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Characterization of U–Nb–Zr dispersion fuel prepared by centrifugal atomization process

Jong-Man Park [a,*], Ki-Hwan Kim [a], Dong-Seong Sohn [a], Chang-Kyu Kim [a], Gerard L. Hofman [b]

[a] *Korea Atomic Energy Research Institute, Res. Reactor Fuel Dev. Project, 150 Dukjin-Dong, Yusong-gu, Taejon 305-353, South Korea*

[b] *Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*

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Abstract

The dispersions of U–Nb–Zr alloy particles in aluminum were characterized in order to assess the applicability of this dispersion as research reactor fuel. Heat treatment revealed that the 9 wt% Nb alloy powder had, as expected, higher γ-phase stability that the 5 wt% Nb alloy powder. A lamellar structure consisting of an α-U phase and γ-phase was observed to start at the grain boundaries during heat treatment. The U–Nb–Zr alloy dispersion exhibited large volume increases during annealing when compared with similar experimental results for U_3Si, U_3Si_2 and U–Mo dispersion fuel systems. The reaction product $(U,Nb,Zr)Al_3$ forms preferentially by diffusion of aluminum in the α-U phase which, in turn, forms during the diffusion process as the metastable γ-phase decomposes. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, increased attention has been paid to the development of aluminum matrix dispersion fuels with increased fissile uranium density to make possible the conversion of research reactors from the use of high-enriched uranium (HEU) to low-enriched uranium (LEU) [1,2]. To date, U_3Si_2 dispersion fuel has been commonly accepted, and is being used to convert reactors requiring a fuel element loading of up to 5 g U/cm^3 [1,2]. Although U_3Si_2–Al dispersion fuel possesses very stable irradiation behavior, new dispersion fuels with loading up to 8–9 g U/cm^3 are required for the conversion of several high performance reactors [3]. Because there is a practical limit of 55% for the volume loading of the dispersed fuel phase in a commercial process, fuel dispersants with uranium densities higher than about 15 g U/cm^3 are required to reach this goal [3]. Since uranium compounds with this density have previously been found to swell excessively [1], it appears that uranium alloys are needed to achieve this density. Since earlier studies have shown the γ-uranium phase to behave rather stably under irradiation [3], uranium alloys which retain the γ-phase are preferred. One group of promising candidates is the uranium–molybdenum alloys, which have a relatively large range of γ-phase that is retainable in a metastable state at a temperature at which the fuel is fabricated and irradiated [4]. It has also been found that γ-uranium reacts much more slowly with the aluminum matrix than dose α-uranium at fabrication temperatures (typically 400–500°C). Such a reaction, caused by interdiffusion of the fuel and aluminum, would produce undesirable swelling of the dispersion owing to the formation of lower-density compounds. It has been found that the addition of both zirconium and niobium to uranium also stabilizes the body-centered-cubic gamma phase [5,6], albeit less effectively. Because of the low neutron absorption properties of Zr and Nb, this ternary alloy system may be another high density candidate fuel [3]. Both U–Mo and U–Nb–Zr alloys of various compositions have recently been selected for screening irradiation tests at ATR [3,7].

In this study, powders of U–5 wt% Nb–3 wt% Zr and U–9 wt% Nb–3 wt% Zr alloys were prepared by the

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[*] Corresponding author. Tel.: +82-42 868 8559; fax: +82-42 868 8346; e-mail: jmpark@nanum.kaeri.re.kr.

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rotating disk centrifugal atomization process, and dispersion of these powders in aluminum were made by extrusion. Samples of these dispersion were given a variety of heat treatments, after which suitability as high-density fuel candidates was assessed.

2. Experimental procedure

Two alloys, U–5 wt% Nb–3 wt% Zr and U–9 wt% Nb–3 wt% Zr, were atomized, using depleted uranium lump (99.9 wt%), niobium (99.9 wt%) and sponge zirconium (99.7 wt%) with a purity of respectively 99.9, 99.9 and 99.7% [1]. The alloying elements were induction melted in an alumina crucible coated with a high-temperature-resistant ceramic, yttria stabilized zirconia. In order to obtain a suitable size distribution of the U–Nb–Zr powders, atomization parameters, such as superheating (at around 100°C higher than the melting temperature) and the rotating speed of the disk (30,000 rpm), were set.

The size distribution and density of U–Nb–Zr powders were measured by sieve analysis and the Archimedian immersion method, respectively. The powders were annealed at various temperatures in a vacuum of 10^{-5} Torr, and the microstructural change and phase transformation behavior of the alloys were determined using X-ray diffraction analysis with CuK_{α} radiation and scanning electron microscopy (SEM). Compositional analysis was done by energy dispersive spectroscopy (EDS).

Rods of 6.5 mm diameter consisting of 25 vol.% U–Nb–Zr powders dispersed in an aluminum matrix were extruded for each of the powder compositions. The extrusion temperature was 450°C and the maximum pressure 65 kgf/cm^2. Specimens of 25 mm length were cut, vacuum-sealed in quartz tubes and annealed in a box furnace, at 400°C and 500°C for up to 400 h. Sample swelling as a function of temperature and time was determined from the dimensional changes. The microstructures and phase identification of the annealed rods were examined by SEM and EDS.

3. Results and discussion

3.1. Characterization of powders

Chemical analyses for the atomized 5 and 9 wt% Nb powders, as shown in Table 1, were found to be U–5.6 wt% Nb–2.9 wt% Zr and U–9.6 wt% Nb–3.1 wt% Zr, respectively, which are near to the desired composition. The atomized particles shown in Fig. 1, appeared to be spherical in shape, having smooth surfaces. The average density and mean size of as-received powders were measured to be 17.2 and 16.3 g/cm^3, and 65 and 69 μm, for U–5Nb–3Zr and U–9Nb–3Zr, respectively.

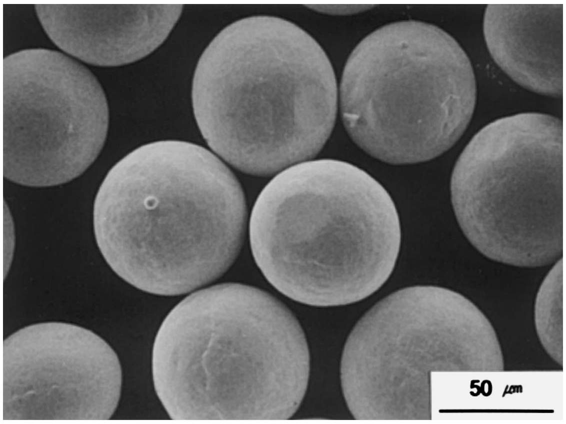

Fig. 1. SEM image showing the shape of atomized U–5Nb–3Zr alloy powder.

3.2. Annealing test on fuel alloy powder

Because atomized powder is achieved under a very high cooling rate of 10^4 K/s, the high-temperature γ-phase was expected to be easily retained. However, in the case of the as-atomized U–5Nb–3Zr alloy powder, a slight amount of orthorhombic α-U phase already existed with the metastable bcc γ-phase (γ_m) matrix, while complete γ_m-phase was achieved in U–9Nb–3Zr alloy. Considering the very high cooling rate during the atomization process as mentioned above, these results imply that there is a threshold limit between 5% and 9% in the niobium content to achieve a stabilized γ-phase after atomization. The relative phase stability of the powders was evaluated by annealing tests. Fig. 2 shows the changes in the X-ray diffraction patterns of the atomized U–5Nb–3Zr and U–9Nb–3Zr alloy powders as the powders were heat treated at increasing temperatures. The amount of decomposed α-U increased and the retained γ_m phase decreased, for both alloy compositions with increasing temperature and time as expected. Also, the higher the niobium content, the slower the decomposition rate.

Table 1
Chemical composition results of U–5Nb–3Zr and U–9Nb–3Zr powders

	U (wt%)	Nb (wt%)	Zr (wt%)	Ni (ppm)	Fe (ppm)	Al (ppm)	B (ppm)	Si (ppm)	C (ppm)
U–5Nb–Zr	Bal.	5.6	2.9	53	<50	59	<0.5	50	90
U–9Nb–3Zr	Bal.	9.6	3.1	<50	<50	<50	<0.5	50	200

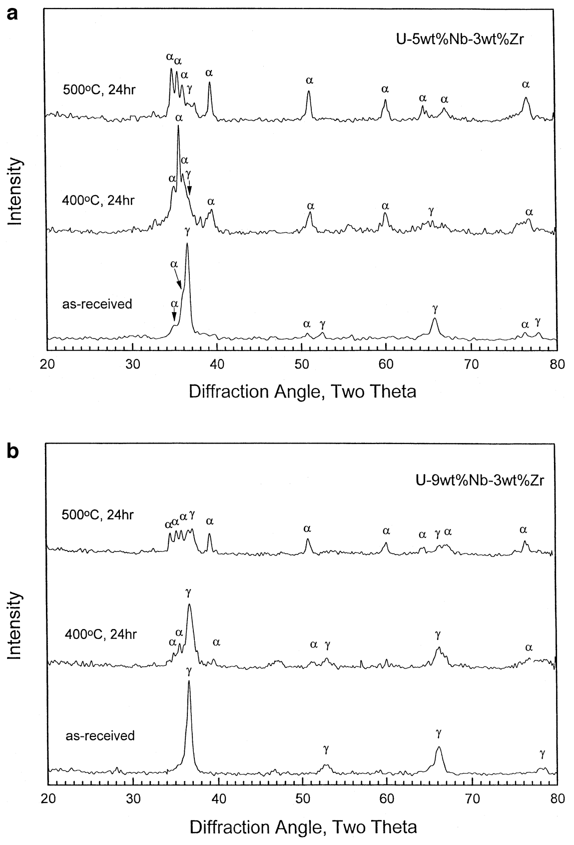

Fig. 2. The variations of X-ray diffraction patterns of the atomized. (a) 5 wt% Nb and (b) 9 wt% Nb alloy powders with heat treatment condition.

These differences in phase stability of the two alloys may also be confirmed by observed microstructural changes. Small grain sizes of about 1–5 μm were observed on both the atomized powders. Segregation (coring) has occurred during solidification as evidenced by higher uranium concentration near the grain boundaries. Fig. 3 also shows the typical microstructural changes of U–Nb–Zr alloy powders after 24 h at 500°C; the samples were chemically etched with a reagent of 50% nitric acid and 50% acetic acid. The decomposition into the α-U and γ-phase from the metastable γ_m matrix appears to start in the grain boundary regions (see Fig. 3(b)), whereas the metastable γ_m-phase remains unaffected in the grain interiors of the 9Nb alloy, in the U–5Nb–3Zr powder, a very fine lamellar two-phase structure has formed throughout the entire grain.

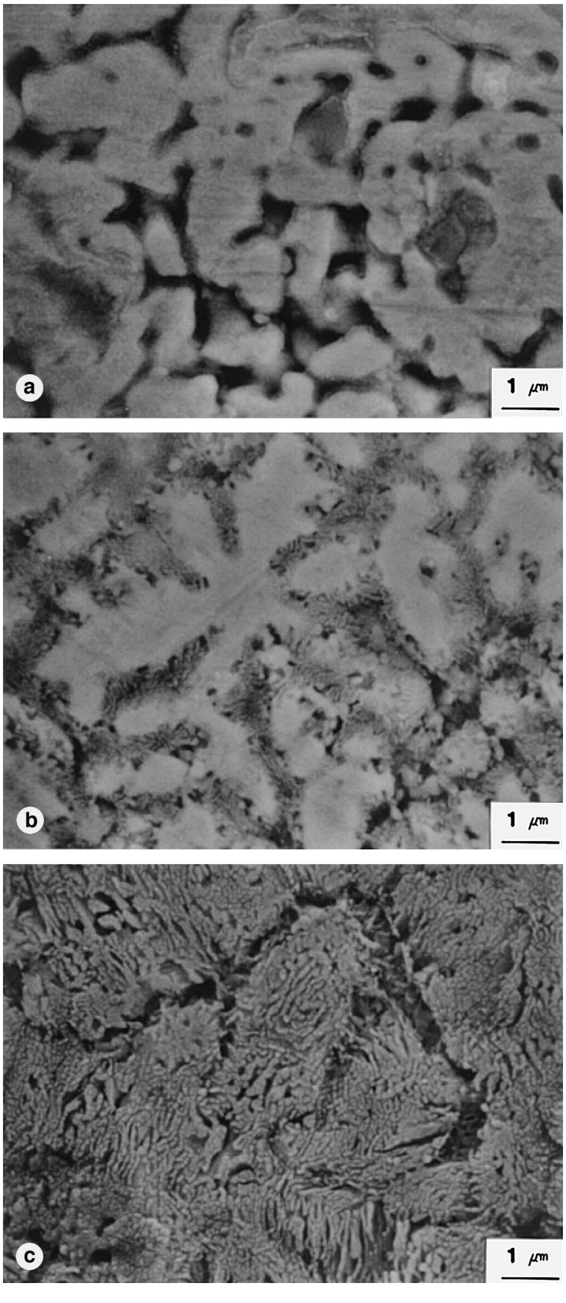

Fig. 3. The microstructural changes of U–Nb–Zr powders: (a) the 9 wt% Nb, as-atomized; (b) the 9 wt% Nb, after heat treatment at 500°C for 24 h; (c) the 5 wt% Nb, after heat treatment at 500°C for 24 h.

3.3. Annealing test on fuel alloy powders dispersed in aluminum

Fig. 4 shows the dependence of the swelling behavior on temperature and time of the two different alloy samples. The volume of the dispersion samples increased rapidly and saturated within a relatively short time. The 5 wt% Nb sample exhibited a slightly larger volume expansion at all temperatures, and the rapid volume increase of the 9Nb sample at 400°C is somewhat delayed compared to that of the 5Nb sample. The maxi-

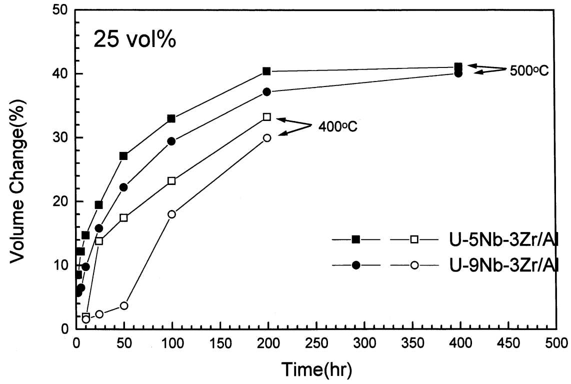

Fig. 4. Volume changes of the atomized U–Nb–Zr fuel meats at 400°C and 500°C.

mum volume increase is about 40% at 500°C after 400 h. Fig. 5 shows a comparison of the present data for U–Nb–Zr with those of other alloy systems previously reported. It is evident that U–Nb–Zr alloy fuel exhibits both more rapid and larger volume growth when compared with U_3Si/Al [8], U_3Si_2/Al [9], and U–Mo/Al [10]. These results appear to correlate with the relatively low gamma phase stability of the U–Nb–Zr alloys, specifically with the presence of a α-U.

The microstructure of a 9 wt% Nb specimen after 24 h at 400°C, which exhibits a volume growth of about 2.4%, is shown in Fig. 6. This example may be used to explain the initial stage of the reaction with aluminum. The reaction product in the microstructure appears to be (U,Nb,Zr)Al_3, an UAl_3 isomorph, as determined by EDS and X-ray diffraction.

At the initial stages, the reaction occurred at preferred sites of the particle surface, after which aluminum appeared to diffuse radially inward, mainly along the grain boundaries where transformation to α-U first takes place.

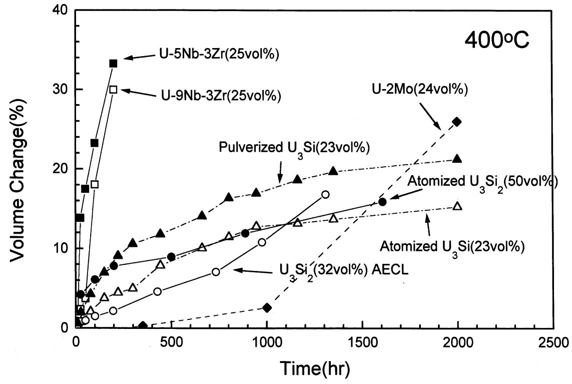

Fig. 5. Comparison of the thermal swelling data of U–Nb–Zr/Al fuel with those of another fuel systems, U_3Si/Al, U_3Si_2/Al, and U–2Mo/Al.

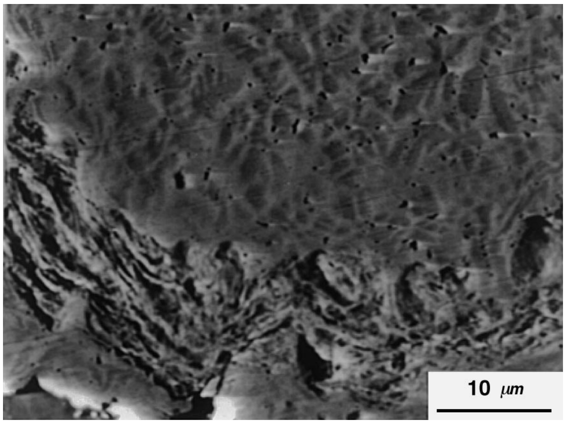

Fig. 6. Microstructure of the 9 wt% Nb fuel meat after 24 h at 400°C.

As the reaction developed, the phase transformation also progressed at a rate and with a final morphology depending on alloy composition. Figs. 7 and 8 show the morphologies of both the 5 wt% Nb and 9 wt% Nb samples after 2 h at 500°C, representing a middle stage of the swelling reaction where the samples had attained a volume growth of 8.5% and 5.7%, respectively. In all cases, the size of unreacted core diminished as the reaction zone grew inward from the particle surface. At the same time, a number of islands, which were revealed by EDS analysis to have a composition close to the γ-phase, remain unreacted in the (U,Nb,Zr)Al_3 layer. However with the 5 wt% Nb sample, there were fewer islands in the reacted zone compared with the 9 wt% Nb alloy fuel. These results can be attributed to the relatively lower γ-phase stability of the 5 wt% Nb alloy and the smaller fraction of γ-phase in the equilibrium two-phase mixture. As the reaction proceeds further, as typically shown in Fig. 9, for a 5 wt% Nb sample that

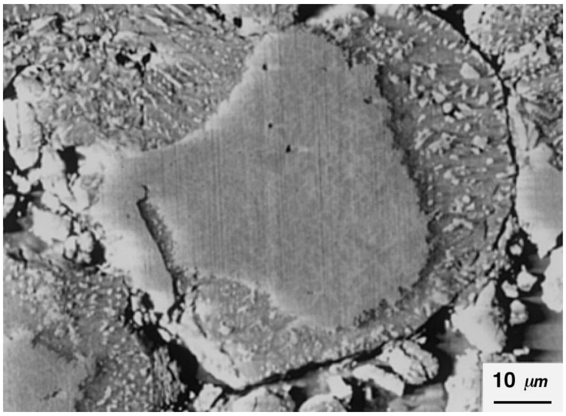

Fig. 7. Microstructure of the 5 wt% Nb fuel meat after 2 h at 500°C.

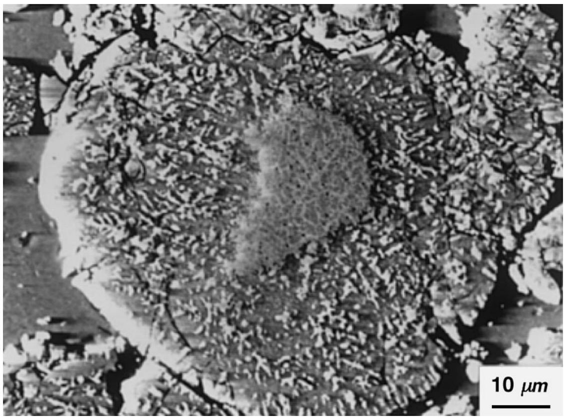

Fig. 8. Microstructure of the 9 wt% Nb fuel meat after 2 h at 500°C.

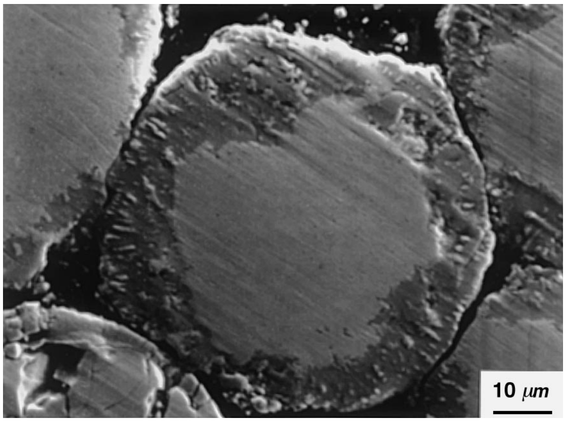

Fig. 9. Microstructure of the 5 wt% Nb fuel meat after 24 h at 500°C.

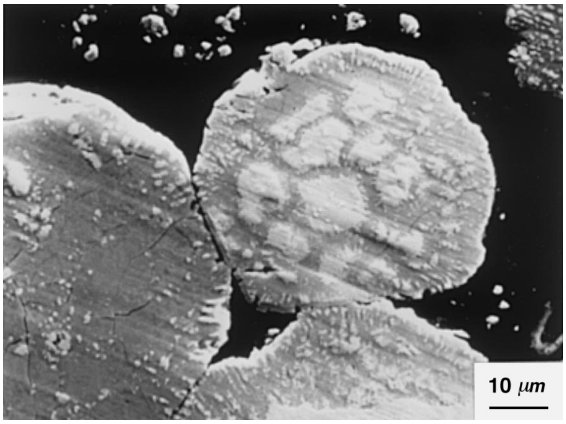

Fig. 10. Microstructure of the 5 wt% Nb fuel meat after 24 h at 400°C.

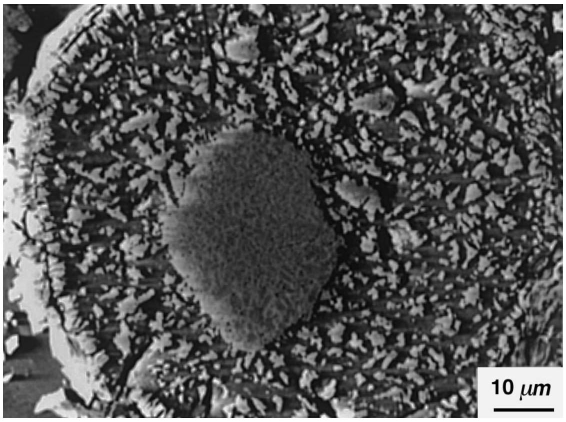

Fig. 11. Microstructure of the 9 wt% Nb fuel meat after 24 h at 400°C.

was heat treated for 24 h at 500°C resulting in volume expansion of about 15–20%, the number of islands left in the reacted zone became fewer, rather than the unreacted particle core shrinking further. This suggests that the majority of aluminum was consumed by reaction with unreacted γ-phase islands before it reached the reaction front at the unreacted fuel core.

However, there appeared to be a temperature effect on swelling reaction morphologies of U–Nb–Zr ternary alloy fuel. Figs. 10 and 11 show the microstructures of the 5 and 9 wt% Nb alloy fuels after 24 h at 400°C, in which the volume growth values were measured to be 13.8% and 2.4%, respectively. The fact that the phase transformation into a lamellar structure occurred predominately at the grain boundary region, at this relatively low temperature, had the effect of aluminum diffusion being more dominant along these boundaries. This resulted in more unreacted islands left in the aluminide zone (for U–9Nb–3Zr), while for U–5Nb–3Zr the morphology consists of larger islands of unreacted U–5Nb–3Zr grains surrounded by reaction product.

Fig. 12 shows the microstructure of U–5Nb–3Zr/Al sample, representing the final stage of the swelling reaction. The specimen was heat treated for 400 h at 500°C and the volume growth was about 40%. Aluminum diffusion is cut off by many cracks formed in the aluminide zone. A considerable amount of unreacted particle core remains. Moreover, these cracks are interconnected and extended to large voids in the aluminum matrix. The reason why U–Nb–Zr/Al alloy fuel exhibits such a large thermal swelling behavior compared to, for example, U–Mo alloys, is still unclear. However, it is likely that the swelling values of more than 40% might be due to the relatively rapid rate of reaction facilitated by the lower γ-phase stability of U–Nb–Zr.

It has been suggested that the formation of large voids may be aided by freeing of absorbed gasses on the Al and alloy powders [11].

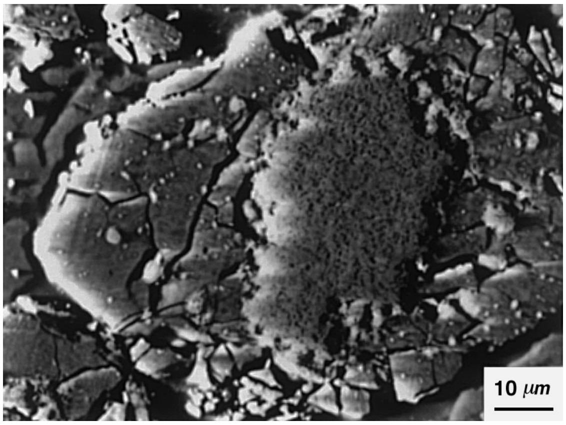

Fig. 12. Microstructure of the 5 wt% Nb fuel meat after 400 h at 500°C.

4. Conclusion

Centrifugally atomized powders of U–Nb–Zr alloys consist of spherical particles with smooth surfaces, irrespective of alloy composition. Heat treatment revealed that the 9 wt% Nb alloy powder had a relatively higher γ-phase stability than the 5 wt% Nb alloy powder. Decomposition of the as-atomized γ structure results in a lamellar two-phase microstructure consisting of α-U and γ_s-(U–Nb–Zr) equilibrium phases. The decomposition initiates at the grain boundaries and proceeds into the grain interiors. The volume growth values of about 40% at 500°C after 400 h for U–Nb–Zr alloy/Al fuel dispersions are quite large when compared with previous swelling data for U_3Si–Al, U_3Si_2–Al, and UMo–Al dispersion fuels. The 5 wt% Nb fuel dispersion exhibits a slightly larger volume expansion that the 9 wt% Nb specimen at any temperature. The reaction product $(U,Nb,Zr)Al_3$, was formed, starting at the particle surface proceeding toward the center of the particles preferentially through the α-U phase, which is formed during the diffusion process as the γ-phase decomposes.

The reaction of matrix aluminum and fuel particles results in unacceptable volume changes. This renders the 5Nb alloy unsuitable for dispersion fuel, however, the 9Nb alloy merits consideration if the temperature and time of dispersion fabrication can be kept suitably low values. Whether the low neutron absorption properties of Nb and Zr compensate for the rather large fraction of these alloy elements needed to maintain γ-stability remains to be evaluated.

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