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AEC RESEARCH AND DEVELOPMENT REPORT

CORROSION OF PLUTONIUM ALLOYS IN NaK

by

H. H. Hyman and J. J. Katz

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2

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CORROSION OF PLUTONIUM ALLOYS IN NaK

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H. H. Hyman and J. J. Katz

*✓ Alloys Al/100
96 atom Pu/100*

ABSTRACT

A plutonium-aluminum alloy containing 4 atom per cent aluminum showed no attack after exposure to purified NaK for one month at 400°C in the absence of any oxide. The same specimen and other plutonium alloys, including pure plutonium, showed marked deterioration in shorter exposures in the presence of oxide films from a welded stainless steel container. Pure uranium was resistant even in the presence of such oxides.

INTRODUCTION

In the development of intermediate-temperature breeder reactors, the behavior of plutonium and plutonium alloys in liquid metal coolants is of considerable interest. Some preliminary experiments have been run on the corrosion of plutonium alloys in purified NaK. The specimens investigated include one of each of the following materials: fine plutonium wire, heavier uranium wire, 10 per cent plutonium - 90 per cent uranium alloy, 98.25 atom per cent plutonium - 1.75 atom per cent aluminum alloy, 96 atom per cent plutonium - 4 atom per cent aluminum alloy, and a larger size uranium sheet.

OBSERVATIONS

Table 1 summarizes the results of the first set of measurements. The temperature of exposure, time of exposure, and changes in weight are given. In every case the specimens acquired a film. In the case of the uranium wire, this appeared to be a reasonably adherent oxide film; the specimen gained weight, and on removal of the film with nitric acid, a corresponding gross loss in weight was observed. In the 4 per cent aluminum in plutonium alloy the tarnish film could not be removed with nitric acid, and this alloy is not attacked by the acid. This specimen showed the least attack of the plutonium samples in NaK, although it did lose weight. This specimen was reserved for an additional exposure. In the case of the other specimens, most notably that of the plutonium-uranium alloy, substantial quantities of the surface flaked off during the experiment and could be picked up as discrete particles after hydrolysis of the NaK. The experimental details are described on page 6.

Table 1

CORROSION OF URANIUM AND PLUTONIUM ALLOYS IN NaK

Expt. No.	Specimen	Temp. (°C)	Time (hr)	Wt. (g)		Apparent Corrosion Rate (mg cm ⁻² hr ⁻¹)
				Before	After	
1	Pu wire	400	144	0.0139	0.0134	-0.04 ^a
2	10 % Pu-90 % U	350	160	0.1651	0.1535	-0.30 ^b
3 ^c	10 % Pu-90 % U	405	160	0.1535	0.1387	-0.39
	1.75 % Al-98.25 % Pu			0.1018	0.0922	-0.25
	4 % Al-96 % Pu			0.1167	0.1144	-0.06
	U wire			0.3657	0.3665	+0.01 ^d
4	U sheet 0.97" x 0.61" x 0.106"	396	160	19.3974	19.4010	+0.002 ^e

^aSample crumpled into 3 major pieces and several small flakes.

^bNumerous small flakes in final suspension. Surface changed in appearance, see Fig. 3.

^cThese four specimens were run in a single exposure.

^dThe weight after the oxide film was removed with 30 % HNO₃ was 0.3582 g, corresponding to a 7.5 mg loss of uranium metal. The uranium loss corresponding to 0.8 mg gain as UO₂ is about 6 mg of metal.

^eThis specimen showed only a spotty tarnish film and was similar in appearance to similar samples tested earlier by the Metallurgy Division (L. Kelman, private communication).

Except for the uranium sheet, these specimens were not selected or prepared as specimens for corrosion testing. They are probably metallurgically unsound samples, and were substantially smaller than normal corrosion specimens. As a result, the surface to volume ratio for the specimen is much larger than commonly employed, and the volume of the testing system is disproportionately large as compared to the size of the specimen being tested. These factors may be considered as intensifying the effects of surface defects in the specimen and trace impurities in the corrosion-testing system. The full-size uranium-metal corrosion specimen was checked in the same equipment and showed much less visible attack as well as a lesser weight change rate.

The specimen of 4 per cent aluminum - 96 per cent plutonium alloy was exposed in a thin stainless steel tube so as to reduce the ratio of equipment to sample size. The results are summarized in Table 2. The negligible weight change for the prolonged exposure agrees with, although it does not necessarily prove, the explanation offered for the film formation observed in the first set of experiments.

Table 2

CORROSION OF Pu-Al ALLOY^a IN NaK

Treatment	Wt. after Treatment (g)	Wt. Change (mg)	Apparent Corrosion Rate (mg cm ⁻² hr ⁻¹)
Coating removed	0.1167 ^b		
160 hr, 400°C in NaK	0.1144 ^b	- 2.3	-0.06
Large container			
Pickled in HCl	0.0785	-35.9	
720 hr, 400°C in NaK			
Rinsed and air dried	0.0845	(+ 6.0)	
Rinsed and mechanically wiped	0.0794	+ .9	+0.005

^a4 atom per cent Al, 96 atom per cent Pu. The sample piece was a nickel-coated cylinder 1/16" in dia. x 3/16" long.

^bSee Expt. 3, Table 1.

EXPERIMENTAL PROCEDURE

The experiments described in Table 1 were run in the equipment shown in Figure 1. Each sample, except for the large uranium sheet in experiment 4, was placed in the perforated basket during the exposure. The sample tube was then connected to the NaK addition line as shown in Figure 2. The sample tube was evacuated, flushed repeatedly with purified helium, and again evacuated, and then NaK was admitted. The sample container was then closed off and set in a vertical tube furnace. The stainless steel container employs an O-ring closure tightened down with six Allen head screws. Originally the gasket employed was a gas-filled stainless steel ring. However, some difficulty was encountered in obtaining a completely leak-free closure, and an aluminum O-ring was substituted in the latest experiments. The thermocouple well and filling tube were welded into the cover plate of the sample container. The body of the sample container consisted of a length of stainless steel pipe with flanges and a bottom plate welded on. The perforated basket was screwed on to the plug which formed the bottom of the thermocouple well. The assembly was tested under both pressure and vacuum and shown to be leak-tight when used in each experiment. The NaK was filtered before attaching to the filling manifold and passed through an additional filter in charging the container. The helium was passed over activated charcoal cooled with liquid nitrogen. Although this type of operation should ensure virtually oxide-free NaK, it must be pointed out that the stainless steel container and especially the welds retain an oxide film which may well be significant in comparison with the amounts of oxide ultimately produced on the specimens, if the films noted are oxide films.

For the next experiment the 4 atom per cent aluminum - 96 per cent plutonium alloy was pickled in hydrochloric acid to remove the previously formed tarnish film and re-exposed.

The container used for this exposure was a length of one-eighth inch stainless steel tubing. The bottom of the tubing was welded shut for safety, but the tube was pinched mechanically approximately two inches above the bottom so that the NaK did not come in contact with the welded area. The tube was connected to the manifold as shown in Figure 2 and evacuated, purged, and filled with purified NaK exactly as the larger tube had been. The top of the tube was pinched off, and the entire tube left in the furnace at approximately 400°C for one month.

All specimens were carefully examined under the microscope before and after the corrosion experiments. In most cases, photographs were taken. The most interesting set of photographs appears in Figure 3, which shows the before and after appearance of the sample of 10 per cent plutonium - 90 per cent uranium alloy used in experiment 2, Table 1. This piece is reported to have been machined from a one-eighth inch diameter casting down to its final size of a one-sixteenth inch diameter cylinder, approximately three-sixteenths of an inch long.

Figure 1

Stainless Steel Sample Tube for Testing Corrosion in NaK

Figure 2

NaK Addition Apparatus

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Before

After

Figure 3

Pu-U Alloy - Corrosion in NaK

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The three specimens of plutonium alloy were originally received with a protective coating of carbonyl nickel, which was peeled off prior to the test. The larger scratch marks on the surface of the alloy before immersion are due to the peeling operation. As can be seen, the original machine marks and virtually all the scratches are obliterated as a result of the exposure.

The behavior of the specimen tested in the smaller corrosion equipment was substantially different.

The specimen as removed from the hydrochloric acid but before the second exposure to NaK was shiny and metallic in appearance but badly deformed in shape. There were several deep pits and voids, some with rather sharp edges. After exposure the stainless steel tubing was cut open, and the specimen pushed out. All of the NaK in the tube was hydrolyzed in butyl alcohol, and the specimen washed with butyl alcohol and air dried. At this time the specimen did not appear to be completely clean, in that particles of nonmetallic foreign matter appeared to be loosely adherent to the specimen. The specimen showed a substantial weight gain, as is shown in Table 2. The specimen was then rinsed further with acetone and mechanically wiped with tissue to remove any film not tenaciously held, and the sample was then reweighed. The specimen showed only a small weight gain and did not appear to be substantially changed in appearance as compared with the sample before immersion in NaK. Although some of the hollows did appear to be filled with nonmetallic deposits, the high spots are shiny metal.

The NaK recovered from each experiment was handled in two portions, one consisting of the bulk of the material in the sample tube, the second portion consisting of the material most intimately associated with the basket and sample. Both were hydrolyzed with butyl alcohol and stored. The bulk of the NaK contained a comparatively small fraction of the particulate matter, which appeared in the fraction most closely associated with the samples. These particles were found to be intensely alpha radioactive, and presumably are flakes from the surface of the specimens. In the case of the pure plutonium wire, the supernatant from the bulk of the NaK was analyzed and found to contain very little plutonium. A 10-ml sample was acidified, treated with potassium dichromate, and salted with aluminum nitrate, and the plutonium was extracted with hexone. The hexone was washed with saturated aluminum nitrate solution, and then the plutonium was washed out with distilled water. The aqueous phase was acidified and salted with aluminum nitrate and re-extracted with hexone, and the plutonium was finally plated and counted. Approximately $0.2 \mu\text{g}$ of plutonium was found in the entire hydrolyzed solution, corresponding to approximately thirty grams of NaK originally. At this time it can not be stated whether this is due to a true solubility of plutonium in NaK or the solubility of plutonium in the sodium butyrate in butyl alcohol solution, or whether it is simply an upper limit due to minute particles in the sample. In the latter

case the actual plutonium content of the NaK would be even smaller than 0.01 ppm. In any event, it is clear that most of the material removed from the samples was not dissolved in the NaK but rather removed as substantial flakes.

CONCLUSION

Certain tentative conclusions can be drawn from this work. It is reasonably certain that a specimen of plutonium alloy such as the four per cent aluminum sample would stand prolonged exposure to purified static NaK in an oxide-free system without significant deterioration. It should therefore be possible to perform experiments involving exposure of plutonium alloys to NaK.

However, it is also true that conditions exist under which nonadherent films may be produced. These films are apparently oxide films which form even in oxygen-free NaK if the outer container is made of welded stainless steel or other material covered with a removable oxide layer. While similar films are observed with pure uranium, they appear to be adherent and protective. It is not known whether the failure of the films in the case of the plutonium alloys is inherent or accidental. The specimens tested were metallurgically unsound and not representative of alloys which might be prepared with the same over-all chemical composition.

Until suitable alloy specimens can be prepared and tested, the deterioration of a plutonium alloy must be anticipated on exposure to NaK in the presence of any oxide.

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