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COMPATIBILITY BETWEEN PuO_2 AND 80 Ni/20 Cr

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COMPATIBILITY BETWEEN PuO_2 AND 80 Ni/20 Cr

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RICHLAND, WASHINGTON

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ABSTRACT

PuO_2 was found to be compatible with an alloy of 80 Ni/20 Cr at 1093°C (2000°F) for 400 hours. The oxidation stability of a PuO_2 -62 wt% (80 Ni/20 Cr) cermet heated in air to 1093°C (2000°F) is superior to that of a UO_2 -62 wt% (80 Ni/20 Cr) cermet. UO_2 , if not protected by cladding, is converted to U_3O_8 in 982°C (1800°F) air even though it is dispersed and impacted in an alloy of 80 Ni/20 Cr. A PuO_2 -62 wt% (80 Ni/20 Cr) cermet can be diffusion bonded to 80 Ni/20 Cr foil by pneumatic impaction at 1093°C (2000°F) and 17,000 atmospheres ($\sim 250,000$ psi). The compatibility of PuO_2 with 80 Ni/20 Cr cladding material is dependent on the silicon content of the 80 Ni/20 Cr. PuO_2 reacts with silicon in 80 Ni/20 Cr foil at 816°C (1500°F). No evidence of PuO_2 diffusion through 0.15 mm thick 80 Ni/20 Cr foil was found after heating at 1093°C (2000°F) for as long as 400 hours.

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COMPATIBILITY BETWEEN PuO_2 AND 80 Ni/20 Cr

INTRODUCTION

The purpose of this study was to determine the compatibility of PuO_2 with an alloy of 80 Ni/20 Cr (NiCr). The study was conducted in support of the General Electric 630A air-cooled maritime reactor development program. (1) Prior to this study, fuel development effort was principally concerned with a 38.2 wt% UO_2 -61.8 wt% NiCr cermet. The UO_2 was enriched in the fissionable isotope U^{235} to 93.2 wt%. An obvious alternative to this highly enriched UO_2 fuel is one containing PuO_2 . Plutonium dioxide needs no enrichment, and is stable in air.

Two specimen types were employed in this study. The first, a thin disc, was used in oxidation studies which compared a PuO_2 -62 Wt% (NiCr) cermet with a UO_2 -62 wt% (NiCr) cermet. The second, a cylindrical capsule, was used in diffusion studies of a PuO_2 -62 wt% NiCr cermet totally clad in NiCr.

The principal analytical tools utilized were the metallograph, electron beam microanalyzer and X-ray diffractometer.

EXPERIMENTAL PROCEDURES - Oxidation Studies

The disc specimens consisted of cermet cores in NiCr circular frames, each sandwiched between two NiCr foils (Figure 1). The discs were densified to nearly theoretical density by high energy rate (pneumatic) impaction at 700°C (1292°F) and 17,000 atm. ($\sim 250,000$ psi). Densification of the core is illustrated in Figure 2. The completed discs containing either PuO_2 or UO_2 cermet cores appeared as shown in Figure 3. The NiCr matrix of the core became diffusion bonded to the circular frame and mechanically bonded to the foils. Prior to testing, two 0.8 mm (1/32-inch) diameter holes were drilled through each PuO_2 -NiCr disc and one through each UO_2 -NiCr disc. Discs were heated for 400 hours in moving air at 982°C (1800°F) and 1093°C (2000°F) in contact with Al_2O_3 trays.

RESULTS AND DISCUSSION - Oxidation Studies

The results of these tests are well illustrated in Figures 4-7. The UO_2 -NiCr discs swelled considerably, whereas the PuO_2 -NiCr discs remained unchanged except for surface oxidation of the NiCr. Metallographic examinations of the

FIGURE 1

Schematic of NiCr-Clad Cermet Disc (not to scale)

FIGURE 2

PuO_2 -NiCr Cermet Before (above) and After (below) Pneumatic Impaction

FIGURE 3

7X

NiCr-Clad Cermet Disc After Pneumatic Impaction

$\text{PuO}_2\text{-NiCr}$

$\text{UO}_2\text{-NiCr}$

5X

FIGURE 4

NiCr-Clad Cermets Before Tests at 982 °C (1800 °F)

$\text{PuO}_2\text{-NiCr}$

$\text{UO}_2\text{-NiCr}$

5X

FIGURE 5

NiCr-Clad Cermets After Tests at 982 °C (1800 °F)

$\text{PuO}_2\text{-NiCr}$

$\text{UO}_2\text{-NiCr}$

5X

FIGURE 6

NiCr-Clad Cermets Before Tests at 1093°C (2000°F)

$\text{PuO}_2\text{-NiCr}$

$\text{UO}_2\text{-NiCr}$

5X

FIGURE 7

NiCr-Clad Cermets After Tests at 1093°C (2000°F)

heated PuO_2 -NiCr discs revealed no changes. Similar examinations of the UO_2 -NiCr discs showed a pronounced change due to the heating in air. The UO_2 particles that were exposed to air were severely pitted (Figure 8). Pitting of the UO_2 and swelling of the discs were caused by oxidation of the UO_2 to U_3O_8 and the accompanying volume change. The calculated increase in volume on conversion of UO_2 to U_3O_8 is 31%. Finely divided U_3O_8 powder was found in each associated alumina tray (Figures 5 and 7). PuO_2 has a significant advantage over UO_2 as a fuel material in an air-cooled reactor system; it is stable in air to its melting point, 2400°C . Finely powdered UO_2 is oxidized in air at room temperature. (2)

EXPERIMENTAL PROCEDURES - Diffusion and Chemical Compatibility Studies

The assembly of a PuO_2 -NiCr test capsule is illustrated in Figures 9 and 10. Prior to assembly, all NiCr parts were cleaned in H_2 at 1100°C for one-half hour. A short NiCr tube was closed on one end by electron beam welding a thin NiCr foil to the tube wall. Then a hydrogen sintered (12 hours at 1200°C) PuO_2 -62 wt% NiCr cermet core was placed in the capsule against the NiCr foil. A loose NiCr foil was placed on top of the cermet disc as an alpha contamination shield, and the annular gap between this foil and the tube wall was filled with NiCr powder. An alpha radiation counter was used to assure that the tube wall was free of plutonium contamination prior to inserting a NiCr end cap into the tube and TIG welding it to the tube wall. At the time the outgas hole in the end cap was closed, the small amount of helium in the capsule was heated, leaving less than one atmosphere of helium in the completed capsule.

The PuO_2 -62 wt% NiCr cermet cores were densified and diffusion bonded to the capsule NiCr foils by pneumatic impaction at 1093°C (2000°F) and 17,000 atmospheres ($\sim 250,000$ psi). The impaction process consisted of loading the welded cermet capsules into small MgO cylinders, packing these cylinders in MgO filled stainless steel cans, 10 cm dia. x 14 cm high (4 in. dia. x 5-1/2 in. high), welding the cans closed, evacuating the entire assembly through an outgas tube during preimpaction heating, and hot impacting (Figure 11). The test capsules were removed after impaction by cutting the stainless steel cans open and fracturing the MgO from the NiCr surfaces. Figure 12 shows an impacted capsule and cross section; the core was artificially blackened to improve clarity.

Near Periphery

Adjacent to Hole

FIGURE 8

UO₂-NiCr Cermet After Testing in Air at 982 °C (1800 °F)

FIGURE 9

Schematic of PuO₂-NiCr Test Capsule (not to scale)

Completed Capsule

Can

Core

Foil

End Cap

2X

FIGURE 10

PuO_2 -NiCr Test Capsule Assembly

FIGURE 11

Pneumatic Impaction Process

NiCr Foil

9X

PuO_2 -NiCr
Cermet

NiCr Foils

Can Wall

End Cap

9X

FIGURE 12

Impacted PuO_2 -NiCr Test Capsule (above) and Longitudinal Cross
Section (below)

Twenty-one capsules were prepared. One capsule from each of five impactations was examined metallographically for evidence of core-foil bonding. This sampling, $\sim 25\%$, showed that each impactation produced a diffusion bond between the PuO_2 -62 wt% NiCr cermet core and NiCr foils. Ultrasonic testing also indicated bonding, but not as conclusively as the metallographic examinations. The remaining 16 samples were used for the diffusion studies. Core location in each of the test capsules was determined radiographically (Figure 13). Sixteen capsules, four per furnace, were heated on Al_2O_3 plates in moving air at 649°C (1200°F), 816°C (1500°F), 982°C (1800°F), and 1093°C (2000°F). One capsule was removed from each furnace at 100-hour intervals until four capsules, each, had remained 100, 200, 300, and 400 hours at each temperature. The capsules were alpha counted before and after the isothermal heat treatments. Comprehensive metallographic examinations of each heat-treated capsule were completed.

The following materials, chosen on the basis of an analysis of the NiCr foil (Table I), were arc-melted into small buttons to test their compatibility under the most severe thermal conditions.

- a. PuO_2 /NiCr foil
- b. PuO_2 /NiCr tubing
- c. PuO_2 /niobium
- d. PuO_2 /silicon
- e. PuO_2 /iron

Arc melting was done on a water-cooled copper hearth in one atmosphere of argon.

One PuO_2 -62 wt% NiCr test capsule was examined by an electron probe microanalyzer. The probe experimental procedures will be reported elsewhere. (3)

RESULTS AND DISCUSSION - Diffusion and Chemical Compatibility Studies

Preimpaction X-ray diffraction and metallographic examinations of the PuO_2 -62 wt% NiCr hydrogen sintered cores showed no reactions between the PuO_2 and NiCr. There was, however, evidence that the PuO_2 had thermally decomposed to alpha Pu_2O_3 and PuO_{2-x} . Decomposition of PuO_2 is expected in the very dry hydrogen atmosphere, -73.3°C (-100°F) dewpoint. The nickel lattice parameter increased with chromium solution as anticipated. (4, 5)

Alpha counting showed no diffusion of plutonium through the NiCr foils or tube walls during heating.

FIGURE 13

Radiographs of PuO_2 -NiCr Test Capsules

TABLE I
ANALYSIS OF NiCr FOIL*

<u>Element</u>	<u>Weight Percent</u>
Ni	76.91
Cr	19.65
Nb	1.16
Si	0.85
Fe	0.67
Co	0.1
Mn	0.06
C	0.035
S	0.003
P	0.001

*General Electric Spec. No. B-50T2026A
Nuclear Materials and Propulsion Operation
Cincinnati, Ohio

Metallographic examination of each test capsule showed a diffusion bond between the NiCr matrix of the PuO_2 -62 wt% NiCr cermet core and NiCr foils. Typical photomicrographs of the core and core-clad diffusion bond are shown in Figures 14 and 15. Note that the etched specimens reveal large numbers of twinned NiCr crystals. Figure 16 illustrates the two-phased structure ($\alpha \text{Pu}_2\text{O}_3 + \text{PuO}_2$) of the PuO_2 particles as impacted and after heat treatment. The light-colored phase in the PuO_2 particles (etched) and the phase in high relief (as polished) is thought to be the $\alpha \text{Pu}_2\text{O}_3$ because it appears to have been preferentially attacked by the oxidizing etchant ($\text{HCl} + \text{H}_2\text{O}_2$).

No reactions were found between the PuO_2 particles and the NiCr in the core. There was, however, a new phase formed in the PuO_2 particles adjacent to the NiCr foils (Figure 17). It seemed likely that an impurity in the NiCr foil had diffused through the NiCr and reacted with the PuO_2 . Identification of an unknown reaction product is generally simplified if some means is used to increase its relative quantity; reacting the components under very severe conditions is one possibility. PuO_2 was therefore arc-melted with some of the NiCr foil. The PuO_2 and NiCr were molten for 5-10 seconds. Figure 17 shows the quenched button; note the degree of liquation between the PuO_2 and NiCr. As a first approximation this indicates compatibility in the liquid state. Photomicrographs of the arc-melted button (Figure 18) revealed a non-metallic reaction product, similar to that shown in Figure 17, which is apparently independent of the metallic phase. The interface between the NiCr mass and ceramic mass is distinct and shows no evidence of an interaction. Spherical NiCr particles within the ceramic mass are unrelated to the dark-colored reaction product. Metallographic examinations of PuO_2 arc-melted with the NiCr tubing used for the cermet capsules showed no such reaction products, providing strong evidence that the PuO_2 had not reacted with NiCr, but with an impurity in the NiCr foil.

The principal impurities, niobium, silicon, and iron, were arc-melted with PuO_2 to enable metallographic comparison of the reaction products, if any, with the reaction product adjacent to the NiCr foil (Figure 17). Even under these severe conditions, no observable reactions occurred between niobium and PuO_2 . The PuO_2 and niobium masses separated as in the PuO_2 /NiCr buttons except for several perfect spheres of each material dispersed in the other. Arc-melted PuO_2 /Si and PuO_2 /Fe both showed metallographic evidence of reactions. The appearance of the PuO_2 /Si reaction product was very similar to that seen in the PuO_2 /NiCr foil reaction zone.

200 Hrs. at 816 °C

800X

Core-Clad Interface

200 Hrs. at 816 °C

800X

Core

FIGURE 14

PuO_2 -NiCr Cermet

200 Hrs. at 816 °C 800X, Etched
Core-Clad Interface

400 Hrs. at 1093 °C 800X, Etched
Core

FIGURE 15

PuO₂-NiCr Cermet

As Impacted

800X, Etched

800X

300 Hrs. at 816 °C

FIGURE 16

PuO₂-NiCr Cermet

300 Hrs. at 1093 °C

800X

Arc-Melted

9X

FIGURE 17

PuO₂-NiCr Cermet

FIGURE 18
Arc-Melted PuO_2 -NiCr

Electron probe microanalyses of the heat-treated PuO_2 -62 wt% NiCr capsule (Figure 17) confirmed that the reaction product was a combination of plutonium and silicon. One dimensional microprobe scans of the specimen provided a clear, qualitative map of the plutonium and silicon distributions. Silicon was found only associated with the plutonium reaction product. The silicon concentration remaining in the foils was for the most part below microprobe detection limits (manual scans were not run with extended period counting). Electron probe microanalyses also detected a PuO_2 /Si reaction zone adjacent to the can wall. This reaction zone was not detectable by metallographic examinations. Evidence of reaction between the PuO_2 and silicon at the core-foil interface was observed metallographically only after 300 hours at 816°C (1500°F). Until further electron probe microanalyses are conducted, this may be considered the limit below which little reaction occurs between PuO_2 and the NiCr foil used in these tests. Other trace elements in the NiCr foil (iron, cobalt, and manganese) were below the limits of detection for the electron probe techniques used. Analyses for carbon, sulfur, and phosphorus, were not performed.

CONCLUSIONS

1. PuO_2 is compatible with an alloy of 80 Ni/20 Cr at 1093°C (2000°F) for at least 400 hours.
2. The oxidation stability of a PuO_2 -62 wt% (80 Ni/20 Cr) cermet in air to 1093°C (2000°F) is superior to that of a UO_2 -62 wt% (80 Ni/20 Cr) cermet. The principal reason for the stability of PuO_2 in air is that it is the highest oxidation state of plutonium. UO_2 , if not protected by cladding, is oxidized to U_3O_8 in air even though it is dispersed and impacted in an alloy of 80 Ni/20 Cr.
3. The compatibility of PuO_2 with 80 Ni/20 Cr cladding material is impaired by silicon as an impurity in the 80 Ni/20 Cr. PuO_2 reacts with silicon in 80 Ni/20 Cr foil after 300 hours at 816°C (1500°F).
4. A PuO_2 -62 wt% (80 Ni/20 Cr) cermet can be diffusion bonded to 80 Ni/20 Cr foil by pneumatic impaction at 1093°C (2000°F) and 17,000 atmospheres ($\sim 250,000$ psi).
5. No evidence of PuO_2 diffusion through 0.15 mm thick 80 Ni/20 Cr foil was found after heating at 1093°C (2000°F) for as long as 400 hours.

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