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ECA-(NpO_2)-10

April 28, 1961

TO: P. H. PERMAR

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EVALUATION OF NpO_2-Al SLUG NO. 15

INTRODUCTION

Neptunium oxide is irradiated in a target slug that is made by vacuum hot pressing NpO_2-Al powder compacts inside an impact-extruded aluminum can.

During preliminary runs in Building 235-F, thoria was used as a stand-in for NpO_2 to determine optimum process conditions. Thoria was selected as a dummy for NpO_2 due to the scarcity of NpO_2 and the similarity in physical properties of the two oxides. It was found however, that some of the ThO_2 was reduced by aluminum to form $ThAl_3$ during hot pressing. If the backup die temperature was permitted to exceed 637°C during the heating and pressing cycle, a $ThAl_3$-Al eutectic was formed which penetrated the grain boundaries of the can, as shown in Figure 1.

The memorandum presents the results of the evaluation of a standard production slug and of experiments designed to establish whether melting and subsequent grain boundary penetration by the eutectic is a problem in hot-press bonding the NpO_2-Al slugs.

SUMMARY

Neptunium oxide was completely reduced by aluminum to form $NpAl_4$ in 30 minutes at 590°C. The reduction is exothermic, as demonstrated by the fact that a sample heated to 610°C at a controlled rate continued its temperature rise to 638°C on its own. Temperature rise above 610°C was attributed to the exothermic reaction between NpO_2 and Al to form $NpAl_4 + Al_2O_3$.

The $NpAl_4$ compound and aluminum form a eutectic mixture that melts at 651 + 2°C; no evidence of intergranular melting in the 1245F aluminum can was observed below 649°C. There is no danger of eutectic penetration of the can under present operating conditions in 235F, using a nominal backup die temperature of 620°C.

There was no evidence of reduction of NpO_2 in the as-pressed slug, which indicates that the bonding of the slug is aluminum to aluminum and does not involve an intermetallic compound of Np and Al. Stud-weld tests showed bond strengths of 12,000 to 12,500 psi between the core and cladding. Two studs pulled at interface between the bottom end cap and the core showed bond strengths of 6,500 and 12,000 psi. Two studs pulled at the top end cap showed bond strengths of 5,500 psi and 6,000 psi between the cap and the core.

Five samples along the length of the core were taken for chemical analysis; the results will be reported when they are available.

DISCUSSION

One production slug was obtained for esperiments to determine whether there was any danger of forming a eutectic between the reduction product of NpO_2 and Al during the hot-pressing operation. Slug 15 contained NpO_2 + Al and was rejected from the process because part of the cladding was pulled away from the top end cap during removal of the slug from the pressing die, and welding was not considered feasible.

The conditions under which slug 15 were made are as follows:

Hot Pressing Conditions for Slug No. 15

	Nominal	Maximum
Backup Die Temperature, °C	615°	632°
Preheat Time, min.	25	-
Pressing Force, tons	13	-
Pressing Time, min.	6	-
NpO_2 Content, g. per slug	42.3	-
NpO_2 Content, wt .%	24.5	-

Slugs 2 through 22 were made at the same conditions and were of acceptable quality.

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Since it is not considered desirable to sample the 235-F production destructively on a routine basis, slug number 15 was fully evaluated to obtain as much information as possible.

Apparatus

All operations on the bare slug were done inside a gloved box to contain contamination. A resistance-heated tube furnace was used for determining reaction temperatures and the eutectic melting point. The furnace was attached to the containment box by a boot so that samples could be moved to and from the furnace.

Furnace temperature was controlled by a thermocouple mounted in contact with the heating element of the furnace. The sample temperature was measured by a thermocouple inserted in a drilled hole in the sample. The chromel-alumel thermocouples were calibrated by comparison against a Bureau of Standards Thermocouple over the temperature range of interest. Thermocouple readings on the recorder were cali- by a potentiometer and were confirmed before and several times during each run. A third thermocouple was located between the sample and the wall of the furnace tube to provide a check on the indicated sample temperature.

Samples were polished and etched inside the box. Each sample was viewed on an uncontaminated metallograph by placing the sample in a plastic bag which had a cover glass "picture window" taped into one wall. By using lens immersion oil both inside and outside the cover glass, it was possible to view the sample at magnification up to 500x with good resolution.

Experimental Procedure and Results

Heating Experiments

The first piece cut from the core was the top end cap plus a short section of the core. This piece was examined metallographically as representative of the as-pressed slug and saved for later tests. Five additional pieces, each about 3/4 inch long were cut from the slug for heating studies, and drilled to a depth of approximately 1/2 inch to accommodate the thermocouple tip.

The first piece was placed in the furnace with the probe balanced at 610°C. The sample temperature began to level off at 610°C after 20 minutes in the furnace, then began to rise rapidly. The sample was removed from the furnace when the temperature reached 638°C. Figure 2 shows this sample; note that part of the NpO_2 was reduced to form a phase later identified as $NpAl_4$.

A second sample was heated to 590°C and held for 30 minutes, then heated to 618°C and held for 20 minutes. All the NpO_2 in this sample was reduced, but no melting occurred, as shown in Figure 3. The phase formed by the reduction was identified as $NpAl_4$ by X-ray diffraction, and no evidence was seen of residual NpO_2. The same sample was heated to 623°C and held for 20 minutes, examined metallographically, then reheated at 625°C and 630°C and re-examined. There was no

difference in the appearance of the sample from that which was seen at 618°C. Metallographic and radiographic inspection revealed no evidence of gross melting in the core or intergranular eutectic penetration into the cladding.

The sample was then heated to 635°C and held for 20 minutes. Metallographic inspection showed that a change had occurred at the surface of the $NpAl_4$ particles in the matrix. The nature of this change is discussed below, in connection with Figure 4.

Three of the remaining samples were heated directly to temperatures of 642°C, 645°C and 648°C. The sample temperature in each case was noted to increase slowly to about 610°C, then increase rapidly to 638°C. The temperatures then decreased slightly to about 635°C before returning to the control temperature. This seemingly anomalous behavior was attributed to loss of heat from the sample to the sample boat after the exothermic reaction had gone to completion. Each of the three samples was examined both radiographically and metallographically. No evidence of melting was seen in any of the samples. As the temperature was increased, it was noted that the secondary "reaction zone" around each of the $NpAl_4$ particles had broadened. X-ray diffraction showed the new structure to be $NpAl_4$ also. There was no NpO_2 lines in the diffraction patterns of either the original or the secondary $NpAl_4$ areas. The structure illustrated in Figure 4 is typical of the temperature range between 635° and 645°C. Note that the $NpAl_4$ originally formed is separated by a band of voids from the $NpAl_4$ that is in contact with the aluminum.

The change in appearance of the $NpAl_4$ particles was attributed to the consolidation of voids within the original $NpAl_4$, which was probably slightly porous, since the reduction of NpO_2 by Al is accompanied by a 4% decrease in volume of the reacting material.

The remaining sample was placed in the furnace with the furnace controlling at 740°C in order to study the thermal arrests involved in heating the sample. The sample behaved in the same manner as those previously heated up to 650°C, however, at 651°C a thermal arrest of about 20 minutes was noted during which the indicated sample temperature increased to 653°C. When the temperature reached 653°C, it rose rapidly again to 685°C. At a sample temperature of 685°C, the furnace power was turned off and the sample was allowed to cool. When the sample temperature had reached 650°C; recalescence occurred and the temperature increased slightly to 652°C. This was followed by an arrest of about 20 minutes, during which the temperature decreased to 649°C. The procedure was repeated for the same sample with a nearly identical occurrence of the thermal arrests. On the basis of these data, the eutectic point for the system Np-Al was placed at 651 $\pm$ 2°C. The composition of the eutectic was not determined.

The core had partially melted and eutectic liquid had escaped through the can wall. A transverse section is shown schematically in Figure 5 to show the location of the fields illustrated in Figures 6 through 9. Figure 6 shows the can wall, which had melted at the grain boundaries to form the eutectic structure. Figure 7 shows the appearance the eutectic mass at the bottom of the slug. The core contained unmelted $NpAl_4$, both in the form of porous reaction product and as primary crystallites from freezing, as shown in Figure 8. The appearance of the can-core interface is shown in Figure 9.

Bond Strength Determinations

Stud-weld tests were made at the core-cladding interface near the bottom end of the slug. Studs were also pulled at the end cap-cladding interface at both ends of the slug. The results of these tests are shown in the following Table.

Bond Strengths in Slug No. 15

Location	Bond Strength, psi	No. of Studs Pulled
Top End Cap	5,500 - 6,000	2
Clad	12,000 - 12,500	4
Bottom End Cap	6,500 - 12,000	2

Dimensional Evaluation

Dimensions on the as-received slug are summarized below: Measurements were made initially from radiographs of the as-received slug and verified by metallographic examination.

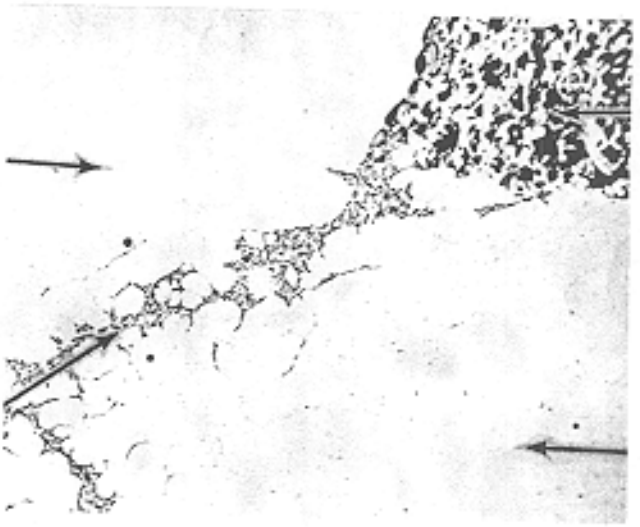
Dimensions of Slug No. 15

Location	Dimension, inches	
	Minimum	Average
Length (Excluding Flash)	-	5.940
Diameter	-	0.938
Clad Thickness	0.032	0.034
End Thickness		
Top	0.185	0.185
Bottom	0.195	0.200

CONCLUSIONS

The eutectic melting temperature for the system Np-Al is 651 ± 2°C, and there was no eutectic penetration of the cladding grain boundaries at temperatures up to 648°C. Under present 235-F operating conditions, using a nominal backup die temperature of 620°C, there is no danger of eutectic penetration of the cans.

HGM/ehj



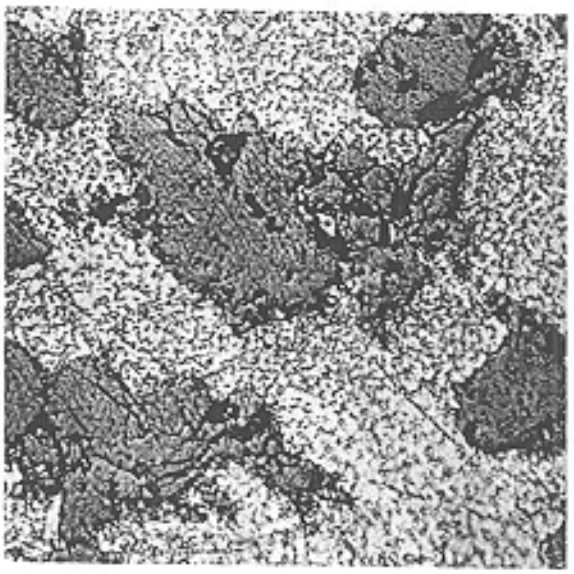
Mag. 50X HF Etch Neg. EA 15,799M

FIGURE 1 Longitudinal Section Showing Eutectic Penetrations in ThO_2-Al Slug

Mag. 500X HF Etch Neg. 33433

FIGURE 2 Transverse Section Showing Partically Reduced NpO_2

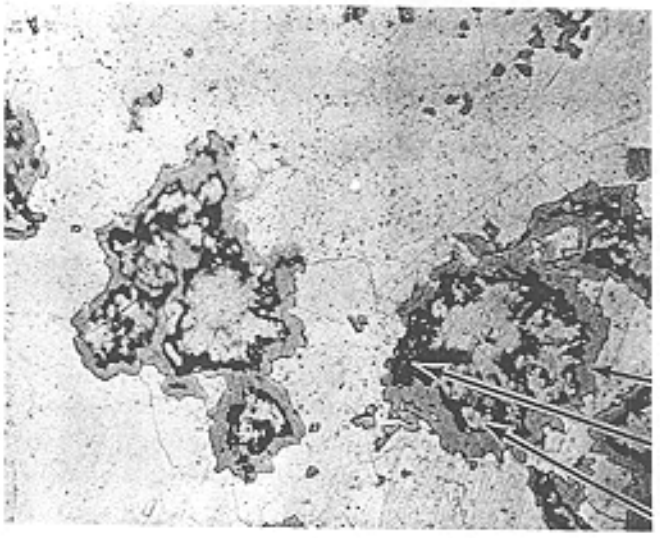
Sample Heated to 610°C; heat of reaction carried temperature.
Dark grey areas are $NpAl_4$; black areas show the location of NpO_2 particles that were lost in preparation of the specimen.



Mag. 500X HF Etch Neg. 33436

FIGURE 3 Completion of Reaction to Form $NpAl_4$

Sample heated for 30 min. at 590°C and 20 min. at 610°C. Appearance of samples heated at temperatures up to 630°C was similar.



Secondary $NpAl_4$

Void

Primary $NpAl_4$

Mag. 500X HF Etch Neg. 33917

FIGURE 4 Secondary "Reaction Zone" of $NpAl_4$

Sample heated to 645° for 20 min.

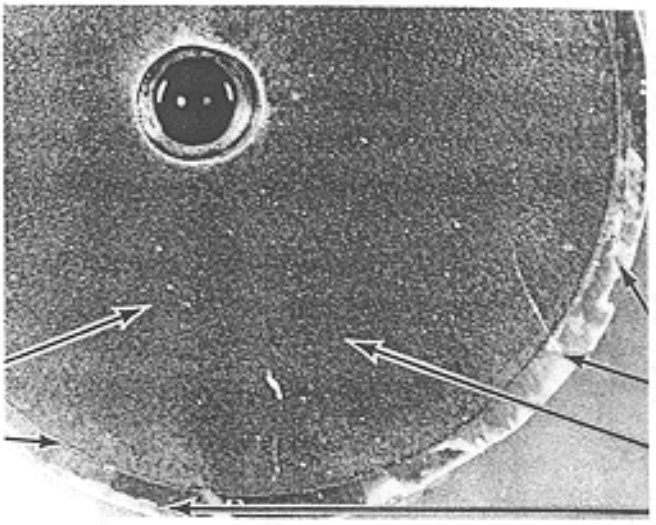


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FIGURE 5 Section after Melting

Locations of the fields shown in Figures 6 to 9 are indicated.

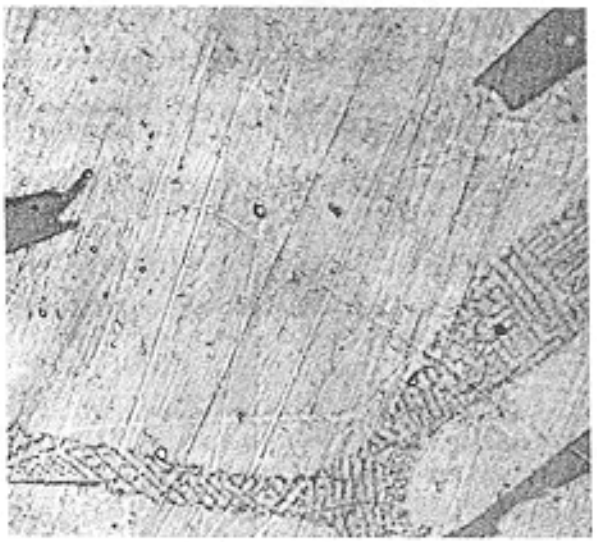

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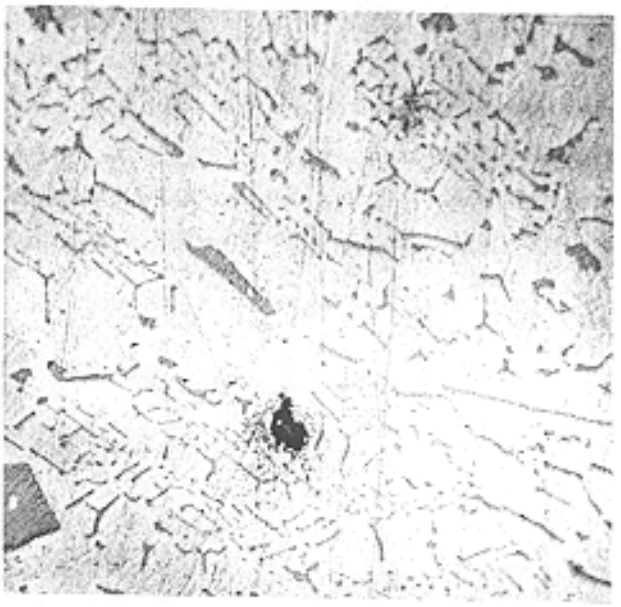
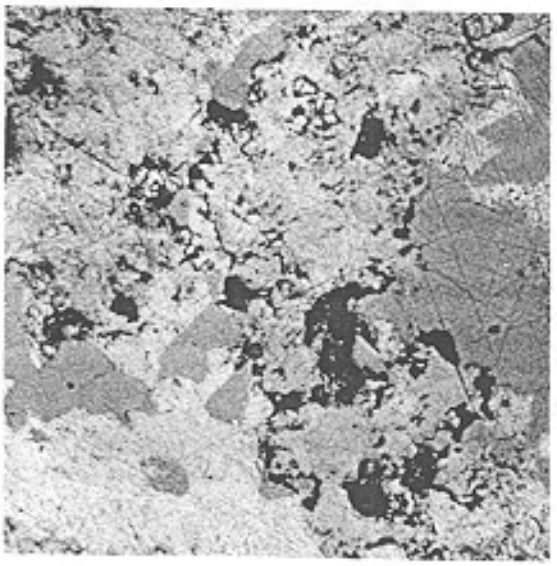
FIGURE 6 Grain Boundary Melting in Can Wall

Sample heated to 685°C. Note eutectic structure surrounding grain of aluminum.



Mag. 500X No Etch Neg. 33563

FIGURE 7 Structure of Eutectic Liquid



Mag. 500X No Etch Neg. 33567

FIGURE 8 Core of Partially Melted Sample

Shows $NpAl_4$ crystallites precipitated from melt and undissolved $NpAl_4$.

Mag. 500X No Etch Neg. 33566

FIGURE 9 Core-Cladding Interface