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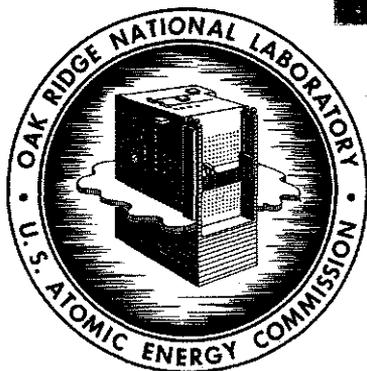
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ORNL-4056
UC-25 - Metals, Ceramics, and Materials

SWELLING OF UAl_3 -Al COMPACTS

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METALS AND CERAMICS DIVISION

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JANUARY 1967

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The UAl_3 , which does not melt congruently, can be formed by melting uranium and aluminum together and then heat treating. It can also be made by hydriding the uranium to produce the powdered hydride, mixing this with the required amount of aluminum powder, and then either hot pressing or cold pressing and sintering. Cold pressing and sintering in a vacuum seems to be the most attractive method for producing the inter-metallic. Irrespective of how it is produced, UAl_3 is brittle and can be readily crushed and screened to particles within the desired size range of $-170 +325$ mesh.³

EXPERIMENTAL PROCEDURE

At the Oak Ridge National Laboratory the sized UAl_3 powder is blended with aluminum powder and cold pressed into a compact using a pressure of 22.5 tons/in.². Stearic acid is normally used as the die lubricant. The cold-pressed compacts are then vacuum degassed at a temperature of 590°C. Swelling of the compacts has been observed after this step, and the degassed compacts may be too large to fit into the assembly that is to be the cladding. The swelling is apparently independent of the method of producing the UAl_3 and of the grade of aluminum powder used. In producing compacts for ORR fuel elements, dimensional changes of the compacts on vacuum degassing were not great enough to cause any difficulty in producing fuel elements, but these compacts contain only approximately 30 wt % UAl_3 instead of the 50 wt % as needed for ATR elements.⁴

In studying the influence of various factors on the swelling of compacts during vacuum degassing, a number of cylindrical compacts 1/2 in. in diameter and 1/2 in. high were made, using various lots of both UAl_3 and the aluminum powder, and vacuum degassed for 2 hr at several temperatures.⁵

³W. J. Werner, J. H. Erwin, M. M. Martin, and C. F. Leitten, Jr., Fuels and Materials Development Program Quart. Progr. Rept. June 30, 1965, ORNL-TM-1200, pp. 9-12. (OFFICIAL USE ONLY).

⁴W. J. Werner, J. H. Erwin, and M. M. Martin, Fuels and Materials Development Program Quart. Progr. Rept. Mar. 31, 1966, ORNL-TM-1500, pp. 18-22. (OFFICIAL USE ONLY).

⁵W. J. Werner, M. M. Martin, and J. H. Erwin, Metals and Ceramics Div. Ann. Progr. Rept. June 30, 1966, ORNL-3970, pp. 107-109.

Heights and diameters of each compact were measured before and after degassing. The percentage increase in height and diameter of a representative number of compacts is shown in Table 1. As indicated in the table, the percentage increase in height on degassing at 525°C or below was generally less than 1%, while degassing at 590°C generally resulted in the height increasing by from 5 to 8%. The percentage increase in diameter is generally less than the increase in height by a factor of 3 or 4.

Table 1. The Effect of Outgassing Temperature on Pellet Size

Pellet Number	Fuel	Matrix	Outgas Temperature (°C)	Percentage Increase in Length	Percentage Increase in Diameter
1	Depleted UAl ₃	X 8001 Al	350	0.30	0.10
2	disk crushed to		400	0.41	0.10
3	-170 +325 mesh		450	0.40	0.20
4			500	0.40	0.20
5			525	0.80	0.20
6			550	2.98	1.19
7	Depleted UAl ₃	X 8001 Al	590	4.75	1.80
	-170 +325 mesh				
8	Depleted UAl ₃	X 8001 Al	590	3.12	1.19
	-170 +325 mesh				
11 ^a	Enriched UAl ₃	X 8001 Al	590	8.21	4.34
12 ^a	hand crushed	101 Al	590	8.94	4.14
	through 170				
	mesh screen				
13 ^a	Depleted UAl ₃	X 8001 Al	590	5.51	1.97
14 ^a	-170 +325 mesh	101 Al	590	5.42	1.78
15 ^a	Enriched UAl ₃	X 8001 Al	590	7.01	3.95
16 ^a	hand crushed	101 Al	590	6.72	3.35
	through 170				
	mesh screen				
17 ^a	Enriched UAl ₃	X 8001 Al	590	8.00	4.54
18 ^a	hand crushed	101 Al	590	7.51	3.75
	through 170				
	mesh screen				

^aSamples outgassed in aluminum degassing furnace.

METALLOGRAPHIC AND X-RAY EXAMINATIONS

The swelling of the compacts on degassing is of concern not only because of the difficulty of inserting the compacts in the frame and cover, but also because of the fear that swelling may continue during subsequent steps in fabricating the fuel element or during irradiation. Previous experiences with uranium oxide dispersants lead one to expect that gas release produces the swelling.⁶ Examination of the surfaces of the compacts with a binocular microscope and metallographic examination of sectioned compacts, however, afford good evidence that swelling is not caused by gas. As can be seen from a macrograph of the surface of a swelled compact, Fig. 1, there are cracks on the surface, generally in a circumferential direction, that give the impression that layers of material are being pulled apart. Figure 2 is a micrograph of a longitudinal section of a compact as pressed, while Fig. 3 is a similar micrograph

⁶R. C. Waugh, The Reaction and Growth of Uranium Dioxide-Aluminum Fuel Plates and Compacts, ORNL-2701 (March 1959).

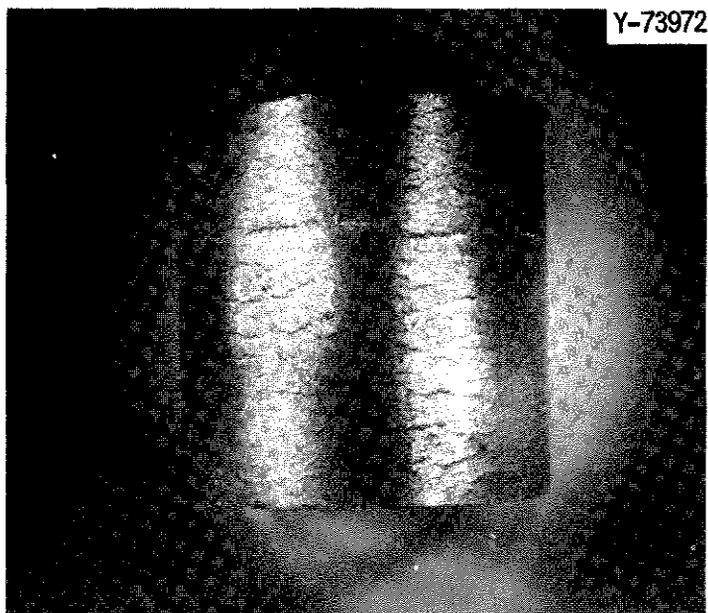


Fig. 1. Surface of a Cold-Pressed UAl_3 -Al Pellet After Degassing 2 hr at $590^\circ C$. 4x.

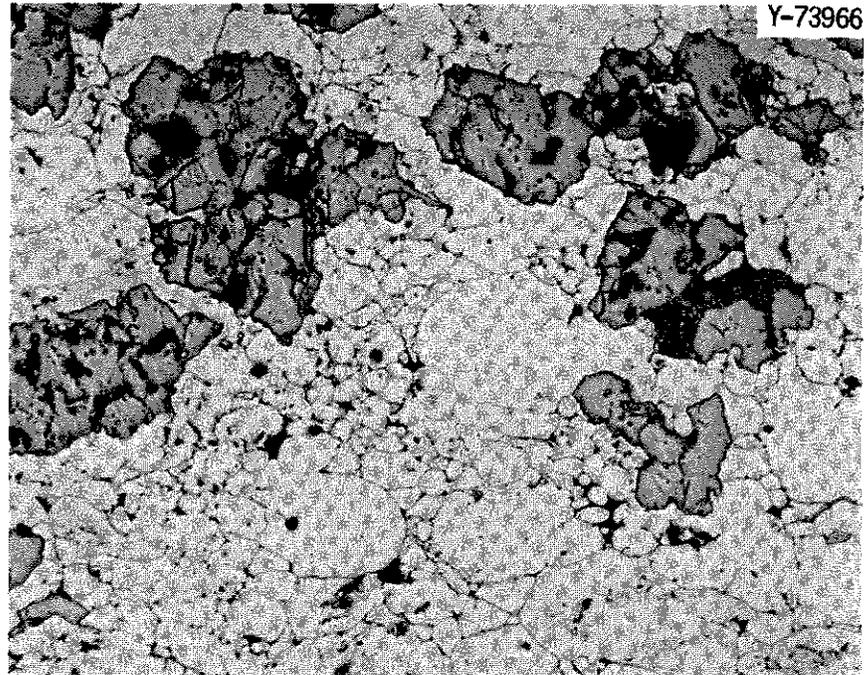


Fig. 2. Longitudinal Section Through As-Cold-Pressed Pellet of UAl_3 . 200X.

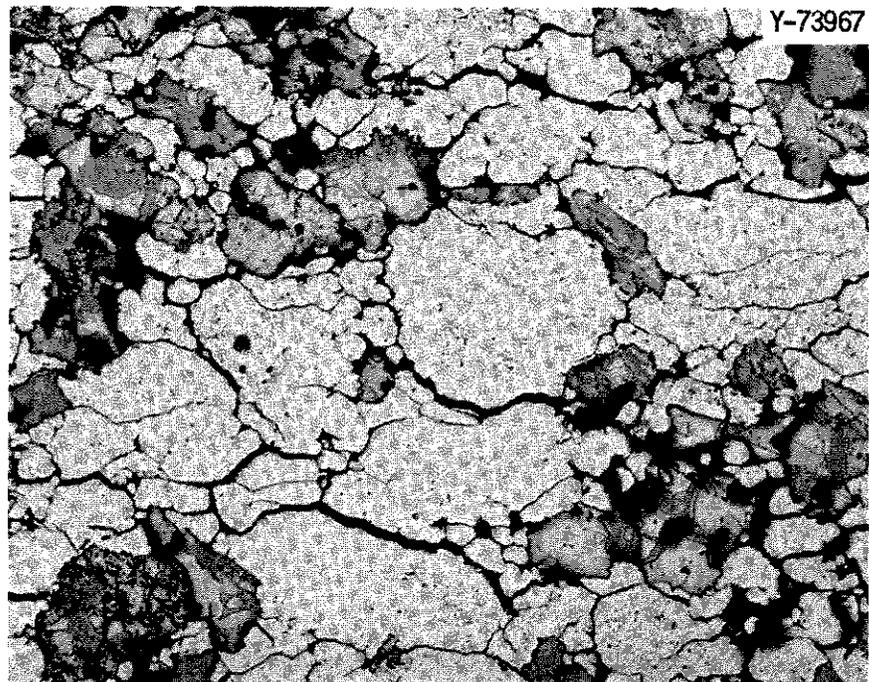


Fig. 3. Longitudinal Section Through Cold-Pressed and Degassed Pellet of UAl_3 . 200X.

of a compact degassed for 2 hr at 590°C. The latter shows that some of the grains have been forced apart, and is clear evidence that at the time the grains were forced apart to produce swelling they were not welded together, but were rather individual particles in mechanical contact. The material is behaving somewhat as though the volume of the intermetallic particles was increasing without a corresponding decrease in the volume of the matrix. As the UAl_3 is converted to UAl_4 by absorption of aluminum, the total volume, however, changes very little. In spite of the very minor change in total volume as the intermetallic is converted, we attempted to determine whether or not the swelling is accompanied by conversion. X-ray diffraction patterns of compacts heated to 525°C indicate that very little of the compound is converted, but that on heating for 2 hr at 590°C something like one-half of the UAl_3 is converted to UAl_4 . Room-temperature metallographic examination of compacts heated to the higher temperature also indicates partial conversion, the noncubic UAl_4 being distinguishable from UAl_3 by polarized light. Moreover, metallographic examination shows that the UAl_4 grows into the UAl_3 from sites at the surface of the UAl_3 rather than growing uniformly from the surface to form hulls around the UAl_3 . This interpretation is also confirmed by observations of reactions of a compact when heated on the heating stage of a microscope as described below.

HEATING-STAGE EXAMINATION

Description of Apparatus

A heating-stage microscope provides a means of observing microstructures directly at temperatures up to 1800°C. The apparatus consists of a small vacuum chamber that sits on the stage of an inverted microscope with a quartz viewing window positioned over the objective lens. The specimen is a right-circular cylinder with one end polished to a metallographic finish, and is inserted in the chamber behind the viewing window for microscopic observation. The specimen is radiantly heated by molybdenum strips that fit around the specimen. The temperature is determined by a Pt vs Pt-10% Rh thermocouple inserted in a well in the specimen about 1/16 in. behind the polished surface.

Figure 4 is an overall view of the heating-stage metallograph. Figure 5 shows a closeup of the furnace open with the top half containing the molybdenum strip heaters on the left and the base with a specimen in place at right center. The thermocouple can be seen in the well in the specimen.

The system can be evacuated to a pressure below 1×10^{-5} torr at room temperature. The pumps are able to maintain a satisfactory vacuum for all but the most reactive materials at high temperature.

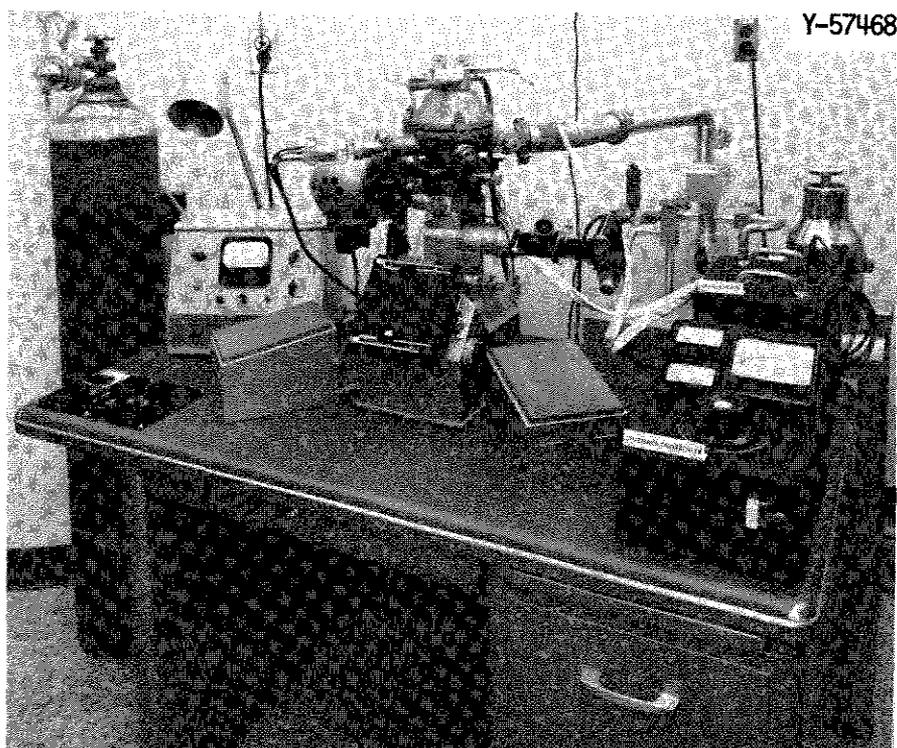


Fig. 4. Heating Stage Metallograph.

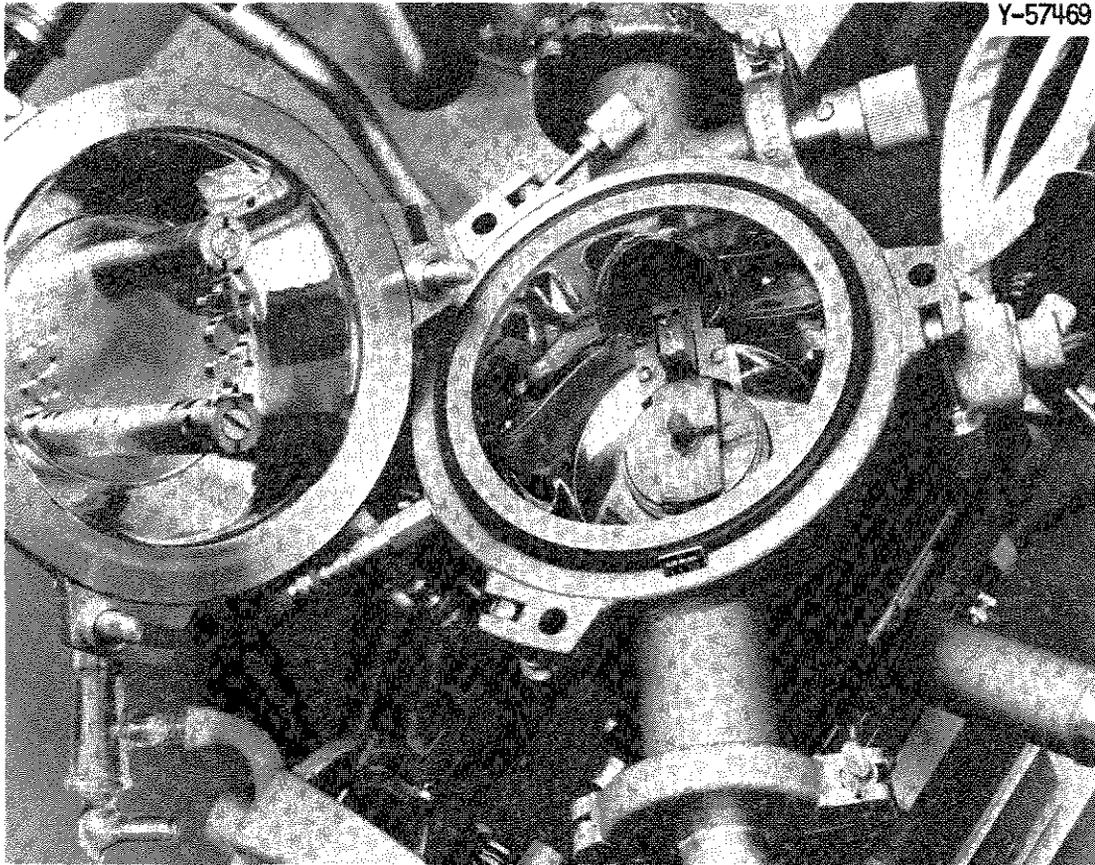


Fig. 5. Heating-Stage Furnace. Top half containing strip heaters is on the left and the base showing a specimen in place is on the right.

Examination Procedures

Five cold-pressed pellets of composition 50 wt % UAl_3 were machined to the shape and size required for the heating stage. These were carefully polished on the face to be observed using standard metallographic techniques, and all were eventually examined on the heating stage. No etching was necessary because there was adequate contrast between the UAl_3 and the aluminum matrix to observe any change that might take place. The results reported below are generally representative of all five samples.

A specimen was placed in the stage and the system evacuated to about 1×10^{-4} torr before heating. A preliminary bakeout at $200^\circ C$ was employed to remove any water vapor that remained from the polishing operation. This bakeout period continued until the pressure stabilized, usually $1/4$ to $1/2$ hr, and then the temperature was raised slowly until some

change in the microstructure was noted. This change usually occurred between 320 and 350°C and the initial indication was in the form of a fine crack in a particle of UAl_3 followed by the growth of a striated structure from this crack. Growth of more of the same phase usually would simultaneously occur at holes and corners of the particle and continue until the entire particle was consumed. Whenever the transformation was first seen, if the power setting remained unchanged, a rise in temperature of about 20 to 30°C was noted, indicating that the transformation is exothermic.

Once the transformation started it was necessary to raise the specimen temperature to force the transformation to completion in some reasonable time. The time to complete the observed transformation varied from one specimen to another, but no attempt was made to determine the reason for the variation.

Figure 6 is a series of photomicrographs taken on the heating-stage metallograph and illustrates the transformation of UAl_3 to UAl_4 . A field taken at room temperature is shown in (a) and again in (b) 1 hr and 10 min after the beginning of the run. The first change in microstructure can be observed at 328°C. Position ① shows some cracks in the UAl_3 and the beginning of transformation; position ② shows transformation beginning at a corner; position ③ is a crack that indicates a change of volume or shape beneath the surface; and position ④ shows the aluminum matrix being pushed up and distorted by the changing UAl_3 grain. The photomicrograph in (c) was taken 10 min after that shown in (b) and at 341°C. The transformation is proceeding rapidly and beginning to appear in other places; positions ①, ②, and ③ are new sites of transformation. The temperature was continuously raised during this run to complete the observed transformation in about 2 hr. The photomicrograph in (d) was taken 25 min later at 434°C. A large crack has occurred at position ①; likewise, a crack has appeared in the aluminum matrix as the particles change shape (position ②). Notice how the area surrounding the particle is out of focus, indicating a sizable change in level across the specimen surface, and how the particle protrudes from the matrix. The field shown in (e) and (f) was taken at 30 and 35 min, respectively, after that shown in (b)

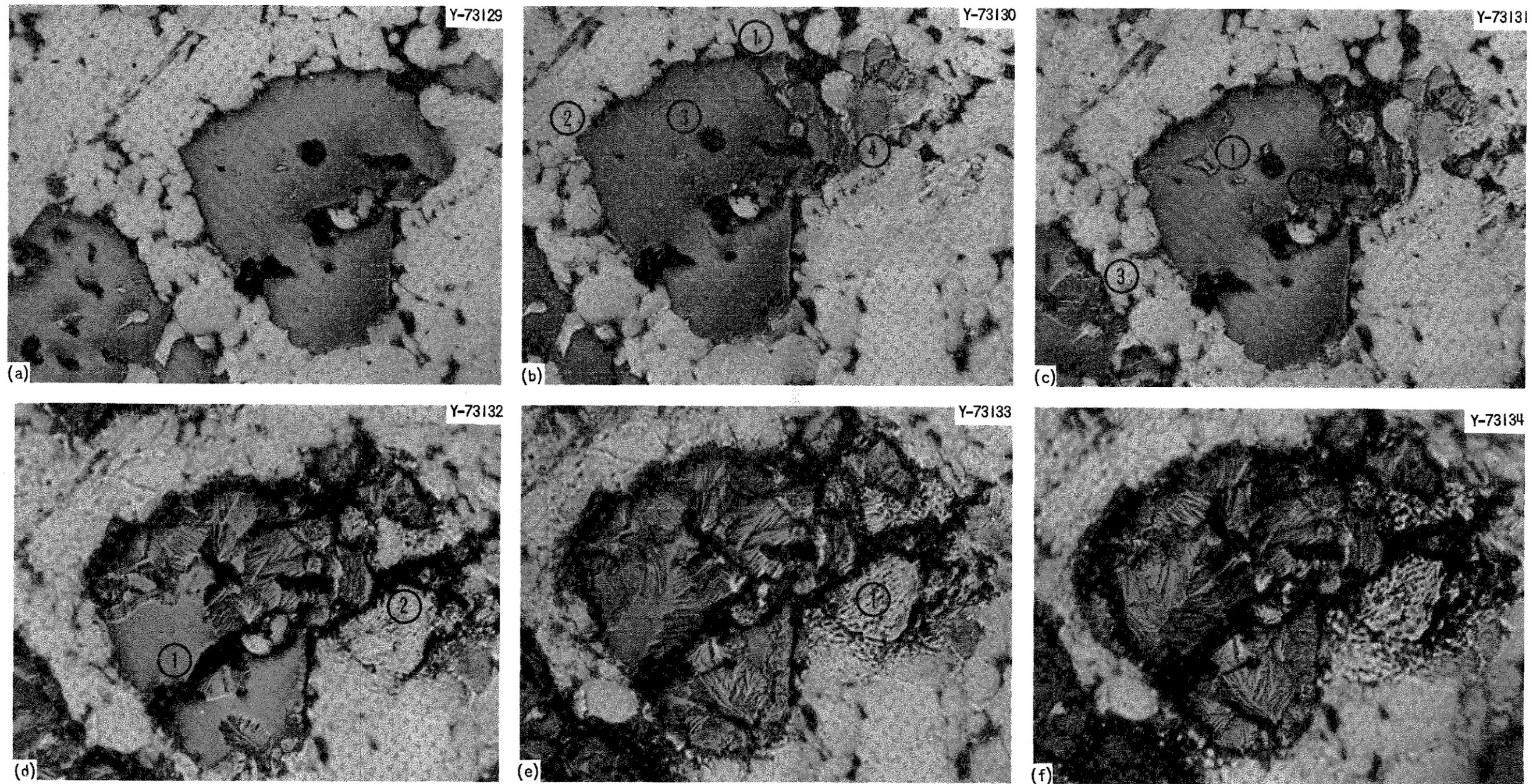


Fig. 6. Photomicrographs from the Heating-Stage Metallograph Illustrating the Transformation of UAl_3 to UAl_4 . 400X.

and shows the transformation apparently going to completion. The aluminum around the particle is severely deformed due to the pressure of the changing particle, as shown in position (L), in (e).

Figure 7 is another field at a lower magnification showing an intergranular crack originating at a particle. The surface is uneven and bulged, indicating the presence of a particle below the surface.

The specimens examined on the heating stage showed conversion taking place at temperatures considerably below those used for vacuum degassing. In order to satisfy ourselves concerning the accuracy of the temperatures read on the heating stage, the temperatures stated above were obtained with a precision potentiometer.⁷ To further check the accuracy of the heating-stage meter, a separate test was made in which a sample of pure copper was heated to its melting point. When incipient melting was observed in the microscope, the meter for the heating stage indicated between 1080 and 1100°C. The melting point of copper is 1083°C.

⁷Rubicon Instruments Potentiometer Model 2745, Division of Minneapolis-Honeywell Company, Philadelphia, Pennsylvania.

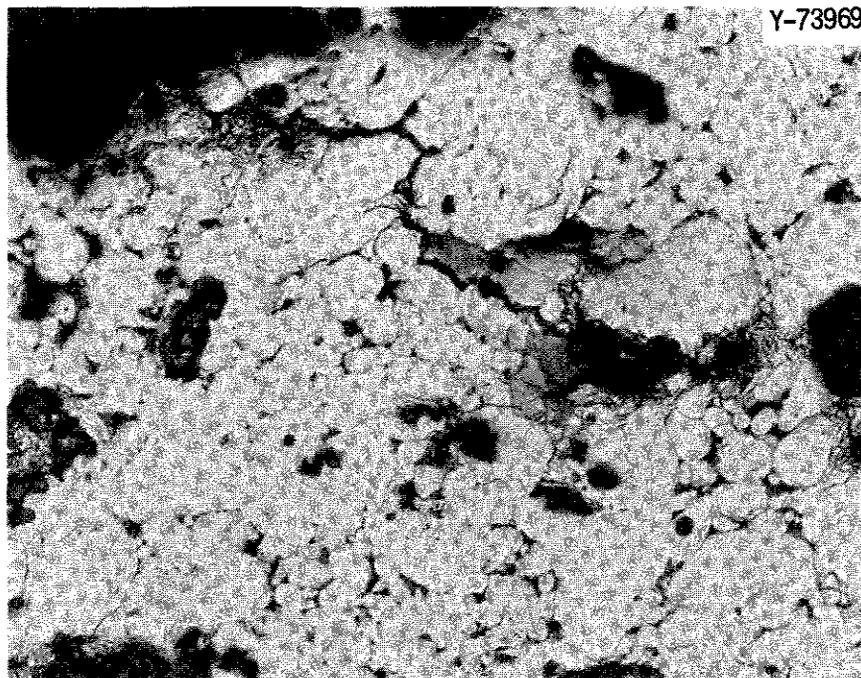


Fig. 7. Heating-Stage Specimen Showing Intergranular Crack Extending from Transformed Particle. 200X.

Two of the specimens examined on the heating-stage metallograph and exhibiting apparently complete transformation were subsequently examined by x-ray diffraction and found to have been substantially transformed to UAl_4 . Some UAl_3 was found in each, however, indicating that microscopic evaluation of complete conversion was not completely accurate. In each run the pressure in the heating stage was watched carefully as swelling took place. If swelling was due to gas evolution, some abrupt pressure rise should have been noted. There was none.

The swelling by solid-state reactions on sintering compacts consisting of two phases has been observed by others, including Williams and Jones.⁸ In almost all cases where appreciable swelling was observed a product had a range of solubility; a marked exception occurs with aluminum-uranium alloys, which according to the accepted phase diagram do not form compounds of variable composition. However, a marked swelling is observed in compacts yielding UAl_4 on sintering. Williams and Jones suggest that swelling is due to diffusional porosity in the UAl_4 phase, and that the so-called UAl_4 compound actually has a variable composition. This could be a factor in the swelling of the compacts described here, but the microscopic observations prove that even if this is a factor the major porosity results from pushing apart of the aluminum particles and not to an unexpected low density of the UAl_4 .

CONCLUSIONS

We postulated that swelling results from irregular growth of the intermetallic particles as they absorb aluminum to form UAl_4 ; this irregular growth simply forces the unbonded grains apart. The observations made on the heating-stage metallograph bear out this postulate.

The difficulties resulting from the swelling of compacts that are to be used as cores in fuel elements may be overcome by degassing at a temperature below which significant amounts of UAl_3 are converted to UAl_4 (in the neighborhood of 500°C), providing that such a temperature is high

⁸J. Williams and J.W.S. Jones, The Formation of Uranium and Beryllium Alloys by the Solid-State Sintering of Mixed Elemental Powders, AERE-MTR 1974 (June 7, 1966).

enough for degassing. Another possibility is that of pressing compacts smaller in the lateral dimensions than required for cores and then coining to the desired dimensions after degassing. A third possibility might be to add sufficient silicon to the UAl_3 to stabilize it in the presence of aluminum.⁹ Preliminary tests have indicated that a silicon addition to UAl_3 in the range 2 to 5 wt % stabilizes the intermetallic in the presence of aluminum at 590°C.

ACKNOWLEDGMENTS

Thanks are due to M. M. Martin and W. R. Johnson for producing compacts and obtaining the dimensional data included above. Also thanks are due to A. E. Richt for calling the authors' attentions to some prior work on swelling of compacts.

⁹Personal communication from C. F. Leitten, Jr., July 1966.

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