ELSEVIER Journal of Nuclear Materials 270 (1999) 315–321

journal of nuclear materials

Thermal compatibility studies of U_3Si_2 dispersion fuels prepared with centrifugally atomized powder

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Received 14 April 1998; accepted 8 December 1998

Abstract

The interaction between atomized U_3Si_2 and aluminum in dispersion fuel samples has been characterized and compared with that of comminuted U_3Si_2. Fuel samples with atomized powder showed a smaller volume increase compared to those with the comminuted powder, irrespective of heat treatment, and volume fraction of U_3Si_2 powder. The possible reasons for this seem to be as follows: (1) the smaller specific surface area of the atomized spherical powder compared to the irregular comminuted powder translating in a smaller U_3Si_2–Al interface area for the former affecting what appears to be a diffusion-controlled interaction process, (2) the atomized fuel samples also contain lower fraction of as-fabricated porosity than the comminuted fuel samples, which may enhance the restraint force in the swelling fuel meat, (3) the comminuted powder particles have distinctive aluminum penetration paths in the form of deformation zones that originated from the comminution process. There appear to be two pronounced penetration paths of aluminum into atomized U_3Si_2 powder; (1) through the phase interface, leaving a central unreacted island, (2) along grain boundaries, leaving several unreacted islands. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 66.10.Cb; 66.30.-h; 68.35.-p

1. Introduction

The term compatibility refers to the effect of varied environments on dissimilar materials in contact with each other [1–6]. In dispersion fuels this manifests itself in dimensional and geometric changes that occur as a result of interdiffusion or other chemical reactions between the fuel dispersant and aluminum matrix [7,8]. The volume expansion produced by thermal annealing is thus a measure of the thermal stability of the dispersion fuels, and it acts as an indicator of expected in-reactor swelling performance.

In the case of uranium silicide compound fuel (U_3Si, U_3Si_2, or U_3SiAl), the reaction products of silicide and aluminum is $U(Al,Si)_3$ which is less dense than the combined reactants. The diffusivity of Al in U_3Si_2 is more rapid than that of U in Al. This may result in the so-called Kirkendall effect and the possible formation of pores in the Al matrix [9]. These pores have been proposed as contributing to volume expansion of U_3Si_2–Al dispersion fuel. It has also been shown that heating uranium and aluminum couple in a vacuum at temperatures greater than 473 K causes pore formation [10–15]. Recently, a similar pore-forming reaction has been reported between uranium silicide and aluminum [16]. As the reaction appears to be diffusion-controlled, it is exponentially dependent on temperature.

U_3Si_2 dispersion fuel for research reactors has been prepared by rolling or extruding the blended powders of

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PII: S0022-3115(99)00005-7

U_3Si_2 and aluminum [17,18]. U_3Si_2 particles are conventionally supplied by the mechanical comminution of as-cast U_3Si_2. In order to simplify the preparation process and improve the properties, a rotating-disk centrifugal atomization method has been used [19]. It is known that this process, in which the powder is prepared by a centrifugal force, has the advantages that the powder has a rapidly solidified microstructure, a relatively narrow particle size distribution, and a spherical shape [20,21].

In this study, the thermal compatibility of U_3Si_2–Al dispersion fuel having the centrifugally atomized powder was evaluated, and compared with the mechanically comminuted U_3Si_2–Al dispersion fuel. The present paper dealt with the issue of, specifically, U_3Si_2–aluminum matrix interdiffusion reaction of the dispersion fuels. The U_3Si_2 fuel rods were made by extruding the blended powders of U_3Si_2 and Al. Because of the absence of radiation enhanced diffusion, the specimen was heated above the expected reactor fuel operating temperature, in order to stimulate any measurable diffusion. Microstructural examinations of the fuel particles after thermal annealing were carried out to determine the nature of the thermal swelling.

2. Experimental procedure

Depleted uranium lumps (99.9% pure) and silicon chips (99.9999% pure) with a slightly hyper-stoichiometric composition (U–7.4 wt.% Si) were charged and induction-melted in graphite crucibles. The molten metal was heated to approximately 200 K higher than the melting point and was fed through a small nozzle onto a rapidly rotating graphite disk on a vertical axis. Liquid alloy droplets were then spread from the disk by a centrifugal force and cooled in an argon atmosphere. The atomized powder was collected in a container at the bottom of the funnel-shaped chamber [22]. Otherwise, the superheated molten metal was poured and cast into a copper mold under a vacuum atmosphere. The as-cast ingot is pressed into coarse particles and milled under argon using a hardened steel mill to obtain the appropriate particle size.

Dispersion fuel rods were prepared by extruding U_3Si_2 and aluminum powders at a working temperature of 673 K and 803 K . These extruded specimens, containing 15 vol.% and 50 vol.% of U_3Si_2 particles, were annealed for incremental times at 673 K for 1608 h and at 803 K for 234 h. After each annealing interval, the dimensional changes of the specimens were measured.

The samples were polished to 0.3 μm diamond paste, and examined by a scanning electron microscope (SEM) to characterize the morphology and the microstructure of the fuels. Electron-probe micro-analysis (EPMA), energy dispersive spectrometry X-ray analysis (EDX), and X-ray diffraction analysis (XRD) using Cu K_α radiation, were used to determine the chemical and the phase composition of the samples.

3. Experimental results

The volume increases versus annealing time for Al–15 vol.% U_3Si_2 and Al–50 vol.% U_3Si_2 dispersion samples annealed at 673 K and 803 K are shown in Fig. 1. The amount of swelling was found to increase with increasing temperature, increasing heating time and the proportion of dispersed U_3Si_2, irrespective of the preparation method of U_3Si_2 powders. The volume change of samples annealed at 803 K was about three times as much as that of fuel specimens at 673 K for the same time. Most of the swelling in the 803 K samples occurred within 10 h, so the swelling appeared to reach a plateau gradually with time. The volume increase of the 50 vol.% fuel samples was about five times greater than that of the 15 vol.% fuel samples. This difference in volume increase is somewhat larger than proportional volume fraction of the U_3Si_2 powder.

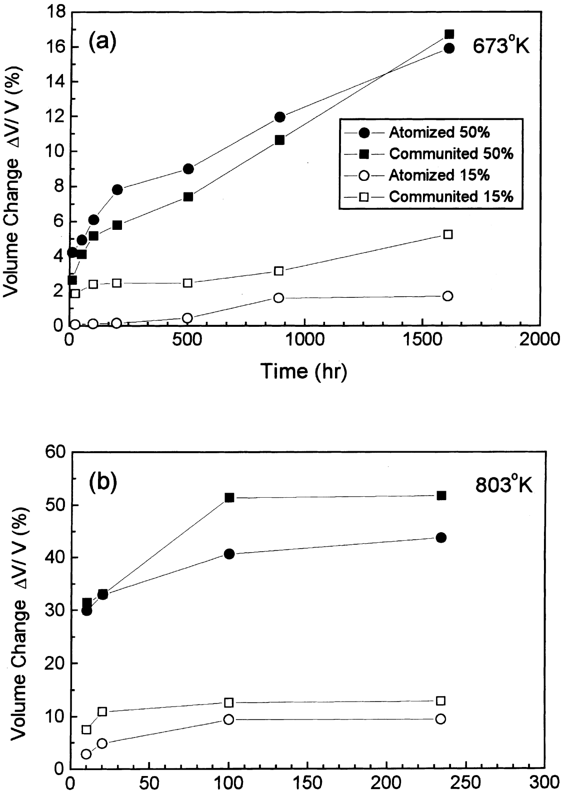

Fig. 1. Volume changes of fuel meat as a function of annealing time at 673 K (a) and 803 K (b).

3.1. Comminuted fuel powder

Back-scattered scanning electron (BSE) images and EPMA traces of the 15 vol.% fuel samples with the comminuted powder after annealing at 673 K for 888 h are shown in Fig. 2. The BSE yield is directly proportional to the average atomic number of the elements present in the area being imaged [23]. Thus, regions with a higher average atomic number appear brighter in a backscattered electron picture, while other regions with lower average atomic numbers acquire successively darker shades of grey. This variation of backscattered electrons with atomic numbers produces a qualitative 'map' of chemical composition except in cracked parts of the sample. The regions in the fuel samples imaged in Fig. 2 may be divided into two general areas: (a) bright-grey islands, (b) very dark-grey regions. Metallographic examinations of the fuel samples prepared with comminuted particles (Fig. 2(a)) showed that most particles had several irregular unreacted islands (bright-grey) with linear features, and cracks (dark-grey), presumably formed during the comminution and extrusion process. EPMA traces of partially reacted regions in a comminuted particle after annealing (Fig. 2(b)) also indicated that there was some penetration of Al in the deformation bands. The composition profiles shown in the probe trace illustrated a considerable penetration of Al atoms in partially reacted regions (very dark-grey), and a slight interdiffusion in the unreacted regions (light-dark). Area scan analyzes of the U_3Si_2 sample with EDX showed that reacted regions (very dark-grey) and unreacted regions (light-dark) were composed of 24 at.% U, 18 at.% Si, 57 at.% Al, that is, $U(Al, Si)_3$, and 61 at.% U, 39 at.% Si, that is U_3Si_2, respectively.

BSE images of the 15 vol.% fuel samples with the comminuted powder after annealing at 803 K for 10 h are shown in Fig. 3. The extent of the reaction product formation exceeded approximately half of the particle cross-section due to the higher heat treatment temperature, and led to a considerable volume change (8%) (Fig. 1). Some voids and cracks have formed in the circumferential region. The smaller particles exhibited almost complete reaction. The coarse comminuted particles showed two aspects of aluminum penetration. The particles were composed of a considerable amount of reacted areas around their circumference and generally had a 'kernel-like' structure with an unreacted center (Fig. 3(a)). In some particles Al diffusion proceeded

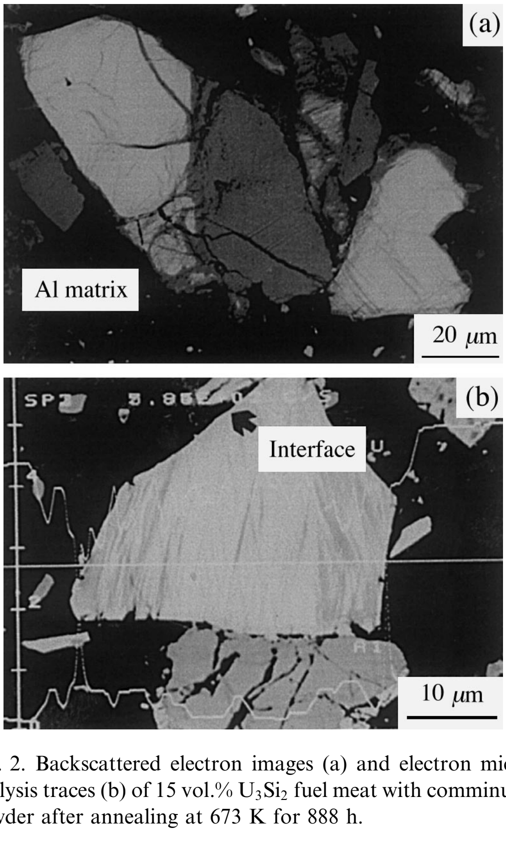

Fig. 2. Backscattered electron images (a) and electron microanalysis traces (b) of 15 vol.% U_3Si_2 fuel meat with comminuted powder after annealing at 673 K for 888 h.

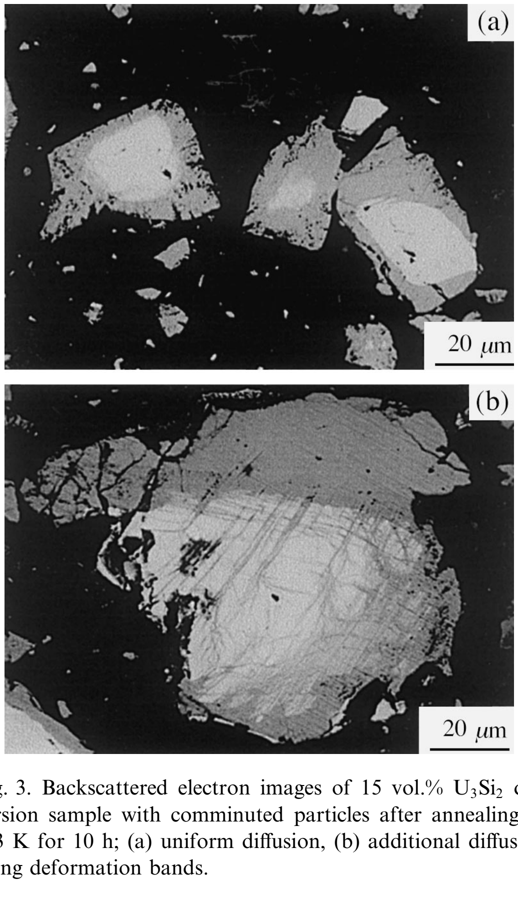

Fig. 3. Backscattered electron images of 15 vol.% U_3Si_2 dispersion sample with comminuted particles after annealing at 803 K for 10 h; (a) uniform diffusion, (b) additional diffusion along deformation bands.

along deformation zones in the particle, presumably due to lack of matrix bonding (Fig. 3(b)). BSE images of the 15 vol.% fuel samples with the comminuted powder after annealing at 803 K for 100 and 234 h are shown in Fig. 4. Fuel samples annealed for 100 h are composed of reacted particles with very small unreacted center, or, occasionally, completely reacted particles (Fig. 4(a)). As the annealing time increased, the unreacted U_3Si_2 regions were gradually reduced. Finally, after 234 h all fuel particles were converted to the $U(Al,Si)_3$ compound (Fig. 4(b)). The reaction caused an overall volume increase of 11% of the dispersion sample.

3.2. Atomized fuel powder

BSE images and EPMA traces of the 15 vol.% fuel samples with atomized powder after annealing at 673 K for 888 h are shown in Fig. 5. Metallographic examinations of the samples (Fig. 5(a)) showed that most particles exhibited a regular and a smooth interface. There was no discernable formation of an intermediate phase layer in atomized particles except in some small particles. EPMA traces of the fuel sample, containing atomized particles (Fig. 5(b)), confirmed that there was no formation of an interaction phase between U_3Si_2 particle and Al matrix, as evidenced by a sharp drop in Al composition in the probe traces. Thus, the atomized sample has reacted to a lesser degree overall compared to the comminuted particle, and the volume increase in the atomized fuel specimens was about half that of the comminuted fuel specimens (Fig. 1).

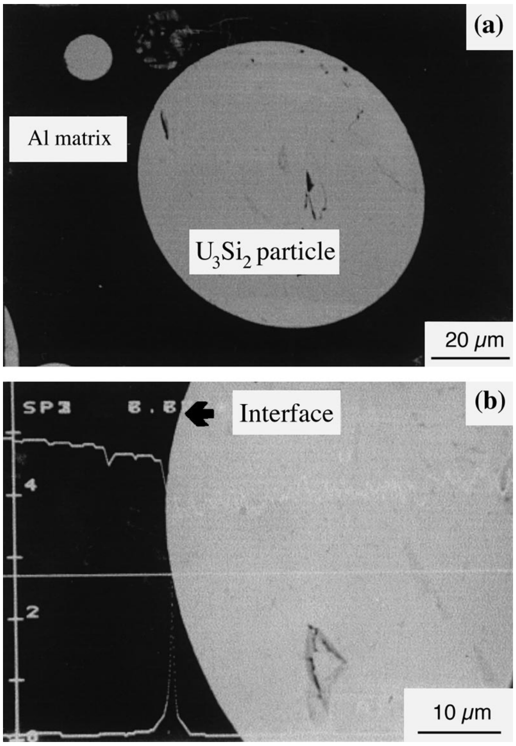

Fig. 5. Backscattered electron images (a) and electron microanalysis traces (b) of 15 vol.% U_3Si_2 fuel rod with atomized powder after annealing at 673 K for 888 h.

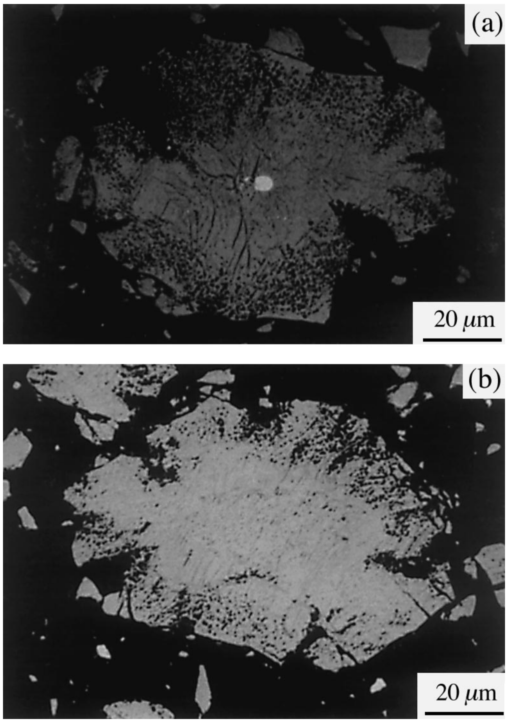

Fig. 4. Backscattered electron images of 15 vol.% U_3Si_2 dispersion sample with comminuted particles after annealing at 803 K for (a) 100 h, (b) 234 h.

BSE images of the 15 vol.% fuel samples with atomized powder after annealing at 803 K for various times are shown in Figs. 6 and 7. The interaction phase layer after 10 h has formed to occupy about half of the particle cross-section (Fig. 6). This resulted in a volume change of 3%, which is less than that of the comparable comminuted powder fuel samples (Fig. 1). There were some cracks and pores around the surface of the reacted regions similar to those in the comparable comminuted samples. The fine particles were generally almost fully reacted. After 100 h at 803 K the 15 vol.% U_3Si_2 fuel samples with atomized powder, were composed mainly of particles with smaller unreacted centers (Fig. 7(a)). The formation of the reaction products after 234 h was virtually complete (Fig. 7(b)). As was the case for the fuel samples with comminuted powder, metallography following the 234 h test at 803 K also revealed that the substantially swollen specimens contained large pores, usually at the aluminum matrix – U_3Si_2 particle interfaces. Many pores were concentrated around the cracks

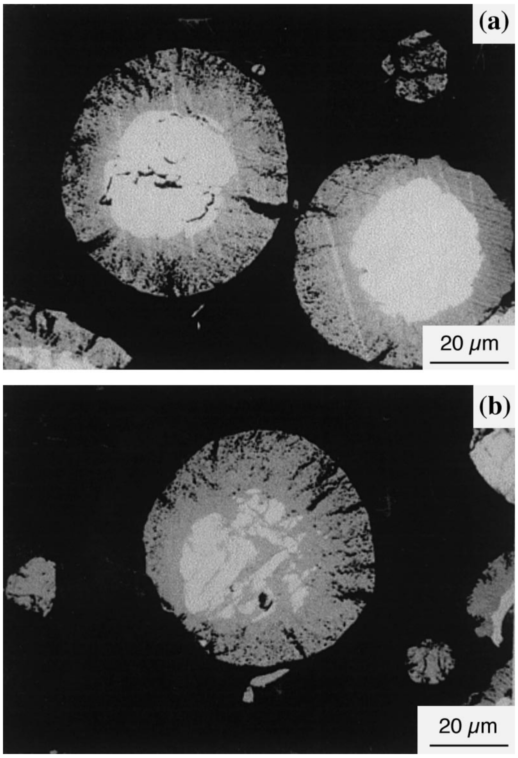

Fig. 6. Backscattered electron images of 15 vol.% U_3Si_2 fuel meat with atomized particles after annealing at 803 K for 10 h; (a) uniform reacted center, (b) several islands in center.

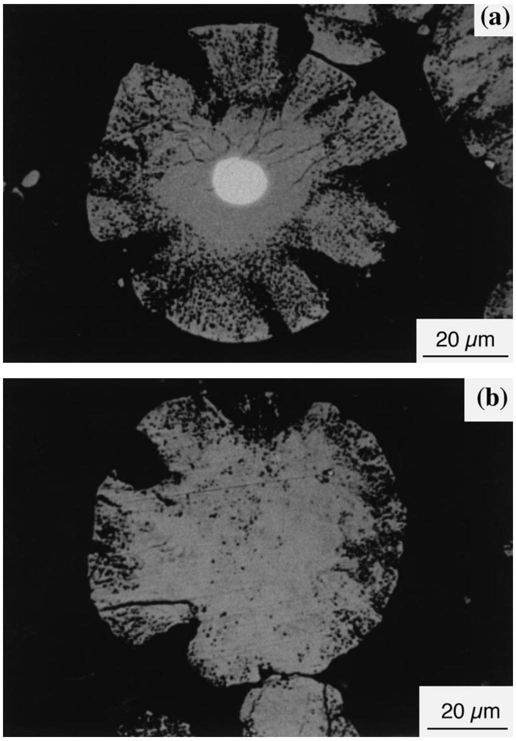

Fig. 7. Backscattered electron images of 15 vol.% U_3Si_2 fuel meat with atomized particles after annealing at 803 K; (a) 100 h, (b) 234 h.

in the peripheral region similar to the comminuted fuel samples, and also, the fuel particles were entirely reacted. In addition, X-ray diffraction patterns of the 15 vol.% fuel samples annealed for 234 h confirmed that the reaction compound was $U(Al,Si)_3$, composed of a solid solution of UAl_3 and USi_3, irrespective of the preparation method of U_3Si_2 powders (Fig. 8).

4. Discussion

As the aluminum reacts with the fuel, the fuel's volume increases due to the difference between densities of the original particle and reaction product, and pores formation [9]. Annealing experiments with dispersion U_3Si_2–Al fuel samples have shown that the growth of the reaction layer at the interface obeys classical diffusion kinetics, i.e., the width of the layer Y is described by: $Y_2 = [K_0 \exp(-Q_{th}/RT)t]$, where Q_{th} is the effective activation energy for interdiffusion in $U(Al,Si)_3$ [2,3], K_0 is a reaction constant, t is time in seconds, T is the absolute temperature, and R is the gas constant. The volume change during thermal annealing is not linearly dependent on the fuel volume fraction. The cause of the additional swelling in the higher loaded samples can be attributed to the higher as-fabricated porosity in the 50 vol.% U_3Si_2 fuel samples compared with the 15 vol.% U_3Si_2 fuel samples, as shown in Fig. 9.

Samples with the comminuted powder showed a larger volume increase compared with those prepared with the atomized powder. The possible reasons can be supposed as follows. The specific surface area of the spherical atomized powder is 30% smaller than that of the irregular comminuted powder, resulting in a correspondingly smaller diffusion interface [24]. In addition, the porosity of fuel meat with atomized spherical powder, believed to be a result of particle cracking that occurs during the extrusion of the samples, is somewhat lower than that of the comminuted irregular powder after extruding, as illustrated in Fig. 9 [25]. After sufficient interdiffusion, trace impurity gases such as hydrogen present primarily on the Al powder surface are released to the as-fabricated pores [2]. The as-fabricated pores are stabilized and extended by the released gases. This results in a weakening of the dispersion and yet greater swelling of fuel core. Moreover, the interdiffusion in the comminuted particles during thermal annealing can be divided into two paths; first, uniform diffusion, through the phase interface, leaving a kernel-like island or several islands; secondly, through defor-

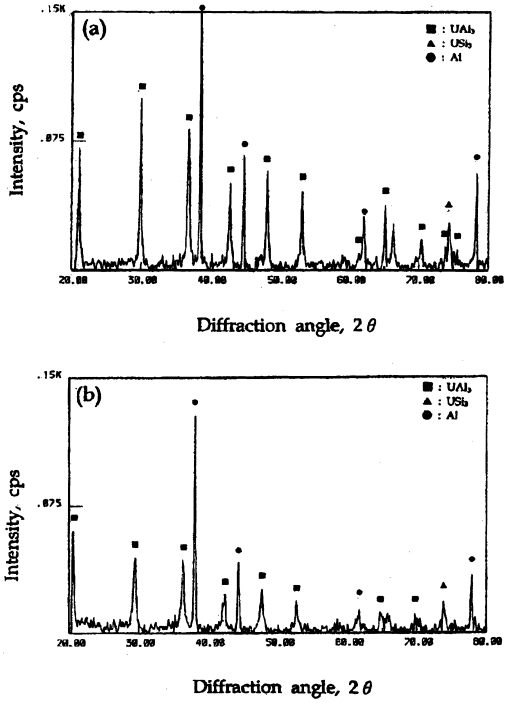

Fig. 8. X-ray diffraction patterns of 15 vol.% fuel samples after annealing at 803 K for 234 h; (a) comminuted powder, (b) atomized powder.

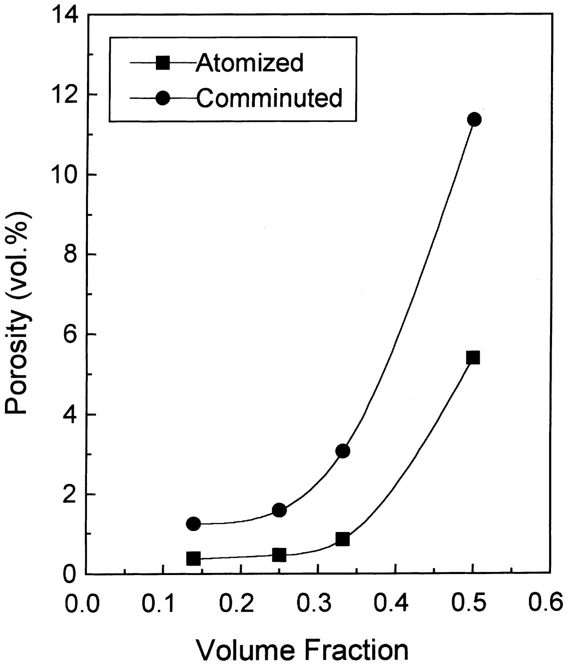

Fig. 9. Void content of extruded fuel cores with comminuted and atomized U_3Si_2 particles.

mation zones or cracks, leaving a network of unreacted islands. These deformation zones may play a role in accelerating the penetration of aluminum atoms. Samples in the atomized powder have somewhat different penetration paths. That is, in addition to uniform diffusion there appears to be diffusion along the many grain boundaries in the much finer grained material (Fig. 10), leaving unreacted islands [26].

The end point of the interaction occurs when all U_3Si_2 had been consumed to form the low density-compound of U(Al,Si)$_3$, as shown in Fig. 8 [16]. U(Al,Si)$_3$ has a composition intermediate between UAl_3 and USi_3, two cubic compounds that are mutually soluble [27]. The Al-to-Si ratio is approximately 3.5, and the composition of the compound lies on the tieline between U_3Si_2 and Al in the ternary phase diagrams. Many features of the observation may be explained by the following simple model. It is postulated that the seven aluminum atoms that react with U_3Si_2 are as follows:

$$U_3Si_2 + 7Al = 3U(Al,Si)_3. \qquad (1)$$

The relatively large fraction of Al involved in this formation and the higher relative diffusivity of Al compared to U and Si results in a vacancy flux toward the Al side of the diffusion front. The vacancies created at the U_3Si_2/matrix interface when not migrating away to free surfaces, may condense to form pores which may be stabilized by gas released during the consumption of Al. Many cracks are also formed in the peripheral region due to the formation of the brittle intermediate phase layer having a lower density. Castleman [28] has attributed the cracks to stresses as generated by volume changes during the reaction of, in his case, U and Al into the intermetallic compounds. The as-fabricated porosity, cracks and vacancy voids are all stabilized in a similar fashion, i.e., by absorbed gases that are released during the interdiffusion process.

It should be pointed out that under irradiation the diffusion mechanism may be different. However, if conditions prevail to cause substantial interaction, ef-

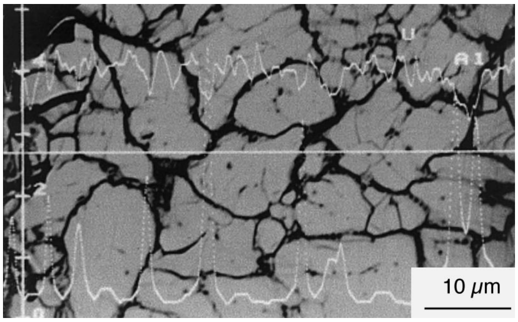

Fig. 10. Backscattered electron images of 15 vol.% U_3Si_2 fuel meat with atomized powder after annealing at 673 K for 530 h.

fects as observed in the present experiment cannot be ruled out. Indeed, some high temperature irradiation experiments with U_3Si_2–Al dispersion fuel appear to confirm this [7].

5. Conclusion

The thermal compatibility of atomized U_3Si_2 dispersed fuel meats was characterized and compared with that of comminuted U_3Si_2.

1. The amount of swelling was found to increase with increasing temperature and heating time and proportion of dispersed U_3Si_2.
2. U_3Si_2 fuel samples prepared from the atomized powder showed a smaller volume increase after annealing compared to those from the comminuted powder, irrespective of the heat treatment temperature and the volume fraction of the U_3Si_2 powder. The following explanation is offered.
   (a) The smaller specific surface area of atomized spherical powder compared to the irregular comminuted powder reduces the overall interdiffusion rate.
   (b) Atomized fuel samples have lower as-fabricated porosity. This provides more void space for released gases and less restraint on swelling.
   (c) U_3Si_2 fuel samples from comminuted powder have different high diffusion penetration paths, that is, along deformation zones which originate from the comminution and extrusion process.
3. There are two pronounced penetration paths of aluminum into U_3Si_2 powder:
   (a) Uniformly through the phase interface,
   (b) Along the grain boundaries.

Acknowledgements

We would like to acknowledge the support of the experimental work by Se-Jung Jang, Hyun-Suk Ahn, Yung-Mo Ko and Don-Bae Lee. Thanks are also due to Dr Il-Hyun Kuk of Korea Atomic Energy Research Institute for considerate comments.

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