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METALLOGRAPHIC AND MICROPROBE EXAMINATION OF ELEMENTAL
REDISTRIBUTION IN LIQUID SODIUM SYSTEMS*

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ABSTRACT

Tubular test specimens fabricated from various metals were subjected to liquid sodium at temperatures ranging from 700 °C-760 °C in a forced circulation loop. Zones of elemental depletion and enhancement were studied using metallographic and microprobe techniques.

*This work performed under the auspices of the U. S. Atomic Energy Commission.

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THE OPERATION AND MODIFICATION OF THE DEEP FIELD MICROSCOPE

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Abstract

The deep field microscope enables the microscopist to photograph specimens of varying size and unusual shape. Because of its great depth of field, this instrument's specimen range far exceeds that of other optical microscopes of equivalent magnification. It has a theoretical depth of field of 6 mm at 38X magnification and a depth of field of 600 μ m at 250X magnification.

Several problem areas and limitations to its use were encountered. This paper discusses the operation of the microscope, its limitations, and examples of its application and range of usefulness. The resolution of the microscope is a function of width of beam of light on the specimen and proper alignment of the light source.

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Alterations to the microscope were made to improve these characteristics and, therefore, improve the resolution.

Introduction

The principle of the deep field microscope was first described by D. McLachlan, Jr.¹ The deep field microscope is designed to photograph non-planer specimens which require a great focal depth, at a magnification between 17X and 236X. The present instrument is manufactured by Electronics and Alloys Inc. This paper describes the operation of the instrument, its advantages and disadvantages, and certain refinements which significantly improve the quality of the photographs.

Theory

In the standard microscope the entire specimen is illuminated, and the area of the specimen in focus is dependent upon the depth of field of the objective and the flatness of the specimen. In the deep field microscope the specimen is illuminated only on the focal plane of the objective by means of a narrow slit of light as seen in Fig. 1. All parts of the specimen which are out of focus

should be in total darkness. The specimen is moved through the plane of focus. Each portion of the specimen is illuminated as it intercepts the light beam causing an image of the specimen to form on the photographic film.

The range of magnification and depth of field is shown in Table I. It should be noted that, with all other factors being equal, the depth of scan is a function of the bellows extension and is inversely proportional to the area which can be photographed.

Description and Operation

A photograph of the instrument is shown in Fig. 2. The light sources are two 50-W tungsten lamps which are collimated through a 2.4×10^{-4} cm slit and condensed through a 40 mm objective to the specimen. These light sources are positioned 90° apart about the vertical axis of the specimen stage. Coarse adjustments of the light beam can be made by physically sliding the condensing lens back and forth in the slit tube. Final adjustments are made with the

knurled knobs located on the base of the instrument. The Zeiss EPT microscope with Luminar objectives is focused on the specimen, which sits at a 45° angle to the horizontal. A motor wound cable, located at the rear of the instrument, lowers the specimen through the plane of light. The integrated scan is recorded on the Graflock camera attachment. The controls for adjusting the intensity of the tungsten lamps are located on the right side of the instrument, and the stage speed controls are on the left side. Vibration is minimized by a 500 lb shock mounted console.

Problems and Solutions

Originally we could not obtain quality photomicrographs because of problems in the following areas: (1) exposure time, (2) continuous focus of the light beam, (3) high magnifications, and (4) motor speed. Alterations to the microscope improved the quality of the photographs taken with the instrument.

The first problem was associated with improper exposure time.

A cable is used to raise and lower the specimen stage. This cable is wound around a 1/2 in. diameter pulley which is turned by a variable speed motor. At its slowest speed the motor moved the specimen stage too fast to expose type 52 film ASA(400), and underexposed photomicrographs resulted. (Type 52 film was used because of its contrast and resolution.) The 1/2 in. diameter pulley was replaced by a 1/8 in. diameter pulley which moves the specimen stage at a slower speed to allow more time for exposure. At 34X magnification two hours are required for exposure of a typical specimen. Four hours are required for a 76X magnification. It is difficult to use color Polaroid[®] film ASA(75) because 20 to 40 hours of exposure time would be required.

Another major problem involved the focus of the light beam on the specimen. Because the microscope objective has a small depth of focus and the film records only that area illuminated at any one time, the quality of the photomicrograph is a function of the

focus of the beam. An illustration of this problem is shown schematically in Fig. 3. As the specimen travels down, the horizontal distance between the specimen surface and the focal plane of the light beam changes. When this happens the specimen surface is no longer illuminated by a focused beam. Illumination by the broad unfocused light beam of more of the specimen depth than the vertical depth of field of the microscope optics results in a loss of definition of surface detail. The depth of A' is greater than the depth of A as shown in Fig. 3. The resulting photomicrograph is in focus only near the focal plane center. The solution would be to change the position of the light source as the specimen travels downward. Therefore, the fine focusing knobs were replaced with a motor and timing chain as seen in Fig. 4. Since the specimen is positioned at a 45° angle to the horizontal, the motor is adjusted to move the light forward one unit as the specimen moves down one unit. The resulting photomicrograph is

then in focus from edge to edge.

Another problem was encountered when photography was attempted with the 16 mm objective. The beam of light always illuminated an area greater than the depth of field of the microscope optics. An attempt was made to narrow the width of the beam of light with a second slit positioned on the specimen side of the condensing lens. However, this decreased the intensity of the light to such a degree that it was impossible to expose the film available within a reasonable time period. A cylindrical lens was placed between the light source and the slit, but only a slight increase in light intensity was obtained.

A problem with uneven film exposure was attributed to uneven motor speed. The manufacturer, Electronics and Alloys, Inc., replaced the Globe Model C-5A-1092 motor which came with the instrument with a Motomatic Model E-550 motor.

Photographs and Results

An example of the improved depth of field of this instrument can be seen by comparing Fig. 5 and 6, which show a manganese nodule photographed at 78X. Only the top of the nodule is in focus in the optical 78X photomicrograph in Fig. 5. A 78X deep field photomicrograph of a similar nodule is shown in Fig. 6. The detail seen in Fig. 6 is not seen in Fig. 5. A 78X photomicrograph of a corroded 8-32 screw thread taken without the light focusing motor is shown in Fig. 7. The out of focus side of the screw is the result of the increased beam width as the specimen travels down. Using the focusing motor improved the resolution as shown in Fig. 8. A photograph taken with the specimen positioned 90° to that of Fig. 8 is shown in Fig. 9. The surface detail is good over an appreciable length of the screw. A 78X photomicrograph of a fractured surface of an electron beam weld is shown in Fig. 10. Welding spikes as well as the fracture weld are clearly visible. The crystal planes of a fractured antimony

specimen at 125X are seen in Fig. 11. Molybdenum coated shards are shown in Fig. 12. A textured surface is seen in Fig. 13.

Conclusion

The deep field microscope has a workable range of 17X to 78X. Increased light intensity is required for color Polaroid.® By changing lighting focus a complete photomicrograph can be taken. The resolution at low magnification is such that quality enlargements can be made. Specimens require no preparation prior to photography. Because the parts of the specimen are at the same distance from the lens, the resulting photomicrographs give isometric pictures making direct measurement possible. The deep focus microscope is a good instrument for photographing small irregular specimens in the 17X to 78X magnification range.

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Applied Optics, 3:9, 1009-1013 (1964).

TABLE I

Theoretical Range of Magnification and Depth of Field¹

<u>Magnification</u>	<u>Objective</u>	<u>Eye-Piece</u>	<u>Focal Length (cm)</u>	<u>Bellows Extension (cm)</u>	<u>Depth of Focus (cm)</u>	<u>Depth of Scan (cm)</u>
10X	2X	5X	48	25.4	1560	1.27
25X	3.5X	10X	30	17.8	556	0.51
50X	5X	10X	25	25.4	178	0.25
100X	10X	10X	16	25.4	40.5	0.13
200X	10X	20X	16	25.4	20.2	0.06
300X	20X	20X	8	19.0	5.5	0.04
400X	20X	20X	8	25.4	4.1	0.03
500X	20X	20X	8	31.7	3.3	0.02

Fig. 1. Working principle of the deep field microscope.

Fig. 2. The deep field microscope.

Fig. 3. Schematic illustrating light focusing problems.

Fig. 4. The timing chain assembly.

Fig. 5. A 78X optical microscope photomicrograph of only the top surface of an Mn nodule.

Fig. 6. A 78X deep field photomicrograph showing greater surface area and detail.

Fig. 7. A corroded screw thread without the aid of the light focusing. 78X.

Fig. 8. A corroded screw thread employing the lighting focus showing greater detail. 78X.

Fig. 9. The screw corroded thread rotated 90°. 78X.

Fig. 10. Welding spikes of an EB weld at 78X.

Fig. 11. Crystal planes of a fractured Sb crystal. 125X.

Fig. 12. Mo coated shards at 78X.

Fig. 13. A textured surface at 78X.

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METALLOGRAPHIC AND FRACTOGRAPHIC ANALYSIS OF
STAINLESS STEEL SPECIMENS AFTER LOW-CYCLE FATIGUE TESTING

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ABSTRACT

The metallographic and fractographic analysis of specimens tested under low-cycle fatigue conditions involved three general categories: (1) characterization of the fractured surface; (2) characterization of the fracture mode; and (3) characterization of the microstructure. The material tested was fully annealed Types 304, 316, and 348 stainless steel. Specimens were tested in air at various strain rates and strain ranges at elevated temperatures.

The characterization of the fracture surface was obtained using optical and electron microscopy. Plots of crack growth rate versus fatigue cycles showed that strain rate (and hence frequency) has only a small effect on the crack propagation rate, whereas the strain range is shown to be the primary rate controlling parameter in the evaluation of Type 304 stainless steel.

Fracture modes were studied by using longitudinal cross sections showing the crack initiation point and final fracture area of the fatigue specimens. The mode of crack initiation, crack propagation, and

final fracture were identified for three materials, two temperatures, three strain rates, and also for tests with various strain wave forms and hold periods at peak strain.

Optical and electron microscopy were used to characterize the microstructure by studying the grain boundary phase, intragranular phases, and subgrain formation developed during testing. The grain boundary phase was identified as $M_{23}C_6$ and is predominantly a chromium carbide in Type 304 and 316 stainless steel; the intragranular phase has not been identified because of its small size. Transmission electron microscopy revealed the formation of numerous subgrains at 650°C for the stainless steels evaluated.

METALLOGRAPHIC AND FRACTOGRAPHIC ANALYSIS OF
STAINLESS STEEL SPECIMENS AFTER LOW-CYCLE FATIGUE TESTING

As part of a research program designed to evaluate the low-cycle fatigue properties of temperature resistant materials, a metallographic analysis was undertaken to study the effects of this testing on the structure, and to correlate the resulting material structures with test conditions.

The metallographic and fractographic analysis of stainless steel specimens tested under low-cycle fatigue conditions involved three general categories: (1) characterization of the fractured surface, (2) characterization of the fracture mode, and (3) characterization of the microstructure. The materials tested were fully annealed Types 304, 316, and 348 stainless steels. Specimens were tested in air at strain rates of 4×10^{-3} , 4×10^{-4} , and $4 \times 10^{-5} \text{ sec}^{-1}$ using strain ranges of approximately 2, 1, and 0.5% at 430°, 650°, and 816°C (800°, 1200°, and 1500°F). All the low-cycle fatigue tests were performed^(1,2,3,4) using an hourglass specimen, and control of the diametral strain was the programmed test parameter.

CHARACTERIZATION OF FRACTURED SURFACE

Examination of the fractured surfaces at relatively low optical magnifications showed that certain specimens had striations or ripples across the fractured surface (Fig. 1). It has been established by Jacoby⁽⁵⁾, Ritter⁽⁶⁾, and others that each of these striations is the result of one cycle in the low-cycle fatigue test, and is formed by the

stepwise advance of the crack front during the cyclic application of stress. It has also been found that these striations appear only when the crack propagates transgranularly. When the crack propagates intergranularly there are no striations, and, in large-grained material, individual grains are obvious when viewed with the optical microscope (Fig. 2).

In the present investigation fatigue striations were studied using both optical and electron microscopy. Typical electron micrographs are presented in Fig. 3, showing striations on the fractured surfaces of two Type 348 stainless steel specimens which were fatigue tested at 430° and 816°C. Although Fig. 3A shows that replica electron microscopy is capable of providing distinct images of fatigue striations, it is often difficult to determine the precise location and orientation of a given field of view with respect to the point of fracture initiation on the original sample surface. In addition, Fig. 3B shows that for specimens tested in air, an increase in the test temperature leads to obliteration of the fatigue striations due to the formation of an oxide scale on the freshly exposed surface.

Using the stereomicroscope, counts were made of the number of striations present on the fractured surfaces of the Type 304 stainless steel tested under the conditions previously described. Measurements were also made of the distance between a given striation and the final fracture point. The results are shown in Figs. 4, 5, and 6, where the number of cycles prior to final fracture ($N_f - N$) is plotted against the measured crack length. From these curves it can be seen that normally

the crack length at failure for a given strain range is longer the lower the strain rate. The one exception occurred in the 2% strain range specimens, where the results were reversed. In most specimens the crack appeared to initiate at several points, with one crack predominating and progressing to final fracture. In the specimens tested at the fastest strain rate, however, the crack appeared to initiate at only one location and then propagate from this point.

The results of these measurements were plotted using the ratio of the crack length after N cycles to that at final fracture versus the number of cycles prior to final fracture (Fig. 7). The top curves are at 0.6% strain range, the middle group at 1% strain range, and the lower group at 2% strain range. From these curves, it can be seen that the strain rate (and hence frequency) has little effect on the crack propagation rate, but that strain range is the important factor. Also, the slopes of the curves decrease as the strain range decreases. Another interesting observation can be made considering a constant crack length ratio. Taking a ratio that corresponds to 70% of the length at failure, the cycles to failure were 95 at 0.6% strain range; 50 cycles at 1%; and 20 cycles at 2%. As indicated, the number of cycles prior to failure is smaller as the strain range increases, i.e., the strain range is the controlling factor in the rate of propagation.

No satisfactory explanation has been offered to explain the power law relation between plastic strain and life. One approach has been based on rate of crack growth. For example, Manson⁽⁷⁾ reported that the rate of crack growth per cycle in stress cycling is a power law of stress and crack length. Since $\Delta\sigma\sqrt{l}$ is a fundamental relation in stress

cycling, perhaps the parameter $\Delta\epsilon_p \sqrt{l}$, where $\Delta\epsilon_p$ is the plastic strain range and l is the crack length, can be used for fully-reversed strain cycling. Assuming a power law relation between the rate of crack growth and $\Delta\epsilon_p \sqrt{l}$, it follows that:

$$dl/dN = C(\Delta\epsilon_p \sqrt{l})^S$$

where S is a constant to be determined. The values of dl/dN were obtained from the curves where the number of cycles prior to final failure were plotted against the measured crack length for the two fastest strain rates and for three strain ranges. These results were plotted against $\Delta\epsilon_p \sqrt{l}$ as shown in Fig. 8. The values fall on a straight line indicating some degree of correlation, but the analysis of the data has not been completed. With additional studies it is hoped to determine if the slopes of these lines are related to the slope of the line relating plastic strain range and cycles to failure.

CHARACTERIZATION OF FRACTURE MODE

In order to characterize the fracture mode, the low-cycle fatigue specimens were sectioned longitudinally through crack initiation point and final fracture area. These cross sections were then mounted in an epoxy resin containing pelletized alumina to help preserve the edge of the fractured surface, and prepared for metallographic evaluation.

The Type 348 stainless steel, Fig. 9, had a duplex grain structure with a fine grained center (ASTM 10) surrounded by a coarse grained outer layer (ASTM 4). The amount of the fine grained material varied from specimen to specimen. In all the specimens tested the fracture

initiated intergranularly in the large grained material and propagated transgranularly.

The Type 316 stainless steel, Fig. 10, was fully annealed with an ASTM grain size of 3 to 4 and a DPH (100 gm) of 171. In the low-cycle fatigue specimens tested at 650°C and a 2% strain range, the crack initiated intergranularly; at the 1 and 0.5% strain ranges the crack initiated transgranularly. Only those specimens tested at the 2% strain range showed cavities or grain boundary separations normal to the stress axis, Fig. 11. At 816°C the crack initiated transgranularly in those specimens tested at 1 and 0.5% strain range for the fastest strain rate, while in all the others the crack initiated intergranularly. No grain boundary separations or cavities were noted in these specimens. The mode of crack propagation changed from intergranular, to a mixture of inter- and transgranular, to transgranular as the strain rate increased at both temperatures.

The Type 304 stainless steel, Fig. 12, was fully annealed with an ASTM grain size of 3 to 4 and a DPH (100 gm) of 139. At 650°C the crack initiated and propagated transgranularly at the fastest strain rate, while at the other strain rates the crack initiated intergranularly and the mode of propagation was a mixture of trans- and intergranular. At 816°C the crack initiated and propagated intergranularly.

Results of the metallographic analyses of the stainless steel specimens are summarized in Tables 1 and 2.

The effects of hold time at peak strain on the structure of Type 304 stainless steel were studied. These tests were run at an axial

strain range of 2% and a strain rate of $4 \times 10^{-3} \text{ sec}^{-1}$ at 650°C with various holding times at peak strain in tension or compression or both. There was a similarity in the topography of the fractured surface of the low-cycle fatigue specimens tested with zero hold time, 30-minute hold time in both tension and compression, and the 30-minute hold time in compression only in that they all showed fatigue striations on the fractured surface indicative of transgranular crack propagation (Fig. 1). The specimens held only in tension had the appearance of the fracture occurring at the grain boundaries (Fig. 2). Metallographic examination of the longitudinal cross section of the hold time specimens indicated that the fracture initiated and propagated transgranularly in all cases except in the specimens held only in tension at the peak strain. In the specimens held in tension only the fracture initiated and propagated intergranularly (Figs. 13 and 14). Grain boundary separations also occurred near the fracture and were quite similar to those normally encountered in elevated temperature stress-rupture evaluations. These separations did not occur in specimens held only in compression or in specimens held in both tension and compression. Fig. 15 shows the grain boundary separations normal to the stress axis of a specimen held in tension for 30 minutes at the peak strain. The structure of the specimen held in tension for 60 minutes at peak strain was similar to that shown in Figs. 12 and 13. The fracture mode characterization is summarized in Table 3.

CHARACTERIZATION OF MICROSTRUCTURE

Optical and electron microscopy were used to characterize the microstructure of Types 304 and 316 stainless steel by studying the grain boundary phase, intragranular phases, and subgrain formation developed during low-cycle fatigue testing. As mentioned previously, the Type 316 stainless steel was fully recrystallized with a uniform equiaxed grain structure (Fig. 10). There was an occasional large oxide particle with stringers of small non-metallic particles, and a second phase dispersed throughout the grains with an occasional blocky intragranular particle. The grain boundaries were generally clean and contained relatively few precipitates. After testing, a grain boundary phase developed, Fig. 16. As can be seen, the grain boundary phase is continuous at 650°C but is discontinuous at 816°C. Fig. 17 shows typical replica electron micrographs of this grain boundary phase. Fig. 18 shows the difference in the grain boundaries when utilizing transmission electron microscopy. In the low stress region, the grain boundaries are relatively clean, but in the high stress regions, there is a high degree of precipitation. Identification of these precipitated phases was made from selected area electron diffraction patterns of thin foils and x-ray diffraction patterns of the chemically extracted residues. These analyses indicated the grain boundary phase to be Cr_{23}C_6 , while the less abundant blocky intragranular particles were identified as Mo_2C . The scattered small particles have not yet been identified, but they have an appearance consistent with their being individual Cr_{23}C_6 particles.

In order to determine the origin of the Cr_{23}C_6 grain boundary phase, specimens were given heat treatments at 650°C to simulate the thermal history of the low-cycle fatigue test specimens. Examination of thin foils indicated that the Cr_{23}C_6 grain boundary phase is primarily thermally induced, but is enhanced by stress. In other words, the low-cycle fatigue specimens tested at 650°C contained more of the grain boundary phase than those specimens only held at temperature for the same length of time.

One of the surprising things was the failure to identify any sigma phase in these specimens. Formation of this intermetallic is usually very detrimental to the mechanical properties. Blenkinsop and Nutting⁽⁸⁾ reported the formation of sigma in a Type 316L stainless steel when aged at 650°C . However, there are two factors influencing the present case which tend to suppress the formation of sigma phase. Firstly, the higher carbon content in the present specimens (0.09 wt. %), compared with that in Blenkinsop and Nutting's samples (0.03 wt. %), leads to heavier carbide formation; and secondly, solutioning at relatively low temperatures (1070°C in the present case) fails to dissolve carbides which are initially present. Both of these factors tend to tie up potential sigma-forming elements into less harmful carbides.⁽⁸⁾ However, the absence of sigma from the specimens examined thus far should not be taken as conclusive evidence that it will never form in this material. It is quite possible that other test conditions, possibly involving longer times or higher test (aging) temperatures could lead to sigma formation.

Thin foils from both the low and high stress regions of a Type 316 stainless steel specimen tested at 1% strain range, $4 \times 10^{-5} \text{ sec}^{-1}$ strain rate at 650°C were examined by transmission electron microscopy (Fig. 19). The photomicrograph taken in the low stress area is representative of the structure in the pre-test condition showing the typical randomly distributed dislocations. The photomicrograph of the high stress region shows that extensive subgrain formation has occurred. These subgrains, approximately 1 micron in diameter, represent regions of the lattice which are slightly misoriented ($\sim 0.5^{\circ}$) with respect to each other, but nevertheless still constitute a single grain. They form during the very early stages of plastic deformation when moving dislocations intersect and interact with one another. Such interaction results in pinning, or immobilization of the dislocations, and leads to the formation of dislocation networks. These dislocation networks form the subgrain boundaries and separate relatively dislocation-free regions which are the subgrains.

The grain boundaries, impurities, and secondary phases in the Type 304 stainless steel were similar to those seen in the Type 316 stainless steel just discussed. After low-cycle fatigue testing at elevated temperatures, a grain boundary phase developed that was similar to that seen in the 316 stainless steel and is presumed to be an M_{23}C_6 carbide, probably Cr_{23}C_6 , Fig. 20. Additional work will have to be done to verify this.

SUMMARY

The metallographic and fractographic analysis of stainless steel specimens after low-cycle fatigue testing involved characterization of (1) fracture surfaces, (2) fracture mode, and (3) microstructure. A summarization of the findings is as follows:

1. It was shown that the strain rate (and hence frequency) has little effect on the crack propagation rate, but the strain range is the predominant factor in Type 304 stainless steel.
2. A curve of the crack growth rate, determined from the striation or ripple density, versus $\Delta\epsilon_p \sqrt{l}$ is shown in an attempt to determine if this slope is related to the slope of the line relating plastic strain range and cycles to failure.
3. The fracture modes were determined and the results shown in tabular form for the three grades of stainless steel studied.
4. The topography of the fractured surface and the internal structure of the low-cycle fatigue specimens tested with zero hold time, 30-minute hold time in both tension and compression, and 30-minute hold time in compression only were similar. The specimens held only in tension at peak strain had grain boundary separations and an intergranular type fracture.
5. A grain boundary phase, Cr_{23}C_6 , developed in the Type 316 stainless steel at the testing temperatures. A similar phase developed in the Type 304 stainless steel. No sigma phase was identified in these specimens.

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TABLE 1
FRACTURE MODE CHARACTERIZATION OF TYPES 304 AND 348 STAINLESS STEEL LOW-CYCLE FATIGUE SPECIMENS

Specimens	Test Temperature, °C	Test No.	Axial Strain Range, $\Delta\epsilon_t$, %	Axial Strain Rate, $\dot{\epsilon}_t$, sec^{-1}	Cycles to 5 % Reduction in Load, N_5	Mode Crack Initiation	Intergranular Crack Length from Point of Initiation, mm	Mode of Crack Propagation to the Shear Point	Specific Observations
304 SS	650	10-12	2.12	4.2×10^{-5}	197	Intergranular	0.3	Inter- + transgranular	Continuous unidentified phase observed in grain boundaries; etch pits in highly strained regions.
	650	10-11	2.15	4.3×10^{-4}	287	Intergranular	0.1	Primarily transgranular	
	650	10-9	2.11	4.2×10^{-3}	524	Transgranular	—	Primarily transgranular	
	650	120	0.58	4.6×10^{-5}	1,533	Intergranular	0.6	Inter- + transgranular	Continuous unidentified phase observed in grain boundaries; etch pits in highly strained region.
	650	296	0.60	4.8×10^{-4}	3,009	Intergranular	0.2	Primarily transgranular	
	650	294	0.62	4.9×10^{-3}	7,176	Transgranular	—	Primarily transgranular	
	816	10-2	2.07	4.1×10^{-5}	80	Intergranular	4.0	Primarily intergranular	Intermittent unidentified phase observed in grain boundaries; subgrains in highly strained regions.
	816	7-3	2.07	4.1×10^{-4}	117	Intergranular	1.2	Primarily intergranular	Continuous unidentified phase observed in grain boundaries; a few etch pits and subgrains in highly strained regions.
	816	7-1	2.08	4.2×10^{-3}	226	Intergranular	1.0	Primarily intergranular	Continuous unidentified phase observed in grain boundaries; few etch pits in highly strained regions.

TABLE 1 (cont'd)
FRACTURE MODE CHARACTERIZATION OF TYPES 304 AND 348 STAINLESS STEEL LOW-CYCLE FATIGUE SPECIMENS

Specimens	Test Temperature, °C	Test No.	Axial Strain Range, $\Delta\epsilon_f$, %	Axial Strain Rate, $\dot{\epsilon}_f$, sec^{-1}	Cycles to 5% Reduction in Load, N_5	Mode Crack Initiation	Intergranular Crack Length from Point of Initiation, mm	Mode of Crack Propagation to the Shear Point	Specific Observations
348 SS	816	10-3	0.53	4.2×10^{-5}	591	Intergranular	0.7	Primarily intergranular	Intermittent unidentified phase observed in grain boundaries; no etch pits in highly strained regions.
	816	7-7	0.54	4.3×10^{-4}	1,055	Intergranular	0.8	Primarily intergranular	Continuous unidentified phase observed in grain boundaries; etch pits in highly strained regions.
	816	7-9	0.56	4.5×10^{-3}	2,346	Intergranular	0.8	Primarily intergranular	Continuous unidentified phase in grain boundaries; subgrains in highly strained regions.
	650	3-7	2.17	4.3×10^{-5}	193	Intergranular	0.2	Transgranular	Large amounts of secondary cracking; grain boundaries were relatively clean compared to 304 SS.
	650	3-8	2.18	4.4×10^{-4}	320	Intergranular	0.1	Transgranular	
	650	3-4	2.19	4.4×10^{-3}	585	Intergranular	0.1	Transgranular	
	650	5-12	0.61	4.9×10^{-5}	5,464	Intergranular	0.4	Transgranular	Limited secondary cracking; crack propagation was very regular, flat, and perpendicular to specimen axis.
	650	3-11	0.62	5.0×10^{-4}	10,948	Intergranular	0.2	Transgranular	
	650	5-3	0.62	5.0×10^{-3}	15,010	Intergranular	0.1	Transgranular	
	816	5-7	2.06	4.1×10^{-5}	122	Intergranular	<0.1	Transgranular	Numerous secondary cracks.
	816	5-5	2.11	4.2×10^{-4}	158	Intergranular	<0.1	Transgranular	
	816	5-1	2.11	4.2×10^{-3}	266	Intergranular	<0.1	Transgranular	
	816	6-10	0.56	4.6×10^{-5}	1,613	Intergranular	<0.1	Transgranular	Crack propagation was very regular, flat, and almost perpendicular to specimen axis; cracks developed at ~60 degree angle to primary fracture surface in the direction of propagation.
	816	6-8	0.58	4.6×10^{-4}	2,718	Intergranular	<0.1	Transgranular	
	816	6-2	0.57	4.5×10^{-3}	4,656	Intergranular	<0.1	Transgranular	Crack propagation was very regular, flat, and perpendicular to specimen axis.

TABLE 2
FRACTURE MODE CHARACTERIZATION OF TYPE 316 STAINLESS STEEL LOW-CYCLE FATIGUE SPECIMENS

Test Temperature, °C	Test No.	Axial Strain Range, $\Delta\epsilon_t$, %	Axial Strain Rate, $\dot{\epsilon}_t$, sec ⁻¹	Cycles to 5 Percent Reduction in Load, N_5	Mode of Crack Initiation ^a	Intergranular Crack Length from Point of Initiation, mm	Mode of Crack Propagation to Shear Point ^a	Specific Observations
650	5-4	2.11	4.2×10^{-5}	93	I	0.6	I	Cavities; two grain boundary phases; secondary cracks on outer surface
650	16-51	2.15	4.3×10^{-4}	193	I	0.4	I and T	Cavities, < specimen 5-4; grain boundary phases; secondary cracks on outer boundary
650	9-2	2.56	3.8×10^{-3}	219	I	0.2	T	Cavities, < specimen 5-4; grain boundary phases; secondary cracks on outer boundary
650	16-2	1.10	4.4×10^{-5}	562	T		T and I	No Cavities; grain boundary phases; no secondary cracks on outer surface
650	16-4	1.16	4.6×10^{-4}	649	T		T	No cavities; grain boundary phases; secondary cracks on outer surface
650	33-32	0.94	4.2×10^{-3}	2,227	T		T	No cavities; grain boundary phases; secondary cracks on outer surface
650	5-8	0.59	4.7×10^{-5}	4,663	T		T	No cavities; grain boundary phases; no secondary cracks on outer surface
650	5-9	0.61	4.9×10^{-4}	2,926	T		T	No cavities; grain boundary phases; no secondary cracks on outer surface
650	27-4	0.50	4.5×10^{-3}	13,394	T		T	No cavities; grain boundary phases; no secondary cracks on outer surface

^aI - intergranular; T - transgranular

Where both modes are given, the predominant method is listed first.

TABLE 2 (cont'd)

FRACTURE MODE CHARACTERIZATION OF TYPE 316 STAINLESS STEEL LOW-CYCLE FATIGUE SPECIMENS

Test Temperature, °C	Test No.	Axial Strain Range, $\Delta\epsilon_t$, %	Axial Strain Rate, $\dot{\epsilon}_t$, sec ⁻¹	Cycles to 5 Percent Reduction in Load, N ₅	Mode of Crack Initiation ^a	Intergranular Crack Length from Point of Initiation, mm	Mode of Crack Propagation to Shear Point ^a	Specific Observations
816	21-2	2.06	4.1×10^{-5}	107	I	0.8	I and T	No cavities; discontinuous grain boundary phase; intragranular phase; secondary cracks on outer surface
816	16-9	2.07	4.1×10^{-4}	215	I	0.5	I and T	No cavities; discontinuous grain boundary phase < specimen 21-2; intragranular phase < specimen 21-2; secondary cracks on outer surface
816	5-10	2.50	3.8×10^{-3}	241	I	0.2	T	No cavities; discontinuous grain boundary phase < specimen 16-9; intragranular phase < specimen 16-9; secondary cracks on outer surface
816	14-9	1.06	4.2×10^{-5}	524	I	1.0	I	No cavities; discontinuous grain boundary phase; intragranular phase; secondary cracks on outer surface
816	14-49	1.08	4.3×10^{-4}	590	I	0.4	I and T	No cavities; discontinuous grain boundary phase < specimen 14-9; intragranular phase < specimen 14-9; secondary cracks on outer surface
816	33-39	0.89	4.0×10^{-3}	1,199	T		T	No cavities; discontinuous grain boundary phase < specimen 14-49; intragranular phase < specimen 14-49; one small secondary crack on outer surface
816	16-10	0.55	4.4×10^{-5}	1,530	I	1.0	I	No cavities; discontinuous grain boundary phase; intragranular phase; no secondary cracks on outer surface
816	5-1	0.59	4.7×10^{-4}	2,046	I	0.3	I and T	No cavities; discontinuous grain boundary phase < specimen 16-10; intragranular phase < specimen 16-10; one small secondary crack on outer surface
816	33-35	0.48	4.3×10^{-3}	5,984	T		T	No cavities; discontinuous grain boundary phase < specimen 5-1; intragranular phase < specimen 5-1; no secondary cracks on outer surface

^aI - intergranular; T - transgranular

Where both modes are given, the predominant method is listed first.

TABLE 3
FRACTURE MODE CHARACTERIZATION OF TYPE 304 STAINLESS STEEL LOW-CYCLE
FATIGUE SPECIMENS HELD FOR VARIOUS TIMES AT PEAK STRAIN^a

Test No.	Time at Peak Strain, minutes		Mode of Crack Initiation	Mode of Crack Propagation
	Tension	Compression		
53-11	0	0	transgranular	transgranular
53-8	3	3	transgranular	transgranular
53-9	30	30	transgranular	transgranular
52-11	0	30	transgranular	transgranular
53-10	30	0	intergranular	intergranular
54-2	60	0	intergranular	intergranular

^aTesting Conditions: $\Delta\epsilon_t = 2\%$, $\dot{\epsilon}_t = 4 \times 10^{-3} \text{ sec}^{-1}$,
650°C in air

Figure 1 - Photomacrograph showing the topography of the fractured surface of Type 304 stainless steel low-cycle fatigue specimen tested at 2% strain range, $4 \times 10^{-3} \text{ sec}^{-1}$ strain rate, 650°C , and held for 30 minutes at peak strain in both tension and compression. (25X)

Figure 2 - Photomicrograph showing the topography of the fractured surface of Type 304 stainless steel low-cycle fatigue specimen tested at 2% strain range, $4 \times 10^{-3} \text{ sec}^{-1}$ strain rate, 650°C , and held for 30 minutes at peak strain in tension. (25X)

430°C

650°C

Figure 3 - Replica electron micrographs of the fractured surface of Type 348 stainless steel after low-cycle fatigue testing under the following conditions:

430°C, 0.5% strain range, $4.5 \times 10^{-5} \text{ sec}^{-1}$ strain rate
816°C, 0.3% strain range, $2.7 \times 10^{-3} \text{ sec}^{-1}$ strain rate

Figure 4 - Plot of crack length versus number of cycles prior to final fracture.

Figure 5 - Plot of crack length versus number of cycles prior to final fracture.

Figure 6 - Plot of crack length versus number of cycles prior to final fracture.

Figure 7 - Plot of the ratio of crack length after N cycles to that at final fracture versus cycles prior to final fracture.

Figure 8 - Plot of $d\ell/dN$ versus $\Delta\epsilon_p \sqrt{\ell}$ for 304 stainless steel tested at 650°C.

Figure 9 - Photomicrograph showing pre-test structure of Type 348 stainless steel (longitudinal cross section) used in low-cycle fatigue testing. (50HNO_3 , $50\text{H}_2\text{O}$, electrolytic etch; 100X)

Figure 10 - Photomicrograph showing pre-test structure of Type 316 stainless steel (longitudinal cross section) used in low-cycle fatigue testing. ($22\text{H}_2\text{SO}_4$, $12\text{H}_2\text{O}_2$ [30%], $66\text{H}_2\text{O}$, electrolytic etch; 100X)

Figure 11 - Photomicrograph of Type 316 stainless steel showing the grain boundary separations or cavities formed during testing at 2% strain range and 650°C. ($22\text{H}_2\text{SO}_4$, $12\text{H}_2\text{O}_2$ [30%], $66\text{H}_2\text{O}$, electrolytic etch; 100X)

Figure 12 - Photomicrograph showing pre-test structure of Type 304 stainless steel (longitudinal cross section) used in low-cycle fatigue testing. ($22\text{H}_2\text{SO}_4$, $12\text{H}_2\text{O}_2$ [30%], $66\text{H}_2\text{O}$, electrolytic etch; 100X)

Figure 13 - Composite photomicrograph of longitudinal cross section of Type 304 stainless steel low-cycle fatigue specimen tested at 2% strain range, $4 \times 10^{-3} \text{ sec}^{-1}$ strain rate, 650°C , and held for 30 minutes at peak strain in both tension and compression. ($22 \text{ H}_2\text{SO}_4$, $12\text{H}_2\text{O}_2$ [30%], $66\text{H}_2\text{O}$ electrolytic etch; 30X)

Figure 14 - Composite photomicrograph of longitudinal cross section of Type 304 stainless steel low-cycle fatigue specimen tested at 2% strain range, $4 \times 10^{-3} \text{ sec}^{-1}$ strain rate, 650°C , and held for 30 minutes at peak strain in tension. ($22\text{H}_2\text{SO}_4$, $12\text{H}_2\text{O}_2$ [30%], $66\text{H}_2\text{O}$, electrolytic etch; 30X)

Figure 15 - Photomicrograph of Type 304 stainless steel specimen held in tension for 30 minutes at peak strain showing grain boundary separation. This separation occurs normal to the stress axis. ($22\text{H}_2\text{SO}_4$, $12\text{H}_2\text{O}_2$ [30%], 66H_2) electrolytic etch; 100X)

650°C

816°C

Figure 16 - Photomicrographs showing the effect of temperature on the grain boundary phase of Type 316 stainless steel after low-cycle fatigue testing at $\Delta\epsilon_t = 2\%$, $\dot{\epsilon} = 4 \times 10^{-5} \text{ sec}^{-1}$ ($22\text{H}_2\text{SO}_4$, $12\text{H}_2\text{O}_2$ [30%], $66\text{H}_2\text{O}$ electrolytic etch; 1000X)

Tested at 650°C

Tested at 816°C

Figure 17 - Electron micrographs of the specimens shown in Figure 16, showing the effect of temperature on the grain boundary phase in Type 316 stainless steel.

Low Stress, 20°C

High Stress, 650°C

Figure 18 - Transmission electron micrographs showing the pre-test structure (low stress, 20°C) and the grain boundary phase formed in Type 316 stainless steel after low-cycle fatigue testing at 1% strain range, $4 \times 10^{-5} \text{ sec}^{-1}$ strain rate, and 650°C.

Low Stress, 20°C

High Stress, 650°C

Figure 19 - Transmission electron micrographs showing the pre-test structure (low stress, 20°C) and the substructure formed in Type 316 stainless steel after low-cycle fatigue testing at 1% strain range, $4 \times 10^{-5} \text{ sec}^{-1}$ strain rate, and 650°C.

650°C

816°C

Figure 20 - Photomicrographs showing the effect of temperature on the grain boundary phase in Type 304 stainless steel after low-cycle fatigue testing at 2% strain range, $4 \times 10^{-5} \text{ sec}^{-1}$ strain rate. (1000X, etched)

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AUTORADIOGRAPHIC INVESTIGATION OF TRITIUM
SEGREGATION IN STAINLESS STEEL

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Abstract

The segregation of tritium in 304 stainless steel was investigated by autoradiographic techniques. Variations in tritium concentration due to defect structure, precipitated phases, and microsegregation of alloy components were observed. The diffusivity of tritium in the metal appeared to be enhanced by the defect structure. The autoradiography was accomplished using high resolution liquid emulsion and a new strippable emulsion. The strippable emulsion enabled in-situ autoradiographs to be evaluated without interference from etching effects on the sample surface.

Introduction

The mechanism of diffusion of gases in metals and the structural effects of metals on the solubility of gases have been of interest for some time. This paper will present

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some of the structural and compositional effects on the distribution of hydrogen in 304 stainless steel.

Since hydrogen is not easy to locate on a microscale, tritium was used and detected by autoradiographic techniques. The selection of stainless steel for this investigation was based on several factors. Type 304 stainless steel is a common containment material for tritium and metals containing tritium because of its corrosion resistance, low solubility and diffusivity for hydrogen, relatively low cost, and high strength. Also, we had first-hand knowledge on the structure and compositional variations in this material.

We were very fortunate to have a convenient source of samples since Mound Laboratory has, for several years, been recovering tritium using uranium beds as a chemical pump. This process involves heating the uranium to a temperature where it will serve as a getter for tritium, then heating it to a higher temperature to decompose the tritide and pumping off the gas. The materials used in this investigation were obtained from storage vessels for contaminated material and uranium tritide, as well as the welded containers for the uranium beds. Another source of samples was coupons used for determining tritium solubilities as a function of tem-

perature at a pressure of about one atmosphere of tritium.

Procedure

The samples were sectioned and mounted for routine metallographic examination. In previous autoradiographic work at Mound Kodak NTB-2 liquid autoradiographic emulsion has been used. This technique was described by R. Gehlbach (Oak Ridge National Laboratory) last year. However, the liquid emulsion required etching of the sample to promote adherence of the emulsion; this technique often disguises the autoradiographs and prevents easy observation of segregation effects. Some difficulty was also encountered in coating thin-walled samples with NTB-2 emulsion because the emulsion tended to flow off the specimen. Because of these problems a new technique was developed. This technique makes use of Kodak AR.10 autoradiographic, strippable emulsion. This emulsion comes on 4-3/4 in. by 6-1/2 in. glass plates. The procedure for applying the emulsion is as follows: A piece of emulsion about the size of the surface of the mount is outlined with a scalpel; the section is then removed from the glass plate gently with tweezers and floated on distilled water, emulsion side down. The emulsion is allowed to float for 2-3 min and then is picked up on the sample by dipping the mount below the

surface of the water and raising it up underneath the emulsion at an inclined angle. The emulsion is then dried on the sample and allowed to expose in a refrigerator. The AR.10 is comparable to the NTB-2 in resolution and sensitivity, and exposures of 1/2 hr to 48 hr were employed depending on the amount of tritium in the samples. With this technique, samples in the as-polished condition were autoradiographed, and areas of segregation could be revealed and associated with microstructures. "Areas of segregation" in this paper are by definition "areas in which increased tritium concentrations were noted due to greater numbers of exposed emulsion particles."

It should be noted that autoradiography is subject to some variables which may give rise to artifacts sometimes not distinguishable from the effects being investigated, for example, the presence on the surface of metals of different reactivity. Such a condition, if the metals are sufficiently reactive, can set up an electrolytic cell effect which can cause reduction of the emulsion on the less active metal making it appear as though radioactive material were present. If the sample is being examined for segregation effects, care must be taken to be sure observed effects are not due to chemical reactions.

Such was the possibility in this work since the ferrite and other areas in the weld samples are more chemically reactive than the parent metal. However, observed tritium segregation effects in the welds did not extend beyond the depth of penetration of the tritium and, therefore, could not have been artifacts. This autoradiographic technique can also be used with etched samples since the strippable emulsion can be readily stripped from the sample and observed with transmitted light on a microscope.

Many of the problems which may be encountered in the use of autoradiographic emulsions are described in the book, Techniques of Autoradiography by Andrew W. Rogers.⁽¹⁾

Results:

Tritium "segregation" was observed in two different areas of weld samples. The weld samples were obtained from the thick-walled containers for the uranium beds and were exposed to tritium at fairly high temperatures (up to about 600°C).

The containers were made from 304L stainless steel for ease in welding. Some of the welds contained delta-ferrite, and some were ferrite free. The fusion weld in the lower right portion of the micrograph shown in Figure 1 is ferrite free.

The top part of the weld is a 308 stainless steel filler

weld. The fusion weld has a large grain size, and an intergranular cell structure can be observed. The cellular structure is due to microsegregation of nickel and chromium. This structure was reported by this author at this conference two years ago. The cell structure is shown at higher magnification in Figure 2. The boundaries of the cells are enriched in nickel and chromium. An in-situ autoradiograph of an as-polished, ferrite-free weld is shown in Figure 3. The cell structure is revealed by the increased number of exposed emulsion particles. This appears to indicate that the solubility of tritium in the Cr-Ni rich metal is higher than in the nominal composition metal. It should be noted however, that if the sample is allowed to stand several hours after preparation before it is autoradiographed, the cell structure can no longer be detected.

The microstructure of a ferrite-containing weld is shown in Figure 4. Preferential segregation of tritium to the delta-ferrite can be observed in the autoradiograph shown in Figure 5. This sample was also autoradiographed in the as-polished condition. This segregation effect was also noted in delta-ferrite in the parent-metal as is shown in Figure 6. The sample was lightly etched to outline the ferrite more clearly,

and liquid NTB-2 (Kodak) emulsion was used for this autoradiograph.

In some of the thin-walled containers used for storage of contaminated materials, the presence of martensite was noted in the microstructure. This material contained a very low level of tritium, and no observable segregation was observed either into the martensite or into the martensite-austenite interfaces. This is shown in the autoradiograph in Figure 7. The sample was lightly etched to reveal the martensite needles.

The deformation substructure of the metal also was found to effect the solubility and diffusivity of tritium in the metal. Samples of cold-rolled and annealed specimens have been studied for diffusivity and solubility as a function of temperature. The studies were done with one atmosphere of tritium in the temperature range of 100 to 300°C. No apparent segregation of tritium into grain boundaries or other areas was observed in the annealed structures as is shown in Figure 8. The tritium in the cold-rolled structure, however, showed gross segregation as is seen in Figure 9. This segregation appears to be into areas of high dislocation density or deformation. These areas do not appear uniform in the substructure, and reasons for this are not completely

understood. The appearance of martensite in the areas showing increased tritium concentrations would seem to contradict the previous observations about martensite. However, it should be noted that the areas containing martensite are also the areas of greatest deformation in the metal. The substructure of the cold-rolled metal can be seen in the electron micrograph shown in Figure 10.

Other evidence of the influence of defect structure on the diffusivity of tritium into the metal can be obtained from the weld samples. The substructure of the weld samples is shown in Figure 11. This dislocation structure is similar to that found in samples which have undergone creep. The presence of the dislocation networks could result in the observed increased tritium penetration into the weld as shown in Figure 12. This autoradiograph was obtained by stripping the emulsion from the sample after it had been exposed, developed, and fixed. The photograph was obtained using transmitted light.

Summary

Apparent tritium segregation has been observed in 304 stainless steel. This segregation has been observed using autoradiographic techniques and has been correlated with

microstructure and defect structure variations in the metal.

Autoradiography has revealed increased tritium concentrations in the following areas:

- (1) The "cell" boundaries, arising from segregation of components during solidification of ferrite-free welds.
- (2) Delta-ferrite in both welds and parent metal.
- (3) Areas of high dislocation density or containing dislocation networks such as cold-rolled metal or weldments.

No apparent increase in tritium concentration was observed in areas such as:

- (1) Grain boundaries or twin boundaries.
- (2) Along martensite needles or platelets when well defined and not apparently associated with gross deformation.

Reference

- (1) Andrew W. Rogers, Techniques of Autoradiography, American Elsevier Publishing Co., New York, 1967.

Fig. 1. Low magnification (26X) optical micrograph of a ferrite-free fusion weld in 304L stainless steel.

Fig. 2. Cell structure in the fusion weld of 304 stainless steel at 320X.

Fig. 3. Autoradiograph of fusion weld in the as-polished condition (500X).

Fig. 4. Microstructure of a ferrite-containing weld in 304L stainless steel (200X).

Fig. 5. In-situ autoradiograph of a ferrite-containing weld in the as-polished condition (200X).

Fig. 6. Autoradiograph of lightly etched parent-metal showing segregation into δ ferrite (1000X).

Fig. 7. Autoradiograph of lightly etched 304 stainless steel containing martensite (1000X).

Fig. 8. Autoradiograph of annealed stainless steel, lightly etched to reveal grain boundaries (500X).

Fig. 9. Segregation of tritium in cold-rolled structure as seen by in-situ autoradiography (1000X).

Fig. 10. Electron micrograph of cold-rolled stainless steel (9000X).

Fig. 11. Substructures of ferrite-free stainless steel weld shown at (1500X).

Fig. 12. Transmitted light autoradiograph of emulsion stripped from a ferrite-containing weld sample (50X).

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X HOT CRACKING IN WELDMENTS OF HAYNES ALLOY NO. 25

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ABSTRACT

Metallographic examination of weldments produced by tungsten inert gas welding of Haynes alloy No. 25 gave evidence of what appeared to be intergranular cracks in the heat-affected zone. This condition was found to result from pull-out of a brittle material during metallographic polishing. When careful metallographic procedures were developed resulting in retention of the intergranular material, it was recognized as the product of a liquation reaction. Segregated carbide precipitates caused melting and hot cracking in the grain boundaries adjacent to the weld pool by means of a multi-component eutectic reaction. Resolidification of the liquid in the grain boundaries formed two distinct phases which were hard and brittle. These were identified by electron microprobe x-ray analysis as a carbide phase and a cored solid

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solution phase. The microstructural characteristics of the base metal indicated that the problem occurred as the result of improper thermal and mechanical treatment of the alloy.

INTRODUCTION

This report involves the metallographic analysis of weldments made during the fabrication of isotopically fueled heat sources for the SNAP-27 program. The cylindrical capsule containing the fuel was enclosed in an outer capsule constructed of Haynes alloy No. 25. The circumferential closure welds of the outer capsule, which served as the strength member of the assembly, were made by tungsten inert gas welding.

A cross-sectional view of the outer capsule is shown in Figure 1 illustrating the weld joint design. The outer and inner portions of the step joint were 0.040" and 0.020" thick respectively, and the entire step joint was 0.060" long. One hundred percent penetration of the weld was required, although it was not required that the weld encompass the entire 0.020" step.

Nondestructive testing¹ was performed on all weldments to detect the presence of defects. Destructive metallographic

analysis was performed on test welds for correlation with NDT results, and example welds made immediately before and after the closure weld of a fueled capsule were examined metallographically to assure that the weld parameters were correct. In general, any well-defined crack was cause for rejection of the weldment. A problem developed in this work involving the interpretation of microstructural detail which neither obviously fit nor misfit the category of well-defined cracks.

The components for the SNAP-27 outer capsule were fabricated from Haynes-25 bar stock which constituted a single heat of material. The wrought bar was solution heat treated in massive form, and the tubular components for the capsule were machined from the bar with no further heat treatment. Characterization of the base metal revealed that the grain size was relatively coarse, carbide particles were distributed in flow lines, within the grains and in grain boundaries, and the machined components exhibited some cold work received from the machining operation.

The nominal composition of Haynes-25 is given by the following specification limits:

Ni	9.00 - 11.00
Cr	19.00 - 21.00
W	14.00 - 16.00
Fe	3.00 Max
C	0.05 - 0.15
Si	1.00 Max
Mn	1.00 - 2.00
P	0.030 Max
S	0.030 Max
Co	Balance

The composition of the material employed in this program was verified by "in house" analyses showing conformance with specification. The silicon content fell on the low side of specification limits at 0.12 percent, and the carbon content fell on the high side of specification limits at 0.13 percent. Phosphorous and sulfur were negligible.

METALLOGRAPHIC EXAMINATIONS

Throughout the metallographic surveillance of weldments in this program, the specimens were examined first in the as-polished condition as this was quite sensitive in revealing defects such as pores or cracks. Examination after etching revealed no "open" defects which were not detectable in the

as-polished condition. "Open" defects were not obscured by smearing as experience showed that smeared metal was not a problem with this alloy.

Three different etchants were employed in studying the weld sections. Figure 2 shows a transverse weld section etched electrolytically in HCl and ethanol. When the specimen is not etched excessively the grain structure in the base metal is not revealed, and the weld is defined in sharp contrast. This is a representative weldment. The large void on the left is a gap at the end of the unmelted portion of the 0.020" step.

Figure 3 shows a transverse weld section etched electrolytically in 10% oxalic acid. The results are essentially the same as the HCl-ethanol etch giving no definition of the grain structure in the base metal. Two weld passes are apparent in this specimen plus the weld overlap area at top left.

Figure 4 shows a transverse weld section etched by immersion in HCl-H₂O₂. This is a much stronger etchant. In addition to the delineation of the weldment, the grain structure in the base metal has been revealed completely showing rather coarse grains.

The heat-affected zone of a weldment is usually described as that portion of the base metal which was not melted, but whose properties or microstructure were altered by the heat of welding. Rather wide heat-affected zones are indicated in Figures 2, 3 and 4 by the presence of microstructural detail extending from the edges of each weldment. Ordinarily the edges of the weldment should be sharp interfaces. None of the detail in the heat-affected zones of these specimens was apparent in the as-polished condition.

The detail in the heat-affected zone revealed by etching in Figure 3 is more prominent near the bottom of the weld, particularly in the unmelted 0.020" step. During welding heat is rapidly conducted away from the weld in both directions, but because of the discontinuity at the end of the step joint, heat builds up excessively in the unmelted step. The effect may vary from essentially no change in a joint with an ideal fit to complete melt-away of the step in a joint with a poor fit. In this case the entire unmelted step must be considered a heat-affected zone.

In some cases the detail in the heat-affected zone appeared even more severe. Two such examples are shown in Figures 5 and 6. Both specimens were slightly overpolished and both

were etched with HCl-H₂O₂. In Figure 5 a crack appears to extend along the left face of the weldment, and in Figure 6 a grain on the left side of the weldment is completely surrounded by what appears to be a crack. When detail such as this was first encountered, its identification as "cracks" was very uncertain as the severity of the detail appeared to vary with the metallographic procedures. When the specimens were etched with HCl-H₂O₂ to reveal the grain structure of the base metal, the detail of concern in the heat-affected zone was consistently observed to be intergranular in nature. A disadvantage of the use of the HCl-H₂O₂ etchant is that it becomes difficult to distinguish ordinary grain boundaries from those revealed due to an unusual grain boundary condition. With the HCl-ethanol and oxalic acid etchants the grain boundaries of concern in the heat-affected zone are revealed sharply without interference.

Figure 7 shows an exceptionally wide weldment in which the entire step joint was consumed. Overpolishing has exposed flow lines revealing the wrought condition of the material. Overpolished specimens consistently appeared worse in the heat-affected zone showing an increased concentration of intergranular voids.

Figures 8 and 9 show enlargements of the detail in the heat-affected zone when severe intergranular voids were present. Often the void sections were discontinuous exhibiting intact segments along the grain boundary between the grain boundary separations.

The unusual grain boundary condition was revealed much more prominently by longitudinal sections. The specimen in Figure 10 was sectioned parallel to the weldment on the side opposite the step joint. The section intersected only the upper portion of the weldment which is revealed at the top. The center portion of the surface represents the heat-affected zone adjacent to the side of the weld. The grain boundary detail shown by the oxalic acid etch is more continuous in this orientation. From the absence of microstructural detail, the lower portion of the surface appears to be outside the heat-affected zone. The distance from the surface to the face of the weldment is greatest at the bottom.

The nature of the unusual grain boundary condition became more obvious with the recognition of brittle pull-out, meaning the dislodgement of a brittle constituent from the grain boundaries during metallographic polishing. Figure 11 shows an unetched specimen sectioned longitudinally in the

heat-affected zone on the step-joint side of the weldment. Severe overpolishing resulted in an excessive amount of brittle pull-out giving the appearance of huge intergranular voids. This is further evidence of a highly unusual condition in the grain boundaries since Haynes-25 is a single phase alloy when completely solution heat treated and contains no brittle intergranular material that is subject to pull-out.

In Figures 12-15 a single transverse weld section is shown in four different conditions to demonstrate the pull-out phenomenon. In Figure 12 the specimen is shown polished and unetched. No detail is apparent. In Figure 13 the specimen is shown etched with oxalic acid. The unusual grain boundaries are well delineated in the heat-affected zone although they do not appear to be void. In Figure 14 the specimen is shown severely overpolished and unetched. The specimen edges are rounded and several "defect" areas are apparent as the result of overpolishing. In Figure 15 the overpolished specimen is shown etched with oxalic acid, and the "defect" areas can be identified as grain boundaries in which brittle pull-out occurred.

The identification of brittle pull-out did not provide an

explanation for all the intergranular voids observed in weldment heat-affected zones as some were recognized to be actual microfissures. These were easily detected when present as they could be recognized at all stages of grinding and polishing. Figure 16 shows a longitudinal section in the heat-affected zone of a specimen known to be severely affected. In spite of the coarse scratches on the as-ground surface, several long, void grain boundaries are quite apparent. When the specimen was polished, as shown in Figure 17, the microfissures were well defined and had essentially the same appearance. Overpolishing undoubtedly would have extended the areas which appear void.

In order to identify the intergranular material which was so highly subject to pull-out, and to define the reactions which occurred during welding, it was necessary to develop an improved metallographic procedure which would result in the retention of the brittle intergranular product. Extensive development work was carried out involving manual, automatic and vibratory polishing techniques and the use of many different polishing cloths, abrasives and lubricants. Of the many procedures attempted, the best results were achieved by a manual technique intended to minimize

polishing time.

Figures 18 and 19 show enlargements of the typical intergranular detail in the heat-affected zone retained by careful polishing procedures. The specimens were wet ground on 180, 320 and 600 grit silicon carbide papers, hand polished at low speed with 3 micron diamond on Texmet polishing paper with heavy pressure for less than one minute employing mineral oil as the lubricant, polished with $\frac{1}{4}$ micron diamond on Microlon D with heavy pressure for less than one minute employing mineral oil, and final polished very briefly with 0.06 micron alumina on Microcloth with light pressure employing water. The large grain boundaries in these specimens can be seen to be filled with solid material. With less than optimum metallographic procedures, pull-out would have occurred and segments of the boundaries would appear to be void.

RESULTS AND DISCUSSION

The study of the retained detail in many areas, such as Figures 18 and 19, gave evidence of the chemical reaction which had occurred. This was identified as grain boundary liquation, defined as melting of material in grain

boundaries at a temperature below the solidus temperature of the alloy. This is a special case of hot shortness.

Ordinarily, hot shortness is the result of trace quantities of impurities which are insoluble in a metal. The segregation of the impurities in grain boundaries results in melting by eutectic reaction at temperatures below the melting point of the metal. During welding severe thermal stresses are present in the heat-affected zone, and the development of a liquid grain boundary film in a local area under tension can produce a physical separation of the grain boundary. Contraction may close the separation, but in some cases resolidification during rapid cooling may result in permanent microfissures - or "hot cracks."

In this case, grain boundary liquation and hot cracking did not result from the presence of insoluble impurities in the Haynes-25, but rather from the presence of carbon which should be present in limited concentration in the alloy in solid solution form. Even though the carbon content is relatively low, second phase carbides will be present if the alloy has been improperly solution heat treated, or if it has been held at temperatures above 1200°F for a significant period of time.

There are a number of types of carbides which occur in super alloys.² MC-type carbides form initially from the melt and exhibit random distribution in the microstructure. $M_{23}C_6$ forms in the solid state as the result of aging at elevated temperature and has a strong predisposition to nucleate at grain boundaries. M_6C may replace $M_{23}C_6$ in alloys rich in molybdenum or tungsten. For Haynes-25 the mechanism of delivery of carbon to the grain boundaries is the precipitation of $(Cr,W)_{23}C_6$ and/or $(Cr,W)_6C$.

If an alloy which contained carbide precipitates in the grain boundaries were slowly heated to elevated temperature ($2150^{\circ}F$ or higher), the carbide precipitates would redissolve in the matrix. However, on rapid heating such as that which occurs in the heat-affected zone during welding, the carbides cannot redissolve as this is a slow diffusion dependent reaction. On arriving at sufficiently high temperature, the carbides interact with the adjacent material forming liquid in the grain boundaries by eutectic reaction.

Figure 20 shows the chromium-rich end of the chromium-carbon binary phase diagram. A eutectic is formed at three weight percent carbon lowering the melting point of chromium approximately $775^{\circ}F$. Similar reactions occur between small

amounts of carbon and every metallic element in Haynes-25 as shown in the following summary.

<u>Element</u>	<u>Approximate Wt. Percent Carbon</u>	<u>Approximate Melting Point Depression</u>
Cobalt ³	2.7	315°F
Chromium ⁴	3.0	775°F
Tungsten ⁵	2.2	1205°F
Nickel ⁶	2.2	255°F
Iron ⁷	4.3	695°F
Manganese ⁸	1.3	27°F

Since the melting temperature of each of the alloying elements is lowered by a small amount of carbon, the reaction which occurs during welding in the heat-affected zone is actually a multi-component eutectic reaction. Resolidification of the liquid film in the grain boundary does not form a solid phase like the adjacent grains of Haynes-25 because the liquid is no longer the same in composition; it is carbon rich. During solidification segregation occurs in the carbon-rich liquid forming more than one phase as dictated by the phase equilibrium relationships.

To illustrate this reaction better, two of the capsule components were intentionally heat treated improperly enhancing carbide precipitation prior to welding. This

provided a specimen for analysis which had experienced severe grain boundary liquation and hot cracking. Figure 21 shows this detail. This is a photograph of a composite illustration made for study at high magnification. Liquation occurred along a continuous grain boundary path extending completely across the 0.020" step.

In the center of the grain boundary liquation area in Figure 21 is a continuous light gray phase with many small fingers protruding to the sides. This represents dendritic growth of the first phase to solidify in the liquid film. The only manner in which this structure can result is by unrestrained growth in liquid. The first phase to solidify is a carbide phase. It is surrounded on both sides by a light colored band, the second phase to solidify, which is much the same in appearance as the adjacent Haynes-25 base metal. This phase is a cored solid solution similar in composition to Haynes-25. The carbide phase is extremely hard and brittle and subject to microcracking. The dark segment in the upper half of the grain boundary liquation area is a void where a small amount of pull-out occurred. With excessive polishing this entire area would have appeared as one continuous fissure. Near the bottom are two large void areas which did

not result from brittle pull-out. These are two microfissures (hot cracks) which resulted from movement of the liquid prior to solidification.

Figures 22 and 23 present further enlargements of the retained detail after severe grain boundary liquation. The many small protrusions from the sides of the carbide phase are particularly apparent in Figure 22, and Figure 23 exhibits similar detail in addition to a wide microfissure at the bottom.

An illustration of exceptionally severe grain boundary liquation is shown in Figure 24. This was the most massive concentration of resolidified liquid in a grain boundary observed in this work and retained during metallographic polishing. The unusual width of the liquid film apparently permitted growth of the carbide phase in a network pattern rather than as the usual platelet at the center of the film. Portions of the fragile carbide network experienced brittle pull-out.

The reaction of carbide precipitates with the metallic constituents of the alloy producing liquation was not restricted to grain boundaries. The individual carbide particles distributed randomly in the microstructure were equally

subject to the same reaction when they occurred in the heat-affected zone. Small, individual, spherical pockets of liquid were formed by this reaction, and resolidification resulted in segregation, just as in the liquid grain boundary films, producing a carbide phase surrounded by a solid-solution alloy phase. Figure 25 shows two small areas which experienced liquation. A star-shaped particle frequently resulted from the rapid nucleation and growth of the carbide phase.

Individual carbide particles distributed in flow lines produced the heat-affected zone detail shown in Figure 26. The interaction of the carbide particles with the base metal formed spherical volumes of liquid of varying size indicative of the thermal gradient across the heat-affected zone during welding. In severe cases a stringer-like effect was created by growth of adjacent liquid pockets which joined together.

In further study of the grain boundary liquation reaction, weldments were examined by sectioning in an additional manner different from the transverse sections and longitudinal sections made vertically at the side of the weldment. Figure 27 is a photograph of a composite illustration made for study at high magnification showing a longitudinal section made

horizontally between the top and bottom of the weldment. The section is near the base of the weldment, but it does not parallel the base due to the curvature of the weld ring. The large voids on the right are the interface of the unmelted step joint, and the segment between the voids is the unmelted 0.020" step.

Numerous grain boundaries which experienced liquation are apparent in Figure 27. They are especially prominent on the right side which is the more extensive heat-affected zone. However, liquation did not occur in all the grain boundaries which touched the weld pool, and those which did experience liquation did not form a continuous network. The orientation of the liquated grain boundaries reflects only the random orientation of the adjacent grains. The relative concentration of microfissures present along with the retained material in liquated grain boundaries can be observed by close examination of this illustration. Seepage of trace quantities of liquid from the voids stained the surface marking the location of each microfissure. These are minute spots, and only a few are present. They appear as very short sections within the liquated grain boundaries.

The phases which resulted from grain boundary liquation were

identified by electron microprobe x-ray analysis. The specimen shown in Figure 21 was employed for this work as it contained the largest examples of the retained reaction products. The determinations were made by scanning slowly across the reaction layer to establish the composition profile for each element of the alloy. The representative results are illustrated by eight curves shown in Figures 28 and 29.

Each of the curves in Figures 28 and 29 is identified with a three line caption which defines the type of x-radiation detected in the analysis, the excitation voltage and beam current, and the counting rate at full scale deflection. The analyses were made under different conditions in order to optimize the qualitative detection of the elements and to illustrate their distribution in the reaction layer more sensitively. The curves made under different conditions cannot be compared quantitatively as their relative positions on the chart are not indicative of the relative concentrations of the elements. The statistical fluctuations in the curves for silicon, carbon and tungsten resulted from the use of lower counting rate scales (higher amplifications) than the scale employed for the other elements.

The tops and bottoms of the curves in Figures 28 and 29 are representative of the concentrations of the elements in the Haynes-25 base metal. The portions of the curves representing the positions of the gray phase in the center of the reaction layer and the surrounding light-colored phase are indicated in the margin. Tungsten, chromium and carbon show sharp enrichments in the gray phase, and the adjacent light-colored phase is slightly enriched in tungsten and chromium. Just outside this phase the Haynes-25 is slightly depleted in these elements. Where tungsten, chromium and carbon are concentrated in the reaction products, cobalt and nickel show corresponding depletions in both phases of the reaction layer. Very small amounts of iron and manganese are present in the alloy, but the curves show definite indication of depletion of these elements in the reaction layer. An insignificant amount of silicon is present in the alloy. The lack of variation in this curve indicates the absence of silicon segregation in the reaction products. Similar analyses were made for phosphorous and sulfur, and the results showed no detectable segregation in the reaction products.

These results indicate that the gray phase in the center of

the reaction layer is a carbide of chromium and tungsten. The ratios of the elements are unknown, although the phase is probably (Cr,W)C as the monocarbides ordinarily form from the melt. The light-colored phase which surrounds the carbide phase does not appear to be significantly different in composition from Haynes-25. However, the portions of the curves which define this phase show considerable slope indicating severe coring. The composition gradients show increased concentrations of chromium and tungsten toward the center of the reaction layer and reversed composition gradients for cobalt and nickel.

Electron microprobe x-ray analyses were also conducted on the reaction products which resulted from the liquation reaction between individual carbide particles and the base metal. The analysis of specimens such as those shown in Figure 25 gave results essentially the same as those described above for the reaction products of grain boundary liquation.

In the metallographic analysis of many weld sections, only occasional evidence was observed of true microfissures. The majority of the intergranular detail which appeared to be void was the result of brittle pull-out. Both conditions

are recognized as being highly undesirable, but it is nonetheless of value to distinguish between them. A series of illustrations is presented in Figures 30-36 to further illustrate grain boundary liquation and the pull-out phenomenon. The specimen is an electron beam weldment of Haynes-25 from the same lot as the material in all the previous illustrations.

Figure 30 shows an unetched transverse weld section prepared by the metallographic procedure described earlier. Some very faint features are apparent in relief on the surface, but the specimen shows no "open" detail.

The identical specimen, still unetched, is shown in Figure 31 after being subjected to additional polishing. Two small voids which were not present in the previous illustration are now present as the result of overpolishing and brittle pull-out.

The overpolished section, etched, is shown in Figure 32, and the two voids in Figure 31 can be recognized as grain boundaries in the weld heat-affected zone. In subsequent illustrations the void grain boundary in the upper right-hand corner is shown in greater detail.

In Figure 33 the specimen is overpolished and unetched, and the void grain boundary has the distinct appearance of a microfissure.

Figure 34 shows the same area of the specimen, etched, before overpolishing, and the grain boundary is shown not to be void, but rather filled with solid material.

Figure 35 shows the same area of the specimen, etched, after overpolishing, and again the grain boundary has the appearance of a microfissure. This illustrates the importance of proper specimen preparation to avoid misinterpretation of the microstructural detail.

Figure 36 is a further enlargement of the same area showing a small segment of the grain boundary material which did not experience brittle pull-out. All grain boundaries which have experienced grain boundary liquation are not equally subject to brittle pull-out. This is probably the result of variations in damage to the brittle constituents by microcracking from thermal stresses which occur on cooling. When pull-out does occur, it originates in the breakup and dislodgement of the first phase to solidify, the carbide phase, followed by the dislodgement of the remainder of the

material in the reaction layer.

The metallurgical factors which promote hot cracking in Haynes-25 appear to be essentially the same as the ordinary causes of embrittlement and cracking. Wlodek⁹ pointed out the probable contribution of $M_{23}C_6$ precipitates to embrittlement and the beneficial effects of fine grain size and low carbon content. Ramsey¹⁰ stated that cold-worked Haynes-25 will crack during welding, and he recommended a limitation of 5% cold reduction and a grain size of ASTM 5 or finer.

The difficulties experienced in this work can be directly attributed to the condition of the base metal. The material was coarse grained exhibiting a variation from $4\frac{1}{2}$ to 1 grain per square inch at 100X. The average grain size was ASTM 3.

The hardness of fully annealed Haynes-25 is Rockwell C 22, and 5% cold reduction increases the hardness to Rockwell C 27. The material employed in this work typically gave a hardness of Rockwell C 30-35, equivalent to approximately 15% cold reduction, and in a few cases the hardness was as high as Rockwell C 42 which is equivalent to approximately 20% cold reduction. The increased hardness of the material was not caused by cold work alone, but was also the result

of carbide precipitates produced by inadequate solution heat treatment and by deformation of the material. Figure 37 illustrates the microstructure of the material near the outer edge of the heat-affected zone where grain boundary liquation is still apparent, and Figure 38 shows the microstructure of the base metal well beyond the heat-affected zone. Both illustrations show gross evidence of stress induced precipitation caused by deformation when the components were machined from bar stock.

The specimens in Figures 39 and 40 were etched electrolytically in 10% sodium cyanide. This etchant is typically employed to reveal the presence of carbides. Figure 39 shows a portion of the base metal containing a high concentration of randomly distributed carbide precipitates in addition to segregated precipitates in grain boundaries. Figure 40 shows a portion of the base metal in which the grain boundaries are well defined by the presence of segregated carbide precipitates.

The specimens in Figures 41 and 42 were also etched electrolytically in 10% sodium cyanide. Figure 41 shows carbide particles distributed in flow lines in stringer-like arrays, and Figure 42 shows the face of a weldment where grain

boundary liquation occurred in the heat-affected zone producing a carbide phase.

The problem of grain boundary liquation and hot cracking experienced in this work was clearly a materials problem. As a result of this experience a new material specification for Haynes-25 was prepared.¹¹ This will serve as the basis for future Mound Laboratory requirements.

The final illustrations, Figures 43-48, show several weldments which illustrate that Haynes-25 is not inherently subject to grain boundary liquation during welding. The weldments were made by tungsten inert gas welding employing material from a source other than that involved in the work described in this report.

The specimen in Figure 43 is a butt weld of sheet material. It was etched electrolytically in oxalic acid and shows a clean interface between weldment and base metal. Figure 44 shows the same specimen etched with HCl-H₂O₂, and a further enlargement of the heat-affected zone is shown in Figure 45. Evidence of grain boundary liquation is not apparent. This material has an average grain size of ASTM 5.

Figure 46 shows the heat-affected zone of a weldment in a

drawn tubular component. The recrystallized base metal has a minute grain size, and the specimen is exceptionally clean and free of grain boundary liquation.

Figure 47 shows a compound weldment in a component made by deep drawing. The specimen was etched electrolytically in oxalic acid and shows a remarkably sharp interface between weldment and base metal. The same specimen is shown in Figure 48 with the grain structure of the recrystallized base metal revealed by the $\text{HCl-H}_2\text{O}_2$ etch. Again it illustrates the fine grain size which accompanies a sound weldment free of defects.

SUMMARY

The metallographic analysis of weldments of Haynes alloy No. 25 revealed unusual microstructural detail which appeared to be intergranular cracks in the weld heat-affected zone. The weldments were produced by tungsten inert gas welding at a step joint in tubular components with a wall thickness of 0.060". The identity of the unusual microstructural detail as cracks was uncertain, as the severity of the detail varied with the metallographic procedure. Etching the metallographic specimens with an etchant which did not reveal the microstructure of the base metal showed the presence of an

intergranular material in the weld heat-affected zone. This material was found to experience brittle pull-out during metallographic polishing, and the intergranular voids developed by overpolishing resembled cracks.

An improved metallographic procedure was developed which resulted in the retention of the brittle intergranular material. It was identified as the reaction product resulting from grain boundary liquation - the melting of material in grain boundaries at a temperature below the solidus temperature of the alloy. Segregation occurred during solidification of the liquid films in the grain boundaries resulting in the formation of two discrete phases. These were analyzed by electron microprobe x-ray analysis and found to be a chromium/tungsten carbide phase and a cored solid solution phase similar in composition to the base metal.

The occurrence of grain boundary liquation in the heat-affected zone was attributed to eutectic reaction between carbon and all the constituents of the alloy. Carbon was present in grain boundaries by virtue of carbide precipitates segregated in the grain boundaries. On rapid heating the carbide precipitates were unable to redissolve, and

melting occurred by eutectic reaction. Evidence of similar eutectic reaction was also observed in the heat-affected zone where carbide particles were isolated within grains and distributed in flow lines.

The momentary presence of liquid films in grain boundaries occasionally resulted in intergranular separations due to mechanical factors. These hot cracks were retained when the material experienced rapid cooling. Careful metallographic preparation revealed the hot cracks in the network of liquated grain boundaries, although they were small and few in number in comparison to the intergranular voids observed originally which resulted from brittle pull-out.

Metallographic examination of the base metal revealed the metallurgical characteristics to which the grain boundary liquation and hot cracking were attributed. The material was coarse grained (ASTM 3); carbide precipitates were observed in abundance in grain boundaries, within grains and distributed in flow lines; and the material exhibited some cold work received during machining. Weldments made in material which did not exhibit these characteristics were free of grain boundary liquation and hot cracks.

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FIGURE 1 - Weld joint design.

FIGURE 2 - Transverse weld section,
HCl-ethanol etch (40X).

FIGURE 3 - Transverse weld section, oxalic etch (40X).

FIGURE 4 - Transverse weld section, $\text{HCl-H}_2\text{O}_2$ etch (40X).

FIGURE 5 - Transverse weld section showing apparent crack, $\text{HCl-H}_2\text{O}_2$ etch (40X).

FIGURE 6 - Transverse weld section showing apparent crack, $\text{HCl-H}_2\text{O}_2$ etch (40X).

FIGURE 7 - Transverse weld section, overpolished, showing flow lines, $\text{HCl-H}_2\text{O}_2$ etch (40X).

FIGURE 8 - Intergranular void in heat-affected zone, oxalic etch (250X).

FIGURE 9 - Intergranular void in heat-affected zone, $\text{HCl-H}_2\text{O}_2$ etch (250X).

FIGURE 10 - Longitudinal section showing portion of weld above heat-affected zone, oxalic etch (35X).

FIGURE 11 - Intergranular voids resulting from excessive brittle pull-out, longitudinal section in heat-affected zone, overpolished, unetched (45X).

FIGURE 12 - Transverse weld section, as-polished (40X) .

FIGURE 13 - Transverse weld section, oxalic etch (40X) .

FIGURE 14 - Transverse weld section, severely overpolished (40X).

FIGURE 15 - Transverse weld section, severely overpolished, oxalic etch (40X).

FIGURE 16 - Microfissures in heat-affected zone, longitudinal section, as-ground (55X).

FIGURE 17 - Microfissures in heat-affected zone, longitudinal section, as-polished (55X).

FIGURE 18 - Retained intergranular detail in heat-affected zone, HCl-ethanol etch (400X).

FIGURE 19 - Retained intergranular detail in heat-affected zone, HCl-ethanol etch (400X).

FIGURE 20 - The chromium-carbon system.

FIGURE 21 - Severe grain boundary liquation and hot cracking, oxalic etch (475X).

FIGURE 22 - Reaction products of grain boundary liquation, oxalic etch (1200X).

FIGURE 23 - Reaction products of grain boundary liquation, oxalic etch (1200X).

FIGURE 24 - Reaction products of severe grain boundary liquation showing network of carbide phase, oxalic etch (750X).

FIGURE 25 - Reaction products of liquation between carbide particles and base metal, oxalic etch (1500X).

FIGURE 26 - Reaction products of liquation between carbide particles in flow lines and base metal, oxalic etch (1000X).

FIGURE 27 - Horizontal section near base of weld showing frequency and orientation of liquated grain boundaries in severely affected area, HCl-ethanol etch (22X).

FIGURE 28 - Electron microprobe traces for iron, carbon, chromium and tungsten.

FIGURE 29 - Electron microprobe traces for manganese, silicon, nickel and cobalt.

FIGURE 30 - Transverse section, electron beam weld, as-polished (45X) .

FIGURE 31 - Transverse section, electron beam weld, overpolished, showing two areas where pull-out occurred (45X) .

FIGURE 32 - Transverse section, electron beam weld, overpolished, HCl-H₂O₂ etch (65X).

FIGURE 33 - Intergranular void produced by overpolishing (320X).

FIGURE 34 - Retained solid material in grain boundary where liquation occurred, oxalic etch (320X).

FIGURE 35 - Intergranular void produced by overpolishing, $\text{HCl-H}_2\text{O}_2$ etch (320X).

FIGURE 36 - Intergranular void produced by overpolishing, HCl-H₂O₂ etch (1500X).

FIGURE 37 - Grain boundary liquation and stress induced precipitation in heat-affected zone, HCl-H₂O₂ etch (600X).

FIGURE 38 - Stress induced precipitation in base metal, $\text{HCl-H}_2\text{O}_2$ etch (100X).

FIGURE 39 - Randomly distributed carbides and segregated carbides in grain boundaries of base metal, NaCN etch (100X).

FIGURE 40 - Segregated carbides in grain-boundaries of base metal, NaCN etch (1000X).

FIGURE 41 - Carbides in flow lines of base metal, NaCN etch (100X).

FIGURE 42 - Carbides in heat-affected zone, NaCN etch (100X).

FIGURE 43 - Transverse section, butt weld, oxalic etch (40X) .

FIGURE 44 - Transverse section, butt weld, HCl-H₂O₂ etch (40X) .

FIGURE 45. - Heat-affected zone, butt weld, $\text{HCl-H}_2\text{O}_2$ etch (150X).

FIGURE 46 - Weld heat-affected zone in fine grained drawn component, $\text{HCl-H}_2\text{O}_2$ etch (150X).

FIGURE 47 - Transverse weld section, oxalic etch (40X).

FIGURE 48 - Transverse weld section, HCl-H₂O₂ etch (40X).

X ⁴⁰
THE CHARACTERIZATION OF SOME Cr_{23}C_6 -MODIFIED
 $(\text{U},\text{Pu})\text{C}$ FUELS FOR IRRADIATION TESTING*

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ABSTRACT

Additions of modifying materials to nonstoichiometric $(\text{U},\text{Pu})\text{C}$ have been proposed, ^(1,2) in an attempt to improve the compatibility of these potential fast reactor fuels with stainless steel cladding. The modifying materials react with the secondary phases to form more refractory and less reactive secondary phase products during the sintering cycle of the fabrication of $(\text{U},\text{Pu})\text{C}$ pellets. Such pellets have been fabricated for thermal and fast flux irradiation studies in which Cr_{23}C_6 has been added as the modifier to hypo-stoichiometric $(\text{U},\text{Pu})\text{C}$ powder. The "ideal" structure of these pellets should be a matrix of $(\text{U},\text{Pu})\text{C}$, with secondary phases of $\text{Cr} + \text{Cr}_{23}\text{C}_6$ occurring as a grain boundary network.

Metallographic, chemical, and electron microprobe techniques have been used to determine the composition of the phases which occurred in Cr_{23}C_6 -modified

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(U,Pu)C fuel pellets. The pseudo ternary (U,Pu)-Cr-C phase diagram has been constructed by extrapolation from the U-Cr-C diagram⁽³⁾ and the pellet compositions obtained have been located on this.

The various characterization techniques that have been employed will be presented along with details of how the data from each is related and used to predict pellet composition.

1. INTRODUCTION

A variety of modified and unmodified (U,Pu)C fuel types have been fabricated and characterized for thermal and fast flux irradiation experiments. The purpose of modification is to eliminate any free fissile metal from the structure and thus minimize the possibility of incompatibility between fuel and stainless steel cladding during irradiation. Small amounts of a modifier, such as Cr, Fe, Mo, Rh, V, or W may be added to carbide to produce phases of a desired stability. At Westinghouse the effects of two of these have been investigated, namely Cr and Fe.

The work discussed in this paper was concerned with Cr additions to (U_{0.8}Pu_{0.2})C fuel materials. In this case Cr was added to the carbide in the form of Cr₂₃C₆ during the powder stage of pellet fabrication. Comprehensive facilities and procedures have been developed to characterize the modifying phases that resulted, so that the material could be certified as acceptable for irradiation.

2. EXPERIMENTAL FACILITIES AND TECHNIQUES

The characterization facilities at WARD are housed in four, double-sided, stainless steel glove boxes, three of which are interconnected and have a recycled, purified argon atmosphere. Water and oxygen contents in the latter are maintained at less than 1 and 100 ppm respectively. The fourth glove box has an air atmosphere and is used for carbon determinations, fusion sample preparation for X-ray fluorescence examination, and scrap oxidation.

(U,Pu)C pellets of all types are routinely analyzed for C, O, N, Pu, Fe, Cr, W, Pu/U, and total metallic impurities. Conventional techniques have been applied wherever possible, e.g., C content is determined by the combustion gravimetric technique.

Standard metallographic equipment and techniques have been employed in every instance of sample preparation, details of which have previously been presented.⁽⁴⁾ A Unitron bench microscope is used in conjunction with a Zeiss Polaroid camera, giving a maximum magnification of X600 on the print.

Specimens are generally hot mounted in electrically conducting mounts. Not only is this essential for vacuum cathodic etching, but the technique has proved useful for control during electrolytic etching. Pellets are usually mounted longitudinally and ground to mid-section before polishing. A 100-mesh diamond disc is used during the grinding operation, while 180 through 600 silicon carbide papers are used during the fine grinding stages. Dried kerosene provides the grinding medium inter-stage cleaning being undertaken in an ultrasonic cleaner containing dried xylene.

Final polish is achieved by the use of 6 μ through 1/4 μ diamond pastes on Metcloth wheels lubricated by a mixture of dried kerosene and silicone oil.

Once prepared, samples are examined macroscopically for cracks and other flaws, and microscopically for porosity characteristics, grain size, pore volume, and location of pores and secondary phases.

Three etching techniques have been used in this work, namely aqueous swabbing, d.c. electrolytic, and vacuum cathodic. Difficulty has been

encountered in selecting standardized etching procedures for the various fuel types in order to delineate microstructures. This, it is felt, is due to the wide range of structures encountered in samples of a particular fuel type. Consequently, a variety of etchants have been employed, the principal ones among which will be enumerated later.

In addition, samples have been sent to LASL for electron microprobe, microhardness and X-ray diffraction examination. Unfortunately, in all cases, the volume of secondary phases was too small to permit their identification by X-ray diffraction techniques.

3. (U,Pu)-Cr-C Ternary Phase Diagram

A tentative, relevant portion of the (U,Pu)-Cr-C ternary phase diagram has been constructed by extrapolation from the U-Cr-C diagram, determined by Briggs, et al.⁽³⁾ The diagram is intended to show tie lines for the quenched-in solid phases, while taking into account the work of Anselin, et al,⁽⁵⁾ concerning the homogeneity ranges of UC and PuC.

The analytical chemistry data has to be adjusted so that the fuel may be represented as a three-constituent system, and consequently the following assumptions had to be made.

- (a) Uranium and plutonium are equivalent.
- (b) Oxygen and nitrogen are equivalent to carbon, so that the adjusted values are included to give an equivalent carbon figure, denoted C_E .
- (c) Total metallic impurities, e.g., tungsten, behave in a similar stabilizing role to that of chromium. Thus, these are considered with chromium equivalent Cr_E .

(d) The system in phase equilibrium.

The diagram is shown in Figure 1. "Ideally," the structure should consist of a (U,Pu)C matrix with Cr_{23}C_6 and Cr metal as the grain boundary phases. However, it is apparent that the region in which the "ideal" composition is located is rather small, so that slight variations in fuel composition may yield alternative secondary phases Cr_7C_3 , Cr_3C_2 , or (U,Pu) CrC_2 . Included in Figure 1 are the analytical composition points for some typical fuel batches.

4. PHASE IDENTIFICATION

Positive identification of these possible phases has involved a variety of approaches based principally on data from analytical chemistry, point counting secondary phase volumes (linear intercept method) and electron microprobe analysis. Phases and their volumes, predicted from analytical chemistry data are compared with data from optical metallography. This includes etched appearance and the point counted secondary phase volumes. Allowance may be made for standard errors encountered in the various procedures. However, any gross anomalies obviously indicated the need for reexamination of one or other of the analytical procedures.

5. RESULTS

The initial step in phase identification was to compare point-counted secondary phase volume with that predicted by the location of the analytical composition on the M-Cr-C phase diagram referred to above. Table I shows

representative data obtained by this procedure. There is reasonable agreement between the two sets of data, suggesting that this type of analytical approach was a fairly valid one. However, positive identification of the phases present was not assumed until microprobe data became available.

Table II summarizes the microprobe data obtained on eight representative samples. It should be noted at this point that tungsten contamination to various levels occurred during the fabrication process due to the use of a tungsten electrode during the arc-melting operation and a tungsten carbide lined ball mill for grinding.

Four distinct secondary phases were identified and characterized. The most abundant was type A which proved to be a chromium carbide. At least small amounts of phase B were found in all samples, with microprobe X-ray intensity values fairly conclusively identifying this as a $(U,Pu)CrC_2$ phase. The microhardness attributed to this phase varied widely in the range 1400-3000 kg/mm^2 , possibly due to the variable compositions arising from different degrees of W contamination.

Phase C occurred in only one batch, which happened to have an exceptionally high oxygen content. It was apparent from the microprobe X-ray intensities that it is the mixed oxide.

Phase D occurred only in the three fuel batches containing relatively high amounts of tungsten contamination, i.e., 1-3 w/o. This compound is indicated to be a $(U,Pu)WC_2$ phase.

Table III illustrates microprobe and microhardness data for the most abundant secondary phase, Phase A, which is obviously a chromium carbide. Several interesting features have been observed from this data, not least of which is an explanation of the discrepancy observed above in the point count analysis.

The Cr intensity for the more pure samples of Phase A appears to be well represented by a value of 90%. This agrees quite well with the w/o of Cr in Cr_7C_3 and not as well with Cr_3C_2 . A fair degree of confidence is placed in the Cr intensity values since a chromium carbide, believed to be Cr_{23}C_6 , gave a Cr intensity reading of 94.1%. The microhardness values also compare better with those reported for Cr_7C_3 . Phase A, therefore, has been tentatively identified as Cr_7C_3 rather than Cr_3C_2 . If Phase A is considered to be Cr_7C_3 , there is also better correlation between the microprobe and analytical phase identification. Thus, there are several strong indications that the MC- Cr_3C_2 tie line does not exist for mixed carbide materials equilibrated at 1550°C.

Phase identification by metallography alone proved to be extremely difficult, particularly in light of lack of contrast observed between the secondary phases. Figure 2 illustrates the typical structure of Cr_{23}C_6 -modified (U,Pu)C electrolytically etched in 2:1 acetic-nitric acid. However, several etches are known, or have been found, to preferentially attack specific phases. In some instances, this has allowed reasonably positive metallographic identification of the other secondary phase, if present, by phase equilibrium considerations.

A 5 v/o bromine in methanol swab etch has been successfully applied in testing for free Cr metal in the intergranular secondary phase area. Figure 3 shows a normal electrolytically etched structure before and after a severe bromine/methanol swab. It can be observed that despite partial attack on the matrix grains, the intergranular secondary phase has remained passive to the etch, indicating an absence of free metal. Point counting and analytical chemistry had indicated that neither of the secondary phases were, in fact, free metal, and later microprobe analysis confirmed these indications.

An 85% orthophosphoric acid swab etch was found to be particularly active in the detection of impurity phases. The isolated instances of high tungsten contamination resulted in the formation of $(U,Pu)WC_2$. Figure 4 shows a mottled secondary phase area, the darker material later positively identified by microprobe analysis as being a high tungsten-containing phase. Consequent equilibrium considerations using a $(U,Pu)-Cr-C-W$ quaternary phase system strongly implied that the phase was $(U,Pu)WC_2$.

A similar response has been found with $(U,Pu)O_2$, formed in one instance, with a recycled fuel batch, which had a very high oxygen content. Results obtained with the same 85% orthophosphoric swab etch is shown in Figure 5. The dark grey phase, adjoining both the matrix and the other, lighter, secondary phase, is the $(U,Pu)O_2$. Confusion between the $(U,Pu)WC_2$, mentioned previously, and $(U,Pu)O_2$ is avoided when the much darker coloration of the latter is taken into account. In addition, the oxide does not apparently mix as intimately with other secondary phases present as does the $(U,Pu)WC_2$.

Figure 4 also shows a structure, indicative of a peritectic reaction, that always occurred when the material contained large quantities of tungsten. The "reaction rims" are not an etching artifact and have also been revealed by a 2:1 acetic:nitric electrolytic and vacuum cathodic etching.

The foregoing discussion has outlined WARD's scheme of operation regarding phase identification in Cr_{23}C_6 modified (U,Pu)C fuel. It is apparent from this discussion that not all the fuel produced contains the ideal secondary phases of Cr_{23}C_6 and Cr metal.

The major unanswered problem lies in the compatibility of Cr_7C_3 and perhaps Cr_3C_2 with the stainless steel cladding material in a sodium environment. Mol⁽⁶⁾ reports that if the composition of the Cr_{23}C_6 -modified UC is not in the "ideal" UC- Cr_{23}C_6 + Cr phase triangle gross carburization of the stainless steel results. Tests were run at a temperature of 800°C for twelve weeks. However, the material used for these tests was not fabricated by the same route as that made by WARD.

The work of Jacoby, et al,⁽⁷⁾ at ANL tends to discount this. Compatibility tests were run at a temperature of 800°C for 1,000 hours (~six weeks) of Cr_{23}C_6 -modified (U,Pu)C against stainless steel in a sodium environment, and no reaction was observed. Microprobe examination of the fuel revealed no free Cr metal, indicating the presence of higher carbides of chromium. Further evaluation of these data is currently being undertaken in an attempt to locate the composition more closely.

Initial results on the irradiation behavior of sodium-bonded, Cr_{23}C_6 -modified (U,Pu)C in a thermal flux have indicated that the swelling rates are comparable to those of the sodium-bonded hyperstoichiometric fuels.⁽⁸⁾

These results were obtained during an irradiation experiment where the hottest pins attained peak burnups of between 48,000 and 53,000 mwd/tonne, at peak ratings of 28.4 to 32.0 kw/ft. The intermediate pins attained 33,000 to 36,000 mwd/tonne at 18.7 to 22.0 kw/ft., while the coolest pins reached 14,000 to 17,500 mwd/tonne at 10.6 to 12.7 kw/ft. Estimated cladding temperatures were 650 to 700°C, 500 to 550°C, and 450 to 500°C respectively.

6. CONCLUSION

Metallographic, analytical chemistry and microprobe observations, in conjunction with known phase data, have been shown to be very effective in the accurate characterization of small amounts of secondary phases in Cr_{23}C_6 -modified, (U,Pu)C fuels. Post-irradiation studies of the fuel should provide a useful correlation between predicted and actual behavioral characteristics of the various compositions discussed.

7. ACKNOWLEDGEMENTS

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Table I.

Comparison of Secondary Phase Volumes of
Cr-Stabilized (U,Pu)C Obtained by Metallographic
Point Count and Calculation from Analytical Chemistry Data

Batch No.	Metallography (v/o)	Analytical Chemistry (v/o)
502	7.3	6.0
503	5.6	7.4
511	7.0	9.5
514	3.5	3.7
518	8.8	7.9

TABLE II

SUMMARY OF MICROPROBE DATA

Sample No.	Secondary Phases (+ Vol. %)	Phase Description*
S1	B, A	A = Cr_7C_3 or Cr_3C_2
S2	B, C	B = MCrC_2
S3	B	C = MO_2
S4	A, B	D = MWC_2
S5	B, A	Matrix = MC
S6	A, D, B	
S7	A, D, B	
S8	A, D, B	

*M = nominally ($\text{U}_{0.8}\text{Pu}_{0.2}$)

TABLE III
DETAILS OF PHASE A AS DESCRIBED IN TABLE II

A. Available Data:

	Weight %			Hardness (kg/mm ²)
	Cr	C		
Cr ₃ C ₂	86.7	13.3	from literature	1000-1400
Cr ₇ C ₃	91.1	8.9		1600
Cr ₂₃ C ₆	94.3	5.7		1000

B. Representative Values for Six Samples:

Microprobe X-Ray Intensities, % ⁽¹⁾					Hardness (kg/mm ²)
Cr	C	U	Pu	W	
90	Present	<1	<1	<1	1520-1950

FIGURE-1

ANALYTICAL COMPOSITION
POINTS FOR SOME Cr-
MODIFIED (UP_U)C FUEL
BATCHES

Figure 2
Magnification X185

Figure 3
Magnification X300

Figure 4
Magnification X600

Figure 5
Magnification X600

ESTIMATION OF FOIL THICKNESS AND PORE SIZE
FROM ELECTRON MICROGRAPHS OF IRRADIATED
AUSTENITIC ALLOYS*

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ABSTRACT

Since irradiation-induced swelling of austenitic alloys has been traced to pore formation, quantitative determinations of pore size, distribution, and volume fraction have become important. Such measurements are made on electron micrographs of thin foils whose thicknesses must be known to make quantitative calculations possible. By adapting a method by Sellars and Smith⁽¹⁾ for determining the foil thickness of alloys containing precipitates, to the present problem of alloys containing pores, reasonable values within the expected range were obtained for the thickness of the specimen foils investigated. Furthermore, pore volume fractions calculated with these foil thicknesses showed good correlation with the bulk density changes observed in Types 304 and 347 stainless steel and Incoloy-800. The errors inherent in the method are discussed.

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X DIRECT OBSERVATION AND IDENTIFICATION OF TRANSMUTATION-PRODUCED
SILICON IN A NEUTRON-IRRADIATED ALUMINUM ALLOY*

^{Si}
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ABSTRACT

A commercial Al-1% Ni alloy exposed to high fluence neutron irradiation contains a very fine dispersion of precipitate. This precipitate coarsens markedly by one-hour postirradiation annealing at progressively higher temperatures. Chemical analysis, electron diffraction and electron probe microanalysis are used to identify this precipitate as silicon produced from aluminum by the transmutation reaction with thermal neutrons $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$, $^{28}\text{Al} \rightarrow ^{28}\text{Si} + \beta$.

INTRODUCTION

Creation of one element from another is common in nuclear fuels where fissioning occurs. Materials used for nuclear reactor structural components can also change their identity by capturing neutrons but this process of transmutation is relatively uncommon since such materials generally have small cross sections for neutron absorption. It is usually assumed, therefore, that no problems will arise in these materials from transmutation products, other than gases, during anticipated reactor lifetimes. However, of the usual reactor structural materials, aluminum

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has a comparatively large cross section for the production of silicon by the reaction $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ with thermal neutrons, followed by a β decay to ^{28}Si . Aluminum is used extensively as a structural material in water-cooled research reactors in which some components will be exposed to high neutron fluences during their many years of service. We might, therefore, expect the microstructures of these components to be modified by the introduction of the silicon, especially since silicon has a low solubility in aluminum. This paper describes the observation and identification of particles of transmutation-produced silicon in an aluminum alloy component from a research reactor at Oak Ridge.

MATERIALS AND IRRADIATION CONDITIONS

The material studied is the 8001 alloy, which is 1100 grade aluminum containing 1.0 wt % Ni for improved corrosion resistance. The irradiated specimens were cut from a reactor component for which no specific chemical analysis was available. The chemical analysis in Table 1 is typical of a similar unirradiated component.

Table 1. Chemical Analyses (wt %)

	8001 Al	
	Unirradiated	Irradiated
Cr	<0.03	
Cu	0.05	
Fe	0.35	
Mg	<0.01	
Mn	0.01	
Ni	1.0	
Si	0.08	0.40
Ti	0.008	
Zn	<0.05	
B	0.0002	
Al	bal	

The 8001 alloy specimens were cut from a water coolant channel sheath from the flux trap of the High Flux Isotope Reactor (HFIR). The sheath was exposed to 2.7×10^{22} thermal neutrons/cm² and a 1.0×10^{22} fast neutrons/cm² at $\sim 60^\circ\text{C}$. The alloy entered the reactor in a 30% cold drawn condition.

Calculations, using integrated, spectrum averaged neutron capture cross sections for aluminum,¹ indicated that we might expect roughly 0.5 wt % Si from transmutation reactions. Actual chemical analyses for silicon are given in Table 1. The analysis for the irradiated specimen includes the unknown amount of silicon originally present in the material. The correlation between calculated and actual silicon contents is reasonably good considering uncertainties in the neutron spectra and cross-section values.

RESULTS

Microstructural Observations

Samples were prepared for transmission electron microscopy by the technique described in a previous paper² on the structure of unirradiated 8001 alloy. The thinned samples were examined either in a Hitachi HU-200E electron microscope operating at 200 kv or an HU-11 operating at 100 kv. Microstructures of the as-irradiated specimens are shown in Fig. 1a. The white, polyhedral spots are irradiation-induced voids. These voids, and their behavior during postirradiation annealing, have been described elsewhere.³⁻⁵ Our interest in this paper is on the dark spots in the background. The contrast associated with these spots varied with local diffraction conditions but never disappeared. These spots are tiny precipitates, not dislocation loops, and are absent in the unirradiated

materials. The strain fields around the particles in the as-irradiated specimens made it impossible to determine the size of the particles with any precision, but they were certainly less than 100 Å diameter.

The particles coarsened during postirradiation annealing. Coarsening was barely evident at temperatures below 150°C (Fig. 1b) although contrast became sharper, but for such temperatures it was still not possible to resolve the morphology of the precipitate. After a 300°C anneal the precipitate coarsened appreciably and took the form of platelets, some of them thick (Fig. 1c). Regions adjacent to grain boundaries became noticeably denuded of precipitate but large particles were developed on the grain boundaries. Annealing at 400°C caused significant coarsening of the precipitate to a polyhedral form growing preferentially at the grain boundaries with a consequent depletion of precipitate within the grains (Fig. 1d). After annealing at 530°C the particles became very large (Fig. 1e) and at 540°C the grain boundary precipitates lost their polyhedral form and became large irregular flakes spreading along the grain boundaries (Fig. 1f).

The alloy in the unirradiated condition contained primary inclusions which did not appear to be influenced by subsequent irradiation. Such particles were usually large and were either rounded or cigar-shaped (see ref. 2) and were easily distinguished from the irradiation-induced precipitate. A further distinction between the two was that the resident particles were attacked more easily by the polishing condition. At the higher annealing temperatures, where the induced precipitate was polyhedral or was spreading along grain boundaries, the resident inclusions maintained their roundness.

Precipitate Identification

In addition to the chemical analyses, the irradiation-induced precipitate was identified by two techniques, electron diffraction and electron probe microanalysis. It was impossible to obtain diffraction patterns from the finely dispersed particles present in the as-irradiated states, but patterns obtained from the thin edges of the more massive particles produced by annealing the 8001 alloy at 400°C (Fig. 1d) yielded diffraction spots giving d-spacings that were consistent with those of silicon. Some faint spots having d-values larger than those of silicon were also present, but these may have arisen from contamination on the surface of the specimen.

The microanalyses were made with a Hitachi HXA-1 microprobe accessory fitted to a Hitachi HU-11 electron microscope operating at 50 kv. The beam was focused on particles at the edges of the hole in thinned foils of the irradiated 8001 alloy annealed at 400°C (Fig. 2). Analyses were made on several particles; the only elements detected were aluminum (from the adjacent matrix) and silicon. A typical x-ray intensity plot is shown in the lower half of Fig. 3. Because of the high background level caused by the β - γ activity of the irradiated samples, severe pulse height analysis (PHA) was necessary to resolve the peaks. Such PHA conditions would conceal any peaks for iron and nickel if they were present. However, when the PHA conditions were altered to reveal iron and nickel in the particles, none was detected; the minimum amounts of iron and nickel capable of being detected under these latter conditions would be about 0.5 wt %.

A probe analysis of one of the rounded resident particles in the 8001 alloy is shown in the upper curve of Fig. 3. In this case, PHA was not necessary since an unirradiated specimen was used. These particles are primarily aluminum and nickel with some iron, but some of the aluminum would come from the matrix. Although silicon was not found in these particles, the lower limit of detectability would probably be about 2 wt % Si.

DISCUSSION AND CONCLUSIONS

Our identification of the silicon was made on coarsened particles. We assume that these are representative of the much smaller particles present in the as-irradiated specimens, but we realize that some contamination of the particles with other impurities may have occurred during coarsening. Such contamination was not obvious.

It is not surprising that the silicon is present as visible particles in the as-irradiated specimens. The amounts of induced silicon are much in excess of its solubility in aluminum at the irradiation temperatures of 45 and 60°C; the solubility in unirradiated aluminum at 250°C is estimated to be only about 0.008 wt %.⁶ Agglomeration of the silicon during irradiation can be expected since the temperature ($\sim 0.36 T_m$) is quite high enough for vacancy diffusion, the process that controls migration of substitutional solutes. This diffusion will be enhanced by the high vacancy concentration produced by displacement damage. The presence of the voids is conclusive evidence of significant vacancy activity.

Spreading of the coarsened precipitate along grain boundaries during annealing at 540°C is also consistent with the expected behavior of silicon. At 540°C the aluminum lattice will dissolve about 1.3 wt % silicon.⁶

and possibly very much more in special localized regions such as grain boundaries. The spreading, therefore, is believed to be caused by the silicon dissolving into the boundaries and into the lattice adjacent to the boundaries. During air cooling from the annealing temperature, the grain boundary regions become supersaturated with silicon which then precipitates into the large flakes in Fig. 1f.

The irradiation-induced precipitates are silicon introduced by the $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$, $^{28}\text{Al} \rightarrow ^{28}\text{Si} + \beta$ reactions with thermal neutrons. There are no other possible sources that would increase the silicon content of the specimens so markedly during irradiation. Although Rau and Ladd⁷ have found precipitates in irradiated vanadium that are thought to be LiV_2O_5 produced when lithium from the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction combines with vanadium and interstitial impurity atoms, the present work is believed to be the first experimental identification of a solid transmutation product in a reactor structural material.

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Fig. 1. Typical Microstructures of the 8001 Aluminum Alloy. Irradiated at $\sim 60^{\circ}\text{C}$ to a fluence of 2.7×10^{22} thermal neutrons/ cm^2 and 1.0×10^{22} fast neutrons/ cm^2 . The voids and irradiation-induced precipitate (a) and its response to postirradiation annealing for 1 hour at 120°C (b), 300°C (c), 400°C (d), 530°C (e), and 540°C (f) are shown.

Fig. 2. Typical Coarsened Particle (400°C Anneal) at Edge of Foil Used for Electron Probe Microanalysis.

Fig. 3. Electron Microprobe Charts from Analyzed Particles in 8001 Alloy Showing Characteristic X-Ray Peaks from the Observed Elements. Upper chart is for a resident inclusion in the unirradiated alloy. Lower chart is for an irradiation-induced precipitate coarsened 1 hr at 400°C.

MICROSTRUCTURE OF IRRADIATED AND TESTED ZIRCALOY-2*

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ABSTRACT

Transmission electron microscopy has been used to study the microstructure of irradiated Zircaloy-2 cladding tubes after post-irradiation burst testing. In the as-irradiated condition the microstructure showed a very high degree of radiation damage consisting of a profusion of small "black spot" defect clusters resulting from atom displacement cascades. These defect clusters were effectively removed by withdrawing the condenser aperture and heating in the electron beam, or by one-hour vacuum annealing at temperatures of 500°C or greater. Rapid heating to temperatures in the range from 750 to 1000°C during burst testing caused recrystallization of the initially cold-worked structure, and complete removal of the radiation-induced defect clusters. This annealing of the defects eliminates dislocation pinning sites responsible for embrittlement, and probably accounts for the ductile failure mode of the ruptured tubes.

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✓ ELECTROLYTIC POLISHING OF HOMOGENIZED DELTA PHASE PLUTONIUM*

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ABSTRACT

A new technique was developed for electrolytically polishing homogenized delta phase plutonium. Homogenized delta plutonium, which is soft (38 DPH), is very difficult to mechanical polish without either scratches or flow metal. Mechanical polishing of delta plutonium is especially difficult because it is performed in a glovebox, but this technique utilizing a newly developed optical electro polisher-etcher, removes all flow metal and scratches. Specimens were satisfactorily electrolytically polished at 12.0 A/cm^2 for 5 to 15 seconds using an electrolyte of 10% nitric acid, and 90% ethylene glycol. Photomicrographs showing the removal of flow metal and scratches are included.

INTRODUCTION

Plutonium alloyed with 1 wt% gallium and stabilized in the delta phase is difficult to mechanically polish when it has been completely homogenized. Homogenized delta plutonium has a hardness of 38-42 (DPH). The usual mechanical polishing technique takes several hours, and the

*This paper is based on work performed under United States Atomic Energy Commission Contract AT(45-1)-1830.

final results very often are not satisfactory, due to scratches and flow metal. Thus an electrolytic polishing technique was developed to remove the scratches and flow metal and to lessen the time required to obtain a metallographic finish.

SPECIMEN PREPARATION

The metal specimens were prepared for electrolytic polishing in three different ways. The first way (which is the standard procedure for this laboratory) was to mount the specimen in cold-setting resin, machine the surface smooth with a lathe, grind through 600-grit silicon carbide cloth, rough polish on a vibratory polisher using silk and $.3\mu$ alumina as the abrasive. The second method was to grind the specimen through 600 grit and then electrolytically polish. The third method was to electrolytically polish the specimen directly from the lathe.

The electrolytes and techniques were developed using a modified version of the optical etcher-polisher which was developed by Arrowsmith and Rencken.¹ Figure 1 shows the etcher-polisher in operation on a glove-box-enclosed metallograph. Figure 2 is a cut-away of the cell itself. Electrical contact between the anode and the specimen is made through a drilled hole in the back of the specimen mount. Specimens that are of a cylindrical shape, of any diameter, after being machined or ground, may be placed directly in the etcher without being mounted in cold-setting resin. This is a very fast means of determining grain size.

By being able to observe the specimen surface continuously, electrolytes could be evaluated very quickly. Another advantage of the optical etcher-polisher was the ease with which the correct voltage and current density could be selected and evaluated. On new materials, or when

evaluating new electrolytes, the experienced metallographer usually does not look at the voltage or current density, but maintains a visual observation of the specimen surface while increasing the voltage. By observation alone, the metallographer can select the correct voltage for either polishing or etching.

RESULTS AND DISCUSSION

A procedure was developed for the electrolytic polishing of homogenized delta phase plutonium. This procedure removes flow metal and scratches caused by mechanical polishing, and reduces the time required to obtain a metallographic finish.

During the experimental stage, several different electrolytes were evaluated. A solution of 10% nitric acid in ethylene glycol was found to be the best. For this electrolyte to work properly, it must first be cured. This can be accomplished by passing a current through the solution (about 30 Vdc) using two small stainless steel plates as the anode and cathode. The curing takes about 1 minute, or until the solution is a yellow-green color. More pitting occurs when the solution is not cured. Two other electrolytes that were evaluated were phosphoric acid in ethylene glycol and tetrakisphosphoric acid in 2-ethoxyethanol and water. Both of these electrolytes were satisfactory, but the amount of surface relief and pitting was excessive when compared to the nitric acid solution. With some adjustment in the composition of the phosphoric acid solution, it could possibly be used for the delineation of grain boundaries. By being able to continuously observe the sample surface while evaluating electrolytes, it was found that phosphoric acid in ethylene glycol did chemically attack delta phase plutonium, and revealed some grain

boundaries. Table 1 lists some of the electrolytes that were evaluated.

Table 1. Electrolyte Evaluation for Electrolytic Polishing of Homogenized Delta Phase Plutonium

Electrolyte	Current Density/cm ²	Remarks
10% Nitric Acid	1.2 amps/cm ² to 12 amps/cm ² 5 second intervals	<u>Good</u> - The higher current density is best. No pitting.
10% Nitric Acid 10% Methanol 80% Ethylene Glycol	Same	<u>Fair</u> - High current density. Small amount of pitting.
17% Water 23% Tetraphosphoric Acid 60% 2-ethoxyethanol	4.0 amp/cm ² 5 second intervals	<u>Fair</u> - Excessive pitting. Gassing ₂ above 4.0 amps/cm ²

After a suitable electrolyte was found, the homogenized delta was electropolished from three different starting surface conditions. The first method was to electropolish the specimen directly from the as-machined condition. Although this worked reasonably well there was an excessive amount of surface relief and edge rounding, due to the length of time required to remove all traces of machining. Thus electropolishing and electroetching delta stabilized plutonium from the as-machined condition was not satisfactory except for quick examination of the grain size.

The second method was to grind the specimen through 600-grit silicon carbide cloth and electropolish. Electropolishing after grinding was much better than electropolishing the machined surfaces because it took less electrolytic polishing time. The polishing time was two minutes at 180 Vdc at 12 A/cm². Current was applied to the specimen five seconds at a

time. If the current was held for longer periods, a heavy oxide layer formed, due to surface heating of the specimen. However, this layer could be removed by allowing the surface to cool five to ten seconds and then applying a voltage of 180 volts for a fraction of a second. With the continuously circulating electrolyte system incorporated in the optical etcher-polisher¹ the specimen surface was cooled rapidly. Figure 3 illustrates three different stages of electropolishing -- the as-ground condition (Fig. 3a), after 20 seconds of electropolishing (Fig. 3b), and after the final electropolish (Fig. 3c). Note the faint grain boundaries and the shadowy surface relief in Fig. 3c. These photomicrographs were taken with the electrolyte flowing past the specimen surface.

The third condition of electropolishing was accomplished using a mechanically polished specimen. The mechanical polish was done in the normal way, except instead of polishing on the vibratory polisher for six to seven hours, the specimen was polished for two hours. The specimen was then placed in the optical etcher-polisher¹ and electropolished for 20 seconds, five seconds at a time. It was found that electropolishing occurred between 1.2 A/cm^2 and 12 A/cm^2 . The higher current density proved to be the most successful since there was less surface relief, and better retention of the inclusions. Just as in the electropolishing of alpha plutonium² an anodic film (or reaction layer) was formed, but it was continually flushed away by the flow of the electrolyte. Figure 4 represents different degrees of electropolishing homogenized delta plutonium from the mechanically polished conditions -- as mechanically polished (Fig. 4a), after a 10-second electropolish (Fig. 4b), after a final electropolish (Fig. 4c), and after a bright field grain boundary etch

(Fig. 4d). Note the scratches that are revealed in Fig. 4b after the removal of flow metal, and then the removal of the scratches in Fig. 4c. The grain boundary delineation was accomplished using an electrolyte developed by Hays,³ which has a composition of 200 ml methanol, 116 g citric acid, and 10 ml of a solution of 25 g potassium nitrate per 100 ml of water. Grain boundaries could also be delineated by the addition of 10% methanol to the electrolytic polishing solution. However, with the addition of methanol there was more surface pitting.

A manifold type arrangement, consisting of three valves located on the inlet side of the pump, was used for switching from one electrolyte to another. One valve was to introduce an electrolyte to the etcher. A second valve was to introduce a rinse, and after rinsing another electrolyte could be introduced using the third valve. This arrangement worked very well, because it was fast and the specimen did not have to be removed from the etcher and exposed to the atmosphere.

By comparing Fig. 4c and 3c, it can be seen that much less relief occurs if the specimens had been mechanically polished first rather than electropolishing directly from the 600-grit silicon carbide. But, for a rapid check of grain size the second method is very adequate.

After electrolytic polishing, sometimes it is advisable to give the specimen a final mechanical polish. For example, if the specimen is not completely homogenized it will be more apparent by mechanical polishing, but not so easily detected in the electropolished condition.

CONCLUSION

A new technique and electrolyte was developed for the electrolytic polishing of homogenized delta phase plutonium, using an optical

electropolisher-etcher. With this technique, specimens can be rapidly polished from the as-machined or as-ground condition. Metallographic examination can be attained in a short time compared to the standard mechanical polishing method.

ACKNOWLEDGMENTS

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FIGURE 1
Polisher-etcher on the Stage of a Glovebox Enclosed Metallograph

FIGURE 2
Etching Cell Configuration

3a

As-Ground

250X

3b

20 sec. Electro-polish

250X

3c

Final Electro-polish

250X

FIGURE 3
Electro-polishing of As-Ground Homogenized Delta Phase
Plutonium

4a 250X
Mechanical Polish

4b 250X
5 sec. Electrolytic Polish

4c 250X
Final Electrolytic Polish

4d 250X
Grain Boundary Etch

FIGURE 4
Electro-polishing of Mechanically Polished Homogenized Delta Phase Plutonium

X ELEVATED TEMPERATURE METALLOGRAPHY OF β -Pu* JTB 11-5002

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INTRODUCTION

This paper discusses elevated temperature metallographic techniques, which were developed to determine the grain size of the beta phase of unalloyed plutonium. Beta plutonium can be either superplastic or brittle depending on the metals' thermal history.¹ When β -Pu is transformed from α -Pu it is superplastic but when β -Pu is transformed from γ -Pu it is brittle; α -Pu is stable up to 115°C, β -Pu is stable between 115 and 190°C, and γ -Pu is stable between 190 and 305°C. Alpha plutonium is simple monoclinic having 16 atoms per unit cell. The crystal structure of β -Pu is complex body-centered monoclinic having 34 atoms per unit cell. Gamma plutonium is face-centered orthorhombic.

An explanation for the large difference in plasticity of β -Pu was considered on the basis grain size but no experimental evidence was available to evaluate the β -Pu plasticity as a function of grain size. Experimental techniques were thus developed to determine the grain size of β -Pu. Because of the reactive nature of plutonium, especially in the higher temperature range of 115°C to 190°C, it was necessary to develop a special elevated temperature metallographic facility; an evacuable oil-filled hot stage allowing the long-term observation of as-polished beta

*This paper is based on work performed under United States Atomic Energy Commission Contract AT(45-1)-1830.

surfaces; a deformation hot stage which permits the direct observation of as-polished surface being deformed by a compression load; a cathodic etcher designed to operate at elevated temperature; and an optical electrolytic etching system designed to operate at temperatures as high as 140°C while permitting the operator to observe the specimen surface during etching and polishing, either electrolytically or chemically.

EQUIPMENT

The metallographic facility developed for the purpose of polishing beta phase plutonium shown in Figure 1 is composed of two major parts. The first section is a stainless steel glovebox with a Plexiglas front, having an inert nitrogen atmosphere. The flow rate of nitrogen through the glovebox is 20 cfh when the facility is idle and 400 cfh when the facility is in use. At a flow rate of 400 cfh the atmosphere is replaced approximately three times per hour. This high flow rate is necessary to prevent the rapid oxidation of the metallographic samples. The equipment included in the first section includes a microscope for examination and etching, two rough polishing and heat treating oil baths, and two vibratory polishers. The second section of the facility is a vacuum chamber with approximately 60 cubic feet of space. The vacuum chamber is connected to the first section of the facility by an airlock. The vacuum system for the second section consists of a 4 in. diffusion pump with the associated mechanical pumps. Access is gained by four neoprene gloves which are attached to the outer wall of the vacuum chamber. When the chamber is pumped down, steel doors are closed over the glove ports on the inside of the chamber, and the gloves are pressed against the doors

by atmospheric pressure. Thus a vacuum tight seal is made against the doors. The pressure may be reduced from atmospheric pressure to 1×10^{-2} torr in two hours. Gas to backfill the vacuum chamber is helium. The equipment included in the chamber is a vibratory polisher, microscope viewport, transfer facility, and a cathodic etcher.

SPECIMEN MOUNTING

Specimens were mounted in mechanical polishing mounts as shown in Figure 2. The mounted specimens for either deformation, transformation, or etching were machined and rough ground using the same procedure. They were machined to a 32 μ in. surface and hand-ground on 320- and 600-grit polishing wheels.

After grinding in the alpha phase, the samples were transferred to the elevated temperature metallography facility. The set screws on the mechanical specimen mounts were loosened to prevent deformation of the specimens caused by the 9% volume expansion during the $\alpha \rightarrow \beta$ phase transformation. The samples were placed in the 320-grit oil bath as shown in Figure 3. The oil bath was filled with Dow Corning 550 silicone fluid which was maintained at 140°C. The bath contained a cast iron backing plate for grinding and a space for heat treating specimens.

After allowing sufficient time for the specimens to be completely transformed, the sample was repositioned and the set screw reset to hold the specimen in position. The specimen holder was gripped from the back using 12" tweezers and was slid across the surface of the grinding paper. At the completion of the 320 grinding step the specimen was washed in two 400-ml containers of boiling tetrachloroethylene (tetrachloroethylene boils at 115°C and has a low reaction rate with beta plutonium). After a thorough

washing, the sample was moved to the 600-grit oil bath which was also maintained at 140°C . The specimen was then ground on the 600-grit cloth using the same procedure as the 320-grit grinding.

ROUGH POLISHING

After being thoroughly cleaned in two rinses of boiling tetrachloroethylene, the specimen was transferred to a vibratory polisher that was adapted for high temperature operation by placing a thin pad of teflon between the polishing bowl and the vibratory unit. Heat was supplied to the polishing bowl by immersing an immersion heater in an oil slurry. The polishing cloth used for the first stage of rough polishing was two layers of nylon. The slurry was composed of Dow Corning 550 silicone oil and $5\text{ }\mu$ aluminum oxide abrasive. The vibratory polisher was operated at a temperature of $130^{\circ}\text{C} \pm 5^{\circ}$. After two hours of polishing on the $5\text{ }\mu$ polisher, the specimen was washed in two changes of boiling tetrachloroethylene and placed on the second vibratory polisher that was covered with two layers of silk and a slurry of silicone oil and $1\text{ }\mu$ aluminum oxide. The sample was allowed to polish until all traces of the $5\text{ }\mu$ polish had been removed and a satisfactory finish obtained.

The specimen holder was washed thoroughly in three changes of boiling tetrachloroethylene and placed in an insulated beaker filled with silicone oil heated to 140°C . Before the oil could be used to transfer the sample to the vacuum chamber, it had to receive a prior treatment that consisted of heating the oil to 200°C under vacuum to outgas it. After outgassing and backfilling with helium, the oil's reaction rate with the as-polished specimen was much reduced over as-received oil. The insulated beaker containing the specimen was moved into the airlock, and the inner door

of the vacuum chamber opened, allowing the beaker to be passed into the chamber.

FINAL POLISHING

The specimen holder was then transferred from the beaker to the third modified vibratory polisher. This polisher was covered with a double layer of silk with a one-inch diameter patch cut from the center to allow the gas to escape as the pressure in the vacuum chamber was reduced. The slurry for the final polish was composed of silicone oil and 0.3μ alumina oxide abrasive. The operation of the vibratory polisher was observed to assure smooth operation, and then the pressure was slowly reduced in the vacuum chamber to allow the trapped gasses to be removed from the slurry without causing violent boiling. The final polish on the silk usually required one hour from the time the pressure was reduced in the chamber.

After completion of the final polish, the vacuum chamber was back-filled with helium and the specimen removed from its mechanical holder. A beaker of spectro quality tetrachloroethylene was heated to 110°C and passed through the airlock. The specimen was then washed in the tetrachloroethylene for 20 seconds and then quickly placed in a beaker of silicone oil maintained at 110°C . This beaker of oil was always kept under vacuum in the vacuum chamber except when it was being used. As long as the as-polished sample was kept in this beaker the oxidation rate was low.

SAMPLE OBSERVATION

To check the specimen for the quality of the polish, the specimen was transferred in the beaker of oil to the microscope viewing port. This

view port consisted of a glass window connected to a 1 in. diameter stainless steel tube. The viewing window, which was approximately 0.06 in. thick and extremely flat in the center section, was the face of a 1-in. diameter vidacone tube. After filling the view port with oil and heating it to the desired temperature, the specimen was placed face down on the window surface and observed with an inverted stage microscope. After checking the quality of the polish, the sample was ready for testing. Samples not suitable for testing were moved back in the polishing procedure to be repolished.

TRANSFORMATION STUDIES

Because of the differences in the beta phase formed from α and γ , the observation of the transformation of the two types of beta phase material was of interest. After polishing, the specimens were transferred to a specially designed oil-filled, evacuable, hot stage as shown in Figure 4 for observation of the transformations. Because of the reactive nature of β -Pu it was necessary to design an oil-filled, evacuable hot stage capable of evacuation to 9×10^{-3} torr, which is the vapor pressure of the specific silicone oil used. The hot stage, which was 4 in. in diameter and 7 in. high, was constructed with Buna-N O-rings for the two flange seals and a teflon seal on the window. The thermocouple feed-through was a Swagelok fitting with teflon ferrules to withstand the high temperature. Heat was applied to the hot stage by a 250-watt heating tape wound on the outside diameter of the hot stage. Fiberfax insulation covered the heating tape to reflect the heat into the aluminum body. The advantages of oil in the hot stage are that a close temperature control can be maintained at beta phase temperatures, possible contamination

spread from plutonium can be controlled easily, and metallographic surfaces can be preserved. The hot stage was designed to operate in the temperature range of 20°C to 260°C and could be controlled to $\pm 0.5^\circ\text{C}$. The window used for the hot stage was a 0.030 in. thick Pyrex disc with an anti-reflective coating. This window coating decreased the reflected light to 0.5% and permitted high resolution observation of samples. The sample was held 0.005 in. above this window by the bottom of the sample holder.

To load the hot stage, it was connected to the transfer facility on the bottom of the vacuum chamber. A mechanical finger was lowered into the hot stage through the floor of the vacuum chamber to transfer the hot stage specimen holder to the transfer beaker and then to return the loaded specimen holder to the hot stage. The hot stage was disconnected from the vacuum chamber and moved to the B & L metallograph where the hot stage was connected to a vacuum system. Figure 6 shows a typical example of a beta specimen formed from the alpha phase transforming from beta to alpha. Specimens of beta formed from gamma were also examined but were difficult to photograph because the sample surface roughened without giving satisfactory contrast between transformed and untransformed areas.

DEFORMATION OF BETA Pu

The delineation of grain structures by grain boundary sliding and slip traces on the deformed surface of as-polished metal is accepted. Because of the elevated temperature of the beta phase plutonium it was felt that the deformation of as-polished samples might provide information on the beta grain size and deformation mode with less difficulty than other alternatives.

After polishing the plutonium in the beta phase, the specimen was quickly cleaned and inserted into the deformation fixture as shown in Figure 7. The specimens were deformed by turning the loading screw. Beta specimens transformed from the α phase were found to deform easily while beta specimens transformed from the γ phase were deformed with more difficulty. After deformation the samples were loaded into the oil-filled, evacuable hot stage, and observed on the B & L research metallograph. Two major problems developed with the system. We found that the structure, developed on the beta specimens transformed from the α phase, was so fine that we could not be sure of what we were seeing, using the 21X objective (the highest power usable on the hot stage). Also, the beta phase material transformed from the gamma phase oxidized so rapidly after deformation that by the time it had been transferred to the hot stage it was severely oxidized.

At this point the deformation of as-polished surfaces looked promising if we could provide greater protection for the as-deformed specimen, increase the magnification at which it was possible to observe the specimen surface, and reduce the time between deformation and observation of the sample. With these problems in mind we designed an oil-filled, evacuable, deformation hot stage which permitted the application of a compressive load on the specimen while the specimen's surface was under observation at magnifications up to 500X. Figure 8 shows a cutaway view of the deformation hot stage. The hot stage consisted of a hardened steel body with O-ring seals on the lid, vacuum chamber connection, and the hydraulic ram. The hot stage was heated by a 500-watt heater wrapped around the body. The temperature was measured by a thermocouple which measured

the temperature less than $1/32$ of an inch from the specimen. The specimen was held in position in the hot stage by a special specimen holder so that the as-polished surface was perpendicular to the optical axis of the metallograph and, at the same time, kept the sample in position to be deformed by the hydraulic ram. The amount of deformation was controlled by the amount of surface deformation desired by the observer looking through the metallograph, but deformation of the specimen could be measured by an external dial indicator. The objective lens of the metallograph was connected permanently to the hot stage by a flexible stainless steel bellows. Certain modifications were necessary to the interior of the lens to make it vacuum tight. Focusing on the specimen was accomplished in the normal manner; the stainless steel bellows expanded and contracted to allow the proper focus to be obtained. The hot stage was normally operated at temperatures of 120°C at a pressure of 25×10^{-3} torr.

Loading the hot stage was accomplished by connecting the top flange of the hot stage to the bottom of the vacuum chamber. A polished sample was placed in the sample holder and lowered into the hot stage through the chamber floor. The hot stage was then disconnected from the vacuum chamber and transferred to the metallograph where it was connected to the vacuum system. The pressure was then reduced to 25×10^{-3} torr while connections were made to the hydraulic system and to the metallograph.

After all connections had been made, the hot stage was backfilled with helium to a pressure of 15 in. of Hg to stop bubbles from forming and interfering with the optical path of the metallograph. The pressure on the hydraulic cylinder was increased until the desired deformation

was obtained. The specimen could be scanned by moving the hot stage, using the metallograph stage. The flexibility of the stainless steel bellows allowed the hot stage to move in a manner which showed a $\frac{1}{4}$ -in. diameter circle of the sample. Figure 9 shows a typical microstructure of deformed beta, which had been transformed from the gamma phase. The grain size is about 50 μ in. and it revealed slip lines. This is the smallest grain size observed for beta formed from gamma. Figure 10 shows a typical microstructure obtained from deforming beta transformed from the alpha phase. The grain size, which was about 5 μ , was much smaller and it exhibited no slip lines.

After deformation, beta transformed from alpha plutonium could be held in the deformation hot stage for six hours without noticeable oxidation, while beta transformed from gamma plutonium could be held only a few minutes after deformation without the surface being obscured by an oxide layer.

The deformed specimens were then quenched back to room temperature. After the $\beta \rightarrow \alpha$ transformation the samples were given a very light etch to remove the oxide layer. The surface features found in the alpha phase corresponded with the photomicrographs taken in the deformation hot stage.

ETCHING OF BETA Pu

Although the beta grain size has been tentatively measured by deforming as-polished beta surfaces, this method of revealing the grain size of a specimen was less positive than conventional etching techniques. Two methods of etching beta phase specimens were attempted.

A cathodic etcher designed to etch specimens in the beta phase was developed. Samples were polished in the normal manner and then washed

thoroughly before being transferred into the cathodic etcher. Cathodic etching proved to be unsatisfactory for developing the grain structure because the cathodic etcher could not remove the oxide layer which continuously forms on the beta polished specimens.

Electrolytic etching of beta phase specimens was the other method of etching attempted. A modified version of the optical electrolytic etcher described by Arrowsmith and Rencken² was developed. Changes were made in the method of closing the cell and in the spacing between the window and the specimens. This etcher allowed the operator to evaluate each new electrolyte quickly since the effect on the beta specimen could be immediately seen. The etching system was operated at 110°C during the etching attempts. As-polished beta specimens were placed in the etching cell, and attempts were made to etch the surface. The beta specimens reacted with all of the electrolytes evaluated. The reaction was in the form of a heavy oxide layer which could not be removed. All of the electrolytes caused the specimens to oxidize faster than the etching process was removing the surface material. Attempts were also made to electropolish specimens directly from the 600-grit cloth. Again the specimens oxidized faster than the electrolytic polishing could remove the layer.

Electrolytes used on beta Pu generally consisted of an ethylene glycol base and several kinds of acid, such as phosphoric acid. The fact that the etching operation was conducted at 110°C eliminated many electrolytes because their boiling points were exceeded.

SUMMARY

Elevated temperature metallographic techniques were developed to determine the grain size of beta plutonium. A significant difference between the grain size of beta transformed from alpha and beta transformed from gamma was observed. The average grain size of beta transformed from alpha was less than 5 μ , which can account for the superplasticity that is observed. The average grain size of beta formed from gamma, on the other hand, was greater than 50 μ , which with its limited slip can account for the brittleness that is observed in this beta.

ACKNOWLEDGMENTS

The author would like to thank Dr. R. D. Nelson for his encouragement and constructive suggestions.

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ELEVATED TEMPERATURE METALLOGRAPHY FACILITY

FIGURE 1
Elevated Temperature Metallography Facility

FIGURE 2
Specimen Holder for $\beta \rightarrow \alpha$ Transformation Studies
Etching β -Pu

FIGURE 3
Specimen Holder for Deformation Studies

FIGURE 4
Tank for Rough Grinding β -Pu at 140°C

FIGURE 5
Oil Filled Hot Stage

FIGURE 6
Beta Formed from a Transforming to the α Phase at 80°C

FIGURE 7
Fixture for Deforming β -Pu at 110 to 180°C

FIGURE 8
Deformation Hotstage

300X

FIGURE 9
Deformation Microstructure of β -Pu that had been Transformed
from γ Pu. The Microstructure Reveals Slip Lines and a Grain
Size of About 50μ . The Mottled Background is a Plutonium
Oxide Layer.

500X

FIGURE 10
Deformation Microstructure of β -Pu that had been Transformed
from α Pu. The Microstructure Reveals no Slip Lines and a
Grain Size About 5μ .

A RESUME OF THE METALLOGRAPHY OF IRRADIATED URANIUM FUEL

-or-

URANIUM DOES ITS THING

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ABSTRACT

A quarter of a century's observations and research of the irradiation behavior of uranium is reviewed from the metallographic point of view. Uranium experiences both volume increase and growth in its nuclear environment as it responds to the effects of energetic particles, fission fragments, and transmutation atoms. The growth phenomena is a characteristic of the anisotropy of the uranium alpha phase crystal structure. The growth rate is high at low temperatures and decreases rapidly as 400°C is approached. Severe distortion is evident in the metallographic structure and the structure becomes completely unrecognizable upon continued exposure. Above about 350°C, swelling is experienced as loss of coherency permits the generation of void volume in the form of boundary tearing. The microstructure is swirled and shows irregular shaped voids. Above 500°C, swelling prevails but its nature changes. Preirradiation grain size and shape is retained, but void volume is generated by the development of crystallographically oriented porosity within the grains. Above 600°C, the boundary tearing and oriented porosity seen at lower temperatures diminish and swelling decreases. Some spherical grain boundary porosity and sub-micron matrix porosity is seen. At beta phase and gamma phase temperatures fission gas porosity develops to produce severe swelling.

✓ METALLOGRAPHY OF SOME URANIUM-PLUTONIUM FUEL MATERIALS*

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ABSTRACT

Techniques for mounting and surface preparation of uranium-plutonium nitrides, uranium-plutonium dioxides and plutonium dioxide cermet are described. Metallography of these materials was conducted in glove boxes containing a nitrogen inert atmosphere. Microstructures of the various material compositions are evaluated in respect to methods for grinding and polishing and subsequent etching treatments. The affects of different etching solutions on microstructure and phase delineation are discussed. Methods are given to bring out the PuO_2 and metal matrix structures simultaneously for critical evaluation of the cermet materials. The results of various preparation techniques are supported by numerous photomicrographs.

INTRODUCTION

Battelle-Columbus has been engaged for a number of years in fast-breeder fuel and coated-particle research programs in which studies are being conducted on the evaluation and property characterization of uranium-plutonium fuel materials for the Atomic Energy Commission. Mixed

*Work performed at BCL under AEC Contract W-7405-eng-92.

uranium-plutonium nitride $[(U,Pu)N]$, uranium-plutonium dioxide $[(U,Pu)O_2]$, and plutonium dioxide $[PuO_2]$ are some of the materials presently being investigated. The interest in mixed-nitrides and -dioxides are for their potential use in liquid-metal fast-breeder reactors. Studies on plutonium dioxide were directed toward the development of coated particle fuels for general application.

The sintering, fabrication, and compatibility studies of the mixed uranium-plutonium nitrides performed in these programs as well as the characterization and property studies of the plutonium dioxide and uranium-plutonium dioxides have entailed the preparation and examination of numerous metallographic specimens. This paper discusses the metallographic practices that have been employed to examine some of these fuel materials. The metallography of uranium-plutonium nitride specimens is discussed in respect to methods of preparation and subsequent annealing treatments. The remaining part of the paper is devoted to techniques employed for examination of uranium-plutonium dioxide and plutonium-dioxide specimens. Emphasis in the latter phase of the work is on delineation of structure and retention of coatings. Each of these materials is discussed separately since in most cases the techniques employed for preparation and evaluation are unrelated. Photomicrographs are presented to show the results of the various metallographic procedures.

Because of the extremely toxic behavior of plutonium all operations in handling these materials were conducted in glove boxes in a nitrogen atmosphere under slight negative pressure.

MIXED-NITRIDE MATERIAL

The (U,Pu)N specimens submitted for metallography were generated in various phases of a comprehensive program intent on the complete evaluation of this material as a fast reactor fuel. Four general types of specimen were examined: (1) low density pellets of $(U_{0.8}Pu_{0.2})N$ and $(U_{0.5}Pu_{0.5})N$ derived from mechanically mixed UN and PuN powder batches, (2) low-density pellets and rods of $(U_{0.8}Pu_{0.2})N$ derived from prealloyed (U,Pu)N powder batches, (3) high-density pellets $(U_{0.8}Pu_{0.2})N$ derived from prealloyed (U,Pu)N powder batches, and (4) diffusion couples of UN/PuN and compatibility couples of $(U_{0.8}Pu_{0.2})N$ against various cladding materials.

The nitride specimens made up of sintered mixed powders were prepared from UN and PuN materials that were separately synthesized by reaction of the metal hydride with nitrogen at temperatures of 300 to 600°C. The powders were subsequently blended to the desired composition, ball milled, cold pressed into pellets and sintered at selected temperatures in 1 atm nitrogen. Nitride specimens were also prepared from prealloyed powder batches which were synthesized by the same hydride-nitride cycle described above, except in this case an arc-cast uranium-20 w/o plutonium button was used in place of the pure metal. Crushed and screened or ball milled powders were cold-pressed into rods and pellets and then sintered at selected temperatures in 1 atm of nitrogen. Powder batches of both hyperstoichiometric and stoichiometric composition were used in preparation of high and low density specimens. Stoichiometric powders were prepared by vacuum degassing at 1100°C for 16 hr to obtain decomposition of the higher nitride. Powder not treated in this manner was considered to be hyperstoichiometric.

Compatibility specimens submitted for metallography contained cladding of Type 304 and Type 316 stainless steel, ORNL stainless steel and vanadium in contact with $(U_{0.8}Pu_{0.2})N$ pellets. In addition to these specimens, a UN/PuN diffusion couple, which was annealed at elevated temperature, was also evaluated.

Procedure for Mixed Nitride Specimens

Mounting and Grinding

Metallographic preparation of (U,Pu)N specimens for determination of their microstructure, phase content, and porosity required mounting, grinding, polishing and chemical etching. Most of the pellet-type specimens which included both the high and low density materials were mounted in Epoxy Resin 815 under vacuum. When edge preservation of the pellet was desired for examination purposes, the heat and pressure curing diallyl phthalate resin was used. This harder mounting material appeared to prevent rounding of edges of (U,Pu)N during polishing. Rod-type specimens which required further study after metallography were mounted in Quick Mount resin under 6 to 12 psi of nitrogen. Pressure was used here to suppress bubble formation during the curing period. In this case, specimens were not embedded in epoxy because the vacuum mounting technique caused impregnation of the specimens with resin which made them unusable for further study.

Diffusion couple specimens which in some cases were in sodium-bonded capsules had to be placed in a bath of butyl alcohol to remove infiltrated sodium. Components of the diffusion couples were mounted both in diallyl phthalate and Epoxy 815 resin.

Grinding of most (U,Pu)N specimens was performed successively on 120-, 240-, 400-, and 600-grit silicon carbide paper. When removal of a large amount of material was required, initial grinding was conducted on an 80-grit paper. Carbon tetrachloride was employed as a lubricant throughout the grinding operations.

Polishing

A combination of two polishing techniques gave good results for high density specimens of $(U_{0.8}Pu_{0.2})N$ as well as for low density specimens of $(U_{0.8}Pu_{0.2})N$ and $(U_{0.5}Pu_{0.5})N$. One technique consisted of a 3-stage polish with the first stage consisting of a rough polish on a fast wheel covered with nylon cloth. A slurry of 2 percent chromium trioxide with additions of 2-5 percent alpha alumina was used as a polishing media. This stage removed most of the coarse-grinding scratches and provided a polish surface which was adequate for a cursory microscopic examination of the material. Additional polishing was conducted on a fast wheel covered by a lintless cloth containing a slurry of 2 percent chromium trioxide in water with 2-5 percent additions of gamma alumina. Although this particular treatment yielded surfaces suitable for some photomicrographs, a third polish was needed to obtain good surfaces for etching of the (U,Pu)N material. This third stage or final polish was done on a slow wheel covered by Gamal cloth containing a solution of 2 percent chromium trioxide in water with 2-5 percent powder abrasive additions. Some high density and all low density specimens were polished by this technique.

A second preparation procedure employed for high density (U,Pu)N material consisted of a 2-stage polish in which the initial stage was

conducted on a Syntron vibrator with a slurry of 2 percent chromium trioxide containing 2 to 5 percent addition of gamma alumina as the polishing media. A lintless cloth backed by a microcloth was used to cover the polishing surface of the vibrator. Most of the (U,Pu)N specimens were allowed to polish overnight. This method gave good results for high density specimens; however, it was unsuitable for low density material because dissolution of the nitride occurred during the prolonged contact with the water slurry. Vibratory polishing was followed by a final polish on a slow wheel covered by microcloth containing a slurry of 2 percent chromium trioxide in water with additions of either rouge or gamma alumina. Excellent polished surfaces of high density (U,Pu)N material which gave good response to the etching solutions were obtained by this latter technique.

The mixed-nitride components of the diffusion couples were polished by the methods given above because the two components of the couples usually separated. The PuN/UN diffusion couple was polished with the three-stage technique described above for polishing $(U_{0.8}Pu_{0.2})N$ specimens. Vibratory polishing was attempted on this material; however, the PuN component partially disintegrated when the above procedure was used.

Etching

A large number of $(U_{0.8}Pu_{0.2})N$ specimens including both high- and low-density pellets as well as low-density rods were chemically etched with a solution of 50 parts lactic acid, 40 parts nitric acid and 4 parts hydrofluoric acid. The best etching results were obtained when the specimen was etched within a short time after polishing. The passivity of the

polished surface to the etch increased notably with time. A swabbing technique gave the best results with this etchant. A specimen was swabbed hard with the etching solution for 15-25 seconds, washed with water, and dried. The specimen was then allowed to set for 3 to 5 minutes and swabbing was repeated until the surface brightened. At this point, the surface was immediately rinsed with a 10 percent solution of hydrogen peroxide in water and then dried. This etchant left an unequal stain on the individual grains of the specimen. Prolonged etching sometimes resulted in grain boundary attack; however, the resultant overstaining then masked the microstructure. Second phases of $(U,Pu)_2N_3$ or $(U,Pu)O_2$ were easily delineated when the etchant was properly applied. Considerable difficulty was experienced in cleaning the low-density specimens since the pores of this material readily absorbed the etchant. Additional rinsing operations were employed to circumvent this problem. Over-etching of $(U,Pu)N$ darkened the surface and sometimes masked the impurity phase of $(U,Pu)O_2$ and $(U,Pu)_2N_3$ when they were present.

$(U_{0.5}Pu_{0.5})N$ specimens did not respond favorably to the etching solution that was used for the $(U_{0.8}Pu_{0.2})N$ material. Several etches were tried but a solution of 50 parts lactic acid, 40 parts nitric acid, and 4 parts hydrofluorosilicic acid gave the best results. The etch was applied with a hard swabbing action which was followed by a rinse with 10 percent hydrogen peroxide in water and drying. This particular etch was found to be suitable for PuN as well as the $(U_{0.5}Pu_{0.5})N$ composition.

Diffusion couples of $(U_{0.8}Pu_{0.2})N$ which contained claddings of Type 304 stainless steel, Type 316 stainless steel, ORNL stainless, and vanadium were etched to show their behavior under various prolonged annealing

treatments. Cladding materials of the couples were etched by the standard methods described in the literature for these materials and the $(U_{0.8}Pu_{0.2})N$ component was etched by the techniques described above.

The UN/PuN diffusion couple was etched with a solution of 50 parts lactic acid, 40 parts nitric acid, 2 parts hydrofluoric acid. A swabbing technique similar to that used above for $(U_{0.8}Pu_{0.2})N$ was employed.

MIXED OXIDE MATERIAL

$(U,Pu)O_2$ materials submitted for metallography consisted of sections of solid and hollow cylinders prepared from mechanically blended UO_2 - PuO_2 powders which were pressed and sintered under various conditions. Specimens were examined for grain size, impurity content and microcracks.

Procedure for Mixed Oxide Specimens

Mounting and Grinding

All $(U,Pu)O_2$ specimens required mounting and grinding to prepare surfaces for polishing and subsequent etching. Most specimens were mounted in Epoxy Resin 815 under vacuum. When edge preservation was needed, the heat and pressure curing diallyl phthalate resin was used. This excluded complete hollow cylinder specimens which required mounting in epoxy resin because of their geometry.

The mixed oxide specimens were ground successively on 120-, 240-, 400-, and 600-grit silicon carbide paper. Carbon tetrachloride or water was used as lubricant.

Polishing

The $(U,Pu)O_2$ material was prepared by a combined vibratory and wheel polishing procedure or by the latter method exclusively. In the first

procedure a Syntron vibrator was used for the first stage of preparation. A slurry of 2 percent chromium trioxide in water with additions of 2 to 5 percent gamma alumina was employed as the polishing media. Lintless cloth backed by a microcloth was used to cover the polishing surface of the vibrator. Although overnight polishing usually resulted in what appeared to be a good polish, preliminary etching of this material indicated a need for a more refined technique. Therefore, further polishing of the specimens was done on a Gamal cloth using a slow wheel with a slurry of 2 percent chromium trioxide in water containing additions of 2 to 5 percent rouge. This additional polishing was effective in eliminating scratches previously observed on etched surface of the mixed oxide specimens. A second polishing technique employed for this material consisted of polishing on a fast wheel covered with a double thickness of nylon using a slurry of 2 percent chromium trioxide in water with additions of alpha alumina. A final polishing of the mixed oxide was made on a moderate speed wheel covered with kitten-ear cloth using a slurry of the same composition but with additions of gamma alumina instead of alpha alumina. The resultant polish was comparable to that obtained by the first technique except the combined vibratory and wheel method gave better edge preservation of the specimen.

Etching

Considerable difficulty was encountered during attempts to etch the $(U,Pu)O_2$ materials. The density and grain size of the material appeared to significantly affect the manner in which the surface of the specimen reacted to the etching solution. The lower density or fine-grain material showed a greater passivity to attack than the higher

density or coarser grain specimens. Three different etching solutions were used for delineation of grain structure of the (U,Pu)O₂ material; each had varying success. With one technique, the specimen was immersed in a solution containing 30 cc water, 20 cc nitric acid and 0.1 gm of cerium nitrate for 30 seconds. This method worked well for large grain specimens. Another immersion etch composed of 5 to 10 parts sulphuric acid and 90 to 95 parts hydrogen peroxide worked with some success on fine grain material and the low density specimens. Although grain delineation in some specimens was apparent, some of the grain structure was obliterated from the attack of the etching solution around the pore areas. Another etching solution of 50 parts water, 25 parts nitric acid and 5 parts hydrofluoric acid applied by swabbing also brought out the grain structure of this material. Etching with this latter technique sometimes worked when the other techniques failed. This etch also attacked the pore areas and grain boundaries of the material. To summarize, no particular etch was found which worked consistently for the (U,Pu)O₂ materials examined in this study.

PLUTONIUM DIOXIDE

The metallography of plutonium dioxide particles as discussed in part in this paper was comprised of the preparation and examination of the following types of specimens: as-received material, heat-treated material, coated microspheres and PuO₂ cermet specimens.

Lots of PuO₂ microspheres were screened to aid metallographic examination by isolation of material into various size fractions. After this operation, samples of the various screen sizes were examined. In addition, portions of the PuO₂ microspheres were annealed under various conditions

and examined to determine the affects of this treatment. Other portions of the microspheres were coated and subsequently submitted for metallography. In addition to this work, specimens from cermets prepared from microspheres were examined on a routine basis.

Procedure for PuO₂ Specimens

Mounting and Grinding

The PuO₂ microspheres, both coated and uncoated, required special handling during mounting and grinding in order to obtain acceptable surfaces for polishing. In the mounting technique employed, a monolayer of the microspheres was obtained in the mold before introduction of the mounting resin. This was accomplished stepwise, by first gluing a $\frac{1}{4}$ -in. center hole stainless steel washer to the bottom pin of a $1\frac{1}{4}$ -in. diameter Bakelite mounting die. A drop of ethyl alcohol was then placed in the washer cavity and the microspheres were placed into the mold. At this point, care was exercised to prevent excess microspheres from entering the mold cavity. During introduction the die baseplate was tapped until the microspheres fanned out to form a monolayer. The alcohol was allowed to dry thoroughly before introduction of the diallyl phthalate mounting resin which was used for most of this work. It is presently felt that this mounting material helped significantly in obtaining good edge preservation of the microspheres.

Grinding of coated and uncoated PuO₂ microspheres was done in the usual manner by passing the specimen mounts successively over 240-, 400-, and 600-grit silicon carbide paper. Carbon tetrachloride was used as a lubricant. Periodic inspection of the mount after short intervals of grinding prevented overgrinding of the mounted microspheres beyond the

point where the maximum diameter was reached. The approach of the maximum surface diameter of the microsphere signaled the end of grinding and the start of polishing.

Cermet specimens were generally mounted in Epoxy Resin 815 which was allowed to gel under vacuum. In some cases, where edge preservation of the cermet was desired, diallyl phthalate was used as a mounting material. Specimen mounts were ground successively on 80-, 120-, 400-, and 600-grit silicon carbide paper using water or carbon tetrachloride as a lubricant.

Polishing

Although various methods of polishing were initially used in the preparation of the PuO_2 microspheres and PuO_2 cermet materials, two polishing techniques were eventually found to give the best results on these materials. The first procedure consisted of an initial polish on a high-speed wheel covered with a double-thickness of nylon cloth followed by a final polish on a medium-speed wheel covered with a kitten-ear cloth. A slurry of 2 percent chromium trioxide in water with additions of 2-5 percent alpha alumina was used for polishing on nylon and the same solution with gamma alumina substituted for alpha alumina was used for the final polish. Although this method was found to be expeditious, edge preservation of the microspheres was not as good as obtained with the second procedure which employed a Syntron vibrator with the latter slurry for polishing. Type Pan-W Pellon cloth was used to cover the polishing surface of the vibrator. To achieve a good polish of the PuO_2 materials, the specimens were allowed to revolve on the vibrator for at least a 48-hr period. Although excellent edge preservation was obtained with this technique, the overall time for preparation was a drawback. Since

good edge preservation was needed for evaluation of the coated particles, this method was used almost exclusively for the PuO_2 studies. Another point of importance that should be brought up here in polishing PuO_2 microspheres is the inherent brittleness of the PuO_2 itself. Because of this brittle behavior, severe fallout of PuO_2 can easily occur during polishing of this material if the right preparation technique is not employed.

Etching

Reduction of PuO_2 to PuO_3 was suspected during certain phases of the fabrication and heat treatment of the cermets; therefore, the main criteria employed for selection of an etchant was the ability to delineate these phases in the presence of metal coatings. Although a number of etchants and procedures were tried, only one solution gave the desired results. The etching procedure consisted of immersing the polished specimen into a solution of 50 parts hydrochloric acid and 50 parts hydrobromic acid containing 2-4 drops of hydrofluoric acid for periods of 10 to 15 seconds. This treatment was followed immediately by rinsing with water and drying. The speed and degree of attack of the etchant seemed to be a function of the amount of hydrofluoric acid present.

DISCUSSION AND METALLOGRAPHIC OBSERVATIONS

Materials as prepared for metallographic examination were viewed under bright field light with a Dynazoom, bench type, metallograph. Photomicrographs were taken of both polished and etched surfaces of representative areas of the materials. The $(\text{U,Pu})\text{N}$ and $(\text{U,Pu})\text{O}_2$ specimens were examined for phase content, porosity, impurities, grain size and uniformity of structure. These properties plus the shape of particles

and the continuity and uniformity of the coatings were of interest in the examination of the PuO_2 microspheres and cermet. Mixed nitride diffusion couples were examined for reactions occurring between the fuel and various cladding materials. The results of some of the examinations are given below in discussions of the photomicrographs.

Polished and etched surfaces of high density $(\text{U}_{0.8}\text{Pu})\text{N}$ fuel pellets prepared by sintering prealloyed powder at 1900°C for 3 hrs are shown in Figs. 1a and 1b. The photomicrographs are typical of specimens polished by the 2-stage technique involving vibratory and wheel preparation. The dark areas in these photomicrographs are porosity. No grain structure is evident in the polished section which is typical of most $(\text{U},\text{Pu})\text{N}$ material. The affect of chemical etching on the polished surface of this pellet is shown by the microstructure presented in Fig. 1b. The specimen was swab etched with a solution of 50 parts lactic acid, 40 parts nitric acid, and 4 parts hydrofluoric acid applied by the technique discussed previously. Grains of the mixed nitride are revealed by differential staining and there appears to be no delineation of the individual grains by chemical attack. This specimen has a single-phase structure characteristic of the prealloyed stoichiometric pellets. The porosity is found to occur principally at the triple points of the grains.

The photomicrographs of Figs. 2a and 2b show etched surfaces of a low density $(\text{U}_{0.5}\text{Pu}_{0.5})\text{N}$ pellet fabricated from mechanically mixed powders and subsequently heat-treated for homogenization purposes. The typical porosity distribution of the material is revealed by examination of the polished surface. Changes in the composition of the grains of the specimen associated with interdiffusion of the UN and PuN constituents are revealed readily by etching (see Fig. 2b). The color variation

from light to dark gray suggests that the lactic, nitric, hydrofluosilicic etch used here is effective for a wide range of (U,Pu)N solid solutions.

Photomicrographs of etched surfaces of $(U_{0.8}Pu_{0.2})N$ pellets fabricated from various powder batches and sintered at different temperatures are shown in Figs. 3 to 6. All of these specimens were etched by standard methods and their microstructures are generally quite similar although differences in density and porosity distribution are readily apparent. The etching solution appeared to attack or stain the hyperstoichiometric prealloyed material and the mechanically-mixed stoichiometric material in much the same manner. Metallographic preparation of low density material was difficult. Fallout during polishing was minimized by limiting the polishing of such material to a fast wheel with a low nap cloth and a slow wheel was used only for a light final polish.

Microstructures of $(U_{0.8}Pu_{0.2})N$ pellets prepared from oxygen contaminated powder and sintered at $2100^{\circ}C$ for 4 hr are shown in Figs. 7 to 10. Nitride powder exposed to the glove box atmosphere for a period of 13 days sintered to the single-phase (U,Pu)N structure presented in Fig. 7. Prolonged storage of the powder for 37 days produced the microstructures shown in Figs. 8 to 10. The change in density and the appearance of a second unidentified phase associated with impurities present in the powder were revealed by the metallographic examination. The etching solution attacked the grain boundaries of the impurity phase; however, over-etching usually caused staining of this phase and masked its presence in the microstructure. The ability of the lactic, nitric, hydrofluoric etching solution to reveal composition variations and impurities in mixed nitride specimens is illustrated by the photomicrograph of Fig. 9. The specimen

changed from a large-grain porous single-phase (U,Pu)N structure at the surface to a fine-grain two-phase structure in the center region. These variations are clearly observed in the photomicrograph.

The microstructure of a UN/PuN diffusion couple is shown in Fig. 11. This material was stain etched with solution of 50 parts lactic acid, 40 parts nitric acid and 2 parts hydrofluoric acid to reveal the interface reactions and also to compare the response of the two components to chemical etching for identification purposes. As seen in the photomicrograph of this couple (Fig. 11) there appears to be some chemical attack along the grain boundaries of the large grain PuN phase (top). The smaller grain UN phase (bottom) was stain etched about the same as the previously illustrated (U,Pu)N material. Changes in composition from interdiffusion are seen by the band at the UN-PuN interface.

A 500X magnification of the surface of a fuel pellet of $(U_{0.8}Pu_{0.2})N$ which was sodium bonded to ORNL stainless steel for 1000 hours at $1000^{\circ}C$ is shown in Fig. 12. Grain structure was revealed by the lactic stain etch normally used for this material. Two different types of reaction products occurred at the contact surface. The inner layer appeared to be an oxide product and the outer zone was tentatively identified as titanium-bearing material produced by the reaction of the cladding with the fuel. No reaction was seen in the ORNL stainless.

Figure 13 shows the interface of a Type 316 stainless steel rod and a $(U_{0.8}Pu_{0.2})N$ pellet which were in direct contact for 1000 hours at $1000^{\circ}C$. Etching showed that the cladding had transformed to a pearlitic structure throughout except near the contact edge where this structure was noticeably absent. An interior view along cracks and in the grains of the fuel

pellet is shown in Fig. 13b. The ability of the lactic, nitric, hydrofluosilicic etch to reveal the unidentified phase and at the same time develop the (U,Pu)N structure is additional verification of the versatility of this solution. Analysis of the metallography resulted in a reevaluation of the capsule and detection of a leak present during the heat-treatment of the diffusion couple. Microstructures observed on these stainless steel and (U,Pu)N specimens, therefore, are not characteristic of results obtained on well bonded and sealed compatibility couples, but they do show how the metallographic examination was used to interpret an unusual event in the history of a specimen.

Typical microstructures of a $(U_{0.92}Pu_{0.08})O_2$ and a $(U_{0.80}Pu_{0.20})O_2$ specimen are seen in Figs. 14 and 15, respectively. These specimens were swabbed and etched with a solution of 50 cc lactic acid, 25 cc nitric acid, and 5 cc hydrofluoric to reveal grain structure. The $(U_{0.92}Pu_{0.08})O_2$ specimen was extremely fine-grained and the etchant consistently gave a uniform response on this material. The $(U_{0.8}Pu_{0.2})O_2$ specimen, on the other hand, etched only with considerable difficulty and the chemical attack was irregular (see Fig. 15).

A typical as-polished surface of as-received PuO_2 microspheres is shown in Fig. 16. The surface contact of the microspheres shows that maximum diameters were obtained in the mounting, grinding, and polishing operations. Good flat edges of the PuO_2 microspheres were also obtained by vibratory polishing for a period of 48 hours. The microstructure of a PuO_2 microsphere is shown in the photomicrograph presented in Fig. 17. Excellent grain delineation was obtained by immersion for 10 seconds in an etch of 50 parts hydrochloric, 50 parts hydrobromic and 2 drops of

hydrofluoric acid. Black areas in the photomicrograph are porosity which appears to be brought out in greater quantity than found in the as-polished structure by etching. The typical as-polished appearance of heat treated PuO_2 microspheres can be seen in in Figs. 18 and 19. Here again the flatness and contact of the individual particles is verification of the mounting, grinding, and polishing technique. Dark areas in the particles are porosity. The outline of a second phase appears at the edges of the as-polished heat-treated particles in Fig. 19.

A photomicrograph of coated PuO_2 microspheres in the as-polished condition is shown in Fig. 20. The uniformity of the 2-layer coatings on the microspheres is readily seen in this illustration. These specimens were mounted in diallyl phthalate and polished on the Syntron vibrator by the technique described previously.

Cermet materials composed of metal-coated PuO_2 particles are shown in Figs. 21 to 23. These photomicrographs were taken from cermets that were vibratory polished in a slurry of 2 percent chromium trioxide and water with additions of gamma alumina. The specimens were usually given a final polish on a fast wheel prior to etching. The PuO_2 and Pu_2O_3 phases present in the oxide particles of the cermet are readily revealed by the hydrochloric, hydrobromic, and hydrofluoric acid etch.

In all of the work described here, metallography was found to be an important tool which immensely aided the evaluation of materials properties and process parameters. One can hardly envision the consequences of undertaking these materials studies without this important tool for examination and although considerable effort was often needed to develop proper metallographic procedures, the final results of the effort always justified this initial investment of time.

500X PL4254
a) Polished section. Black areas are porosity.

500X PL4255
b) Etched surface. Large grains are single-phase (U,Pu)N. Black areas are porosity.

FIGURE 1. MICROSTRUCTURES OF SINTERED $(U_{0.8}Pu_{0.2})N$ PELLETS PREPARED FROM PREALLOYED STOICHIOMETRIC POWDER.

250X PL6714
a) As-polished surface. Black areas are porosity.

250X PL6401
b) Etched surface. Diffusion boundary (gray) represents (U,Pu)N solid solutions of different compositions. Black areas are porosity.

FIGURE 2. HEAT-TREATED $(U_{0.5}Pu_{0.5})N$ PELLETS PREPARED FROM MECHANICALLY-MIXED POWDERS OF UN AND PuN.

250X PL4248
Etched surface of single-phase
(U,Pu)N.

FIGURE 3. $(U_{0.8}Pu_{0.2})N$ PELLET PREPARED
FROM PREALLOYED HYPERSTOICHIOMETRIC
POWDER.

500X PL4491
Etched surface showing single-phase
(U,Pu)N and porosity distribution.

FIGURE 4. $(U_{0.8}Pu_{0.2})N$ PELLET
PREPARED FROM PREALLOYED HYPER-
STOICHIOMETRIC POWDER.

500X PL4507
Etched surface of single-phase (U,Pu)N.
Black areas are porosity.

FIGURE 5. $(U_{0.8}Pu_{0.2})N$ PELLET PREPARED
FROM MECHANICALLY-MIXED STOICHIOMETRIC
POWDER.

500X PL4478
Etched surface showing single-phase
(U,Pu)N and porosity (black).

FIGURE 6. $(U_{0.8}Pu_{0.2})N$ PELLET PREPARED
FROM PREALLOYED STOICHIOMETRIC POWDER.

250X (center area) PL5988
Etched surface showing single phase
(U,Pu)N grains and porosity (black).

FIGURE 7. MICROSTRUCTURE OF $(U_{0.8}Pu_{0.2})N$
PELLET PREPARED FROM OXYGEN
CONTAMINATED POWDER.

250X (center area) PL6631
Etched surface showing stained grains
of (U,Pu)N phase and delineated smaller
grains of unidentified impurity phase.

FIGURE 8. MICROSTRUCTURE OF $(U_{0.8}Pu_{0.2})N$
PELLET PREPARED FROM OXYGEN CONTAMINATED
POWDER THAT WAS STORED IN OPEN VIALS FOR
37 DAYS.

125X (edge) PL6439
Etched surface area showing stained grains of the (U,Pu)N phase and delineated grains of impurity phase. Porosity in black.

FIGURE 9. MICROSTRUCTURE OF $(U_{0.8}Pu_{0.2})N$ PELLET PREPARED FROM OXYGEN CONTAMINATED POWDER STORED IN OPEN VIALS FOR 37 DAYS.

500X (center) PL6648
Etched surface showing stained grains of the (U,Pu)N matrix and delineated phases.

FIGURE 10. MICROSTRUCTURE OF $(U_{0.8}Pu_{0.2})N$ PELLET PREPARED FROM POWDER STORED IN OPEN VIALS OVER 37 DAYS.

125X PL6427
Etched surface showing stained grains of UN (bottom) and delineated grains of PuN (top). Diffusion zone occurs at the center. Porosity in black.

FIGURE 11. UN/PuN DIFFUSION COUPLE

500X PL4434
Etched fuel component of diffusion couple showing surface reactions.

FIGURE 12. (U_{0.8}Pu_{0.2})N DIFFUSION COUPLE SODIUM BONDED TO ORNL STAINLESS STEEL FOR 1000 HRS at 1000 C.

250X (a) Stainless Steel PL4185
Steel transformed to a pearlitic
structure throughout. Depleted zone

125X PL4198
(b) Interior of $(U_{0.8}Pu_{0.2})N$ Pellet.
Note unidentified phase formed in con-
junction with a crack in the pellet and
precipitated within the $(U,Pu)N$ grains.

FIGURE 13. $(U_{0.8}Pu_{0.2})N$ -TYPE 316 STAINLESS STEEL DIRECT CONTACT BONDED FOR 1000 HRS
AT 1000 C.

250X

Etched surface

PL6682

FIGURE 14. $(U_{0.92}Pu_{0.08})_2O_2$ SPECIMEN

250X

Etched surface of an edge section

PL6887

FIGURE 15. $(U_{0.8}Pu_{0.2})_2O_2$ SPECIMEN

250X

As-polished

PL4114

FIGURE 16. PuO_2 AS-RECEIVED MICROSPHERES

500X

Etched

PL5553

FIGURE 17. PuO_2 AS-RECEIVED MICROSPHERES.

250X As-polished PL5801

FIGURE 18. HEAT-TREATED MICROSPHERES

250X As-polished PL4558

FIGURE 19. HEAT-TREATED MICROSPHERES

250X As-polished PL5653

FIGURE 20. COATED PuO_2 MICROSPHERES

250X (center view) As-polished PL4586

FIGURE 21. CERMET SPECIMEN

250X (interior view) PL5776
As-polished)

FIGURE 22. CERMET SPECIMEN

250X (interior view) PL5554
 PuO_2 and Pu_2O_3 microstructure at
oxide particles revealed by etching.

FIGURE 23. CERMET SPECIMEN

✓ METALLOGRAPHIC EVALUATION OF EXPLOSIVELY BONDED
AND EXPLOSIVELY COMPACTED MATERIALS

by

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1146000

ABSTRACT

Explosive bonding and explosive compacting processes have been used with success to join similar and dissimilar metals classified as incompatible when fusion or diffusion joining methods are used and to fabricate metal matrix composites. Some of the advantages and disadvantages of the two explosive processes are described along with some of the specific techniques used at Battelle-Columbus Laboratories. Metallographic methods for evaluating the techniques are discussed and demonstrated by photomicrographs of numerous materials that have been explosively bonded and compacted.

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INTRODUCTION

Over the past few years, many new materials have been developed for the aerospace and nuclear industries in response to the demands by both government and industry for material systems that are capable of performing in increasingly extreme conditions of stress, temperature, and atmosphere. A major constraint in the use of some of the developed materials has been the problem of joining and fabricating the materials. In many cases, explosive bonding and explosive compaction now appear to be the best methods for solving these problems.

Explosive bonding and explosive compaction are essentially simple processes that require no complicated and costly equipment. Using explosive bonding, a high strength metallurgical bond usually can be formed between similar metals and also between certain dissimilar metals classified as incompatible when fusion or diffusion joining methods are used.

Many applications for explosive bonding are being studied at BCL. Some of the successful and more useful applications being

studied include bonding of tubular joints, spot welding, tube sheet-to-tube joints, seam welding, tubular cladding and fabrication of reinforced structures.

In explosive compaction pressures that are an order of magnitude greater than those available from other techniques usually can be achieved permitting compaction of a large variety of materials and combinations of materials. At Battelle-Columbus Laboratories (BCL), parts have been compacted explosively into a number of shapes including solid cylinders, tubes, fluted tubes, and nozzles.

This paper describes some of the explosive processing used at BCL, the metallographic techniques utilized for specimen preparations, and the results obtained from metallographic examinations of several explosively bonded and several explosively compacted materials.

EXPLOSIVE BONDING TECHNIQUE

A schematic diagram of one technique for explosive bonding is shown in Figure 1. In this, a chemical explosive is used to impinge the mating metal surfaces at high velocities under high pressure at the collision interface.

Various types of explosives can be used to obtain the pressures suitable for explosive bonding. At the present time, Battelle-Columbus is using a non-nitroglycerin dynamite consisting of a mixture of nitrostarch, ammonium nitrate, and several other lesser components. This explosive is a dry powder which has a detonation velocity of 8,000 to 12,000 ft/sec depending on the thickness of the explosive layer, the degree of confinement, and the packing density. The explosive is relatively insensitive making it safe for normal handling. Another attractive feature is its cost of less than \$1/lb.

When the important explosive-bonding parameters (explosive weight/unit area of cladding surface, and initial interface clearance) for a given system are controlled so that the

dynamic angle between the colliding surfaces is maintained within certain critical limits, a portion of the colliding surfaces, called a jet, becomes fluid and is expelled⁽¹⁾. Usually, the surfaces of metals and alloys are covered naturally with films of oxides, nitrides, adsorbed gases, or with coatings intentionally placed on the surfaces. These films or coatings usually prevent mating metal surfaces from bonding by conventional processes even under very high pressure. However, the severe deformation and extension of the colliding surfaces during explosive bonding act to remove or break up the unwanted surface films leaving behind film-free surfaces pressed into intimate contact.

Under optimum conditions of explosive bonding, the collision region is unstable and generates a wavy interface as shown by the photomicrograph in Figure 2. The wavy interface appears as a combination of direct metal-to-metal bonding and melted zones distributed in noncontinuous pockets. An explosive bond with a characteristic wavy interface and little or no melt between two metal plates can be observed in the photomicrograph

in Figure 3. Bonds between two similar or dissimilar metal plate materials which have a characteristic wavy interface with pockets of melted zones are shown by the photomicrographs in Figures 4, 5, and 6. The quality of the bond has often been found to be related to the pockets of melted material distributed along the interface. In compound forming systems, the pockets of melted material might be brittle. Consequently, in these systems the melted zones should be kept at a minimum or eliminated.

In some materials a certain amount of cold work develops during explosive bonding in the vicinity of the bond interface. The amount of cold-worked metal usually can be revealed by Knoop hardness traverses across the bond and by etching. An example of a bond which has very little cold work associated with it is shown by the photomicrograph in Figure 7. Figure 8 shows a bond with a rather large amount of cold work associated with it.

A stack of metal plates can be explosively bonded successfully as well as two metal plates. An example of a stack of alternating layers of mild steel and stainless steel plates

explosively bonded together is shown by the photomicrograph in Figure 9.

In addition to bonding plates of material, explosive bonding can be used to join monolayer composites as shown by the schematic diagram in Figure 10. For this, two thin metal foils are separated by the filaments being used in the system; the filaments in the bonded composite serve as a reinforcement of the matrix material. The photomicrograph in Figure 11 shows a monolayer composite of stainless steel filaments and aluminum fabricated explosively. Several alternating foil-filament layers can be explosively bonded also in one operation; however, the maximum number of layers which can be bonded in one operation may be limited.

During explosive fabrication of foil-filament composites, the pressure from the explosive detonation causes the foils to flow around the hard filaments and the top foil is accelerated against the bottom foil at a high velocity. If the explosive bonding conditions are right, a jetting phenomenon occurs between the

foils, and around the filaments. The jetting causes melted zones to form on the sides of the filaments. This is shown in the photomicrograph in Figure 12. These zones can be prevented from forming either by controlling the type of explosive and the explosive loading, or by using a thick buffer between the foil and the explosive⁽²⁾. A composite without melted zones around the filaments is shown in Figure 13.

EXPLOSIVE COMPACTION TECHNIQUE

The basic elements required for the explosive compaction process are not complex. All that is necessary is a container filled with metal powder wires, or other small pieces, around which the explosive is placed. The detonator for the explosive is located at one end of the container so that, following detonation, the front of the explosion moves uniformly down the entire circumference of the container. A schematic diagram illustrating the basic features of the process as normally used is shown in Figure 14⁽³⁾. The detonating explosive subjects the container to

a very high pressure which compacts the powder. Densities approaching a theoretical density often can be obtained. Fracturing of the compact sometimes occurs but usually can be prevented if a proper energy balance exists during the explosion. The energy balance is controlled by the proper explosive loading, the type of explosive used, the container wall thickness, and the strength and density of the material to be compacted.

Numerous materials have been explosively compacted at BCL to demonstrate the versatility of the process. One of the first composites fabricated by explosive compaction consisted of copper-coated steel wires as shown by the photomicrograph in Figure 15. Aluminum was successfully reinforced by beryllium wire explosively compacted in aluminum powder. Note the uniform structure and negligible wire fragmentation in a beryllium wire-aluminum composite compaction as shown by the photomicrograph in Figure 16.

Composite compactations have been processed successfully also by dispersing material fibers in powdered metal or alloy

matrices. Figure 17 is a photomicrograph showing boron fibers explosively compacted in a titanium matrix. The photomicrograph in Figure 18 shown graphite fibers explosively compacted in an aluminum matrix. Also, tungsten fibers have been compacted satisfactorily in a beryllium matrix as shown in Figure 19.

METALLOGRAPHIC TECHNIQUES

Explosively bonded and/or explosively compacted materials usually can be prepared for metallographic examination by conventional means. However, much care is required to metallographically prepare composites of the types described in this paper which contain hard fibers in a soft matrix. These types of composites are sectioned either with an abrasive cutoff wheel or they are potted in an epoxy resin and then sectioned. The sectioned samples are mounted and vacuum-impregnated with Epon 815 epoxy resin. The polishing techniques vary slightly for the wide variety of materials; however, the least relief at the bonded interface between hard and soft materials has been obtained by vibratory polishing on silk cloths charged with diamond paste.

The metallographic etchants used for the materials discussed in this paper are summarized in Table 1.

TABLE 1. ETCHANTS USED

Etchant	I	98 pts ethyl alcohol, 2 pts HNO_3
Etchant	II	30 pts glycerin, 30 pts HCl , 10 pts HNO_3
Etchant	III	10 percent oxalic acid solution
Etchant	IV	90 pts HCl , 10 pts HNO_3
Etchant	V	95 pts HCl , 5 pts HNO_3 , 1 g CuCl_2
Etchant	VI	50 pts lactic, 30 HNO_3 , 10 HF
A.P.		As polished

CONCLUSIONS

A wide variety of materials have been bonded and compacted successfully by explosive fabrication techniques. In many cases, explosive fabrication appears to be the best method for meeting the metals-joining demands of the future. Explosive fabrication techniques require a relatively simple, inexpensive capital facility; this requirement and the low cost of explosive

materials indicate a bright future for the commercial use of explosive fabrication techniques.

Metallography has proved to be a practical means of determining the integrity of explosively fabricated materials.

REFERENCES

1. Wittman, R. H., "The Explosive Bonding Process", Battelle Technical Review, pp 12-23, July 1967.
2. Fleck, J. N., Leonard, R. W., "Explosive Fabrication of Metal Matrix Composites", AIME, Spring Meeting, May 1969.
3. Leonard, R. W., "Direct Explosive Compaction of Powder Materials", Battelle Technical Review, pp 13-17 (November-December 1968).

FIGURE 1. SCHEMATIC OF ONE TYPE OF EXPLOSIVE BONDING(2)

100X

Etchant I

FIGURE 2. EXPLOSIVE BOND BETWEEN INCONEL AND MILD STEEL

100X

Etchant I

FIGURE 3. EXPLOSIVE BOND BETWEEN INCONEL AND MILD STEEL

100X

Etchant V

FIGURE 4. EXPLOSIVE BONDED INCONEL 718 TO INCONEL 718

100X

Etchant V and VI

FIGURE 5. EXPLOSIVE BOND BETWEEN FANSTEEL 80 AND STAINLESS STEEL

250X

Etchant IV

FIGURE 6. EXPLOSIVE BOND BETWEEN TD NICKEL AND INCONEL 718

100X

Etchant I

FIGURE 7. EXPLOSIVE BOND BETWEEN STAINLESS STEEL AND MILD STEEL

100X

Etchants II and III

FIGURE 8. EXPLOSIVELY BONDED STAINLESS STEEL TO STAINLESS STEEL

20X

Etchant I

FIGURE 9. EXPLOSIVELY BONDED LAYERS OF MILD STEEL AND STAINLESS STEEL PLATES

FIGURE 10. SCHEMATIC OF THE SET-UP FOR EXPLOSIVE BONDING A MONOLAYER COMPOSITE

500X

As Polished

FIGURE 11. EXPLOSIVELY BONDED STAINLESS STEEL FILAMENTS
IN A MATRIX OF 6061 ALUMINUM

500X

As Polished

FIGURE 12. EXPLOSIVELY BONDED STAINLESS STEEL FILAMENTS
IN A MATRIX OF 6061 ALUMINUM

500X

As Polished

FIGURE 13. EXPLOSIVELY BONDED STAINLESS STEEL FILAMENTS
IN A MATRIX OF 6061 ALUMINUM

(a) Experimental setup for compaction of cylindrical billet.

(b) Relationship between the detonation front in the explosive and the shock front in the powder.

FIGURE 14. SCHEMATIC OF EXPLOSIVE COMPACTION OF POWDER

100X

As Polished

FIGURE 15. COPPER-COATED STEEL WIRE EXPLOSIVELY COMPACTED

100X

As Polished

FIGURE 16. BERYLLIUM WIRE EXPLOSIVELY COMPACTED IN A MATRIX OF ALUMINUM

150X

As Polished

FIGURE 17. BORON FIBERS EXPLOSIVELY COMPACTED IN A MATRIX OF TITANIUM

100X

As Polished

FIGURE 18. GRAPHITE FIBERS EXPLOSIVELY COMPACTED IN A MATRIX OF ALUMINUM

100X

Etchant VI

FIGURE 19. TUNGSTEN FIBERS EXPLOSIVELY COMPACTED
IN A MATRIX OF BERYLLIUM