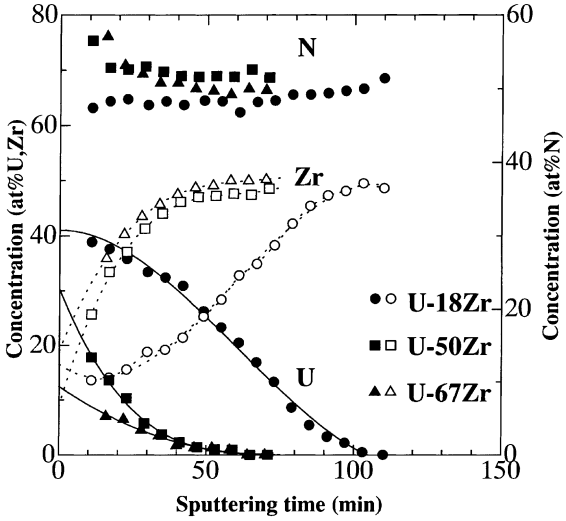

Fig. 4. Ar^+ sputter profiles of U, Zr and N in the U–18, –50 and –67 at.% Zr alloys.

The surface compositions of the (U,Zr)N phases, which were approximated by extrapolating the profiles to 0 min sputter, are likely to equal the bulk compositions of the U–Zr alloys. Therefore, the reaction layers on the U–Zr alloys at 1273 K under 0.19 kPa nitrogen were

$$(\mathrm{U,Zr})\mathrm{N}/\mathrm{ZrN}/\alpha\mathrm{Zr(N)}/\text{alloy matrix.}$$

The reaction layer structure and its sequence agree well with a theoretical sequence which was predicted by the previous theoretical analysis of U–Zr–N system [5].

The thickness of the (U,Zr)N layer cannot be precisely determined because of the unknown sputter rate. For the U-rich alloy of U–18 at.% Zr, the intensities of uranium and zirconium signals became constant after ~100 min sputtering. On the other hand, for the U–50 and 67 at.% Zr alloys, those became constant after ~50 min sputtering. This suggests that the (U,Zr)N layers formed at the surface of U–Zr alloys are thicker for U-richer alloys. Assuming a sputter rate of about 2–4 nm/min, the thickness of the (U,Zr)N layers are roughly estimated to be 0.2–0.4 μm for the U–18 at.% Zr and 0.1–0.2 μm for the U–50 and 67 at.% Zr alloys. The thickness of the (U,Zr)N layer developed on the ZrN layer of the U–18 at.% Zr alloy was also roughly estimated from the EPMA analysis. An effective thickness of UN over the ZrN layer was determined from U–Mα intensity ratio of the U–18 at.% Zr to UN standard at 6 keV of acceleration voltage and maximum depth of electron loss in UN to be about 0.07 μm. The UN thickness was converted into the thickness of (U,Zr)N layer. As a result, the thickness of (U,Zr)N layer was found to be about 0.17 μm. The thickness value was roughly close to that estimated from the sputtering rate.

References

[1] G.L. Hofman, A.G. Hins, D.L. Porter, L. Leibowitz, E.L. Wood, Argonne National Laboratory Report Conference-860931-6, 1986.
[2] D.D. Keiser, R.D. Mariani, J. Nucl. Mater. 270 (1999) 279.
[3] M. Tokiwai, R. Ikeda, K. Toumi, T. Matsuda, in: Proceedings of 1999 Fall Meeting of the Atomic Society of Japan, Kashiwazaki, 10–12 September 1999, I58.
[4] M. Akabori, A. Itoh, T. Ogawa, M. Ugajin, J. Alloys Comp. 213/214 (1994) 366.
[5] T. Ogawa, M. Akabori, J. Alloys Comp. 213/214 (1994) 173.
[6] P.W. Palmberg, G.E. Riack, R.E. Weber, N.C. Mcdonald, Handbook of Auger Spectroscopy, Physical Electronics, Edina, MN, 1972.