218
9-6-74

Dr-932

LA-5593

UC-25

Reporting Date: April 1974

Issued: August 1974

Compatibility of
Hafnalloys 105 and 150 with $^{238}\text{PuO}_2$

by

C. C. Land
D. E. Peterson

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

MASTER

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$4.00 Microfiche \$1.45

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

COMPATIBILITY OF HAFNALLOYS 105 AND 150 WITH $^{238}\text{PuO}_2$

by

C. C. Land and D. E. Peterson

ABSTRACT

The compatibility between two Hafnalloys (hafnium-platinum-palladium formulations) and $^{238}\text{PuO}_2$ (plutonia) was investigated after their exposure at 1000°C for 2000 and 5800 h. Hafn alloy samples with and without preapplied surface layers of hafnia were studied. To interpret the oxidation behavior of the two alloys, thermodynamic and diffusion calculations of their reactivities with plutonia were correlated with experimental observations. The two Hafnalloys prove to be unsuitable materials for plutonia storage at 1000°C for 2000 hours or longer, because oxygen and plutonium diffuse into the alloy lattice and the container becomes brittle. Calculations indicate that they also would not make suitable containers for plutonia at 800°C .

I. INTRODUCTION

A study of the compatibility between $^{238}\text{PuO}_2$ (plutonia) and two hafnium alloys (Hafn alloy-105 and -150) with and without preapplied HfO_2 (hafnia) coats was performed at Los Alamos Scientific Laboratory (LASL) in cooperation with TRW Systems, Inc. The objective of the study was to determine whether the Hafnalloys could be used as fuel-container materials in isotopic heat source systems.

Reactions between plutonia and the Hafnalloys at 1000°C were investigated with metallographic techniques, and an electron microprobe was used to identify the elements in the reaction products. Levels of oxygen diffusion into the alloys were measured as a function of heating time and also were related to microhardness determinations.

Theoretical predictions based on thermodynamic and diffusion calculations were correlated with experimental observations to provide information on the mechanisms involved.

II. EXPERIMENTAL

The plutonia pellets, 0.559-cm-diam by 0.457-cm-long, were supplied by LASL. They contained the following major impurities, in parts per million by weight: 250-1000 Ca, 110 Cr, 160 Fe, 200 C, 1100 Th, 3100 Np, and 6600 U. Individual concentrations of other impurities were less than 100 ppm.

The two Hafnalloys are hafnium-platinum-palladium formulations developed by TRW, and have compositions of Hf-1 wt% Pt-0.5 wt% Pd (Hf-105) and Hf-1.5 wt% Pt-1.5 wt% Pd (Hf-150). Both alloys exceed the solid solubility limit of platinum and palladium in α -Hf, hence both are two-phase alloys. Hafn alloy pellets (0.584-cm-diam by 0.317-cm-thick) and capsules (0.749-cm-diam by 1.40-cm-long, with 0.076-cm wall thickness) were supplied by TRW. Half the pellets were given a preoxidation treatment by TRW to produce a 75-125- μm -thick surface coating of hafnia. Basic hardness data were obtained for this as-received material before the experimental work began.

Both Hafnalloys were exposed to the plutonia pellets at 1000°C in short-term (2000-h) and long-term (5800-h) tests. Each of four test assemblies consisted of a control capsule and a test capsule. The control capsule contained a preoxidized, as well as an as-machined, Hafn alloy pellet of the same composition as the capsule. The test capsule differed only in that a plutonia pellet was sandwiched between the two Hafn alloy pellets. Each capsule was welded closed and loaded into a molybdenum cup (55-mil wall thickness). The cups, with the enclosed capsules, were then encapsulated individually in Nickel 200 (90-mil wall thickness), and these capsules, in turn, were encapsulated in pairs (one control and one test capsule) in Hastelloy X (90-mil wall thickness). Tungsten inert gas welding was used in making all closures. Each Hastelloy X capsule, with its contents, constituted one test assembly. A diagram of a test assembly is shown in Fig. 1.

The test assemblies for the two short-term tests were loaded into one tube furnace and the two for

the long-term tests into another, where they were held at 1000°C for 2000 and 5800 h, respectively.

The Hafn alloy capsules were then recovered from the test assemblies and pressure-potted in polyester resin before being cut into longitudinal sections with a slow-speed diamond saw.

Half of each capsule (with its contents) was analyzed by LASL's Analytical Chemistry Group—the Hafn alloy pellets and capsules for oxygen content, and the plutonia pellets for hafnium and palladium content.

The sections of the remaining capsule halves were ground on 400, 600, and 4/0 grit metallographic papers and polished for 40 h on a Syntron vibratory polisher, using Linde A abrasive and a nylon polishing cloth, with water as the lubricant. These polished sections were examined metallographically, swab-etched in 50 H₂O-1 HNO₃-1 Hf (by volume), and reexamined. Hardness traverses were then made on the etched specimens with a Leitz microhardness tester using a 50-g load and a diamond pyramid indenter. Traverses on pellets were made from the area of contact between pellets to the outside of the pellet; those on capsules were made from the area adjacent to the plutonia pellet to the outside of the capsule. Before and after each series of hardness measurements, the accuracy of the hardness tester was checked with standard test blocks having hardnesses in the range of interest. The samples used for the metallographic tests were also used for electron microprobe analysis to identify the elements in any reaction products formed during exposure to the 1000°C test temperature.

III. RESULTS AND DISCUSSION

Hardness data and oxygen content for the two Hafn alloys are shown in Table I. Baseline hardness data for the control specimens are plotted in Fig. 2, and those for the test specimens in Fig. 3. Average hardness numbers are plotted in all cases, because there was little variation across the pieces. Each alloy, hafnia-coated or not, hardens at an individual rate. The treated samples harden more slowly than the untreated samples; the Hf-105 test samples harden more slowly than the Hf-150 test samples; and the test capsules of both alloys harden more slowly than any of the test pellets, probably because they were not in direct contact with the plutonia. However, all test materials hardened appreciably.

Oxidation behavior of the test pieces (pellets and capsules) after 5800 h is plotted in Fig. 4. The un-

Fig. 1.
Schematic of a Hf-105 test assembly.

TABLE I
HARDNESS DATA^a AND OXYGEN CONTENT^b
FOR THE HAFNALLOYS

Sample	Hf-105, Treated		Hf-105, Untreated		Hf-150, Treated		Hf-150, Untreated	
	Hardness	Oxygen Content	Hardness	Oxygen Content	Hardness	Oxygen Content	Hardness	Oxygen Content
As-received material	200	420	230	15	260	1 100	330	20
Control pellet after 2000 h	250	550	270	180	370	1 400	200	160
Control pellet after 5800 h	230	560	200	400	300	1 700	190	70
Test pellet after 2000 h	350	2 000	490	5 800	690	5 800	890	15 000
Test pellet after 5800 h	700	12 000	770	21 000	700	7 400	860	20 000
Capsule after 2000 h	---	---	290	---	---	---	310	---
Capsule after 5800 h	---	---	560	3 200	---	---	690	7 700

^aAll hardness numbers are averages based on 11 indentations across the sample. All hardness numbers are DPH at 50-g load.

^bOxygen content is given in parts per million by weight.

treated test pellets of both Hafnalloys show higher oxidation rates than do the treated pellets. The untreated test pellets actually reach the maximum solubility of oxygen in α -Hf (approximately 2 wt%) in the 5800-h test period. The Hf-150 capsule picked up twice as much oxygen (8000 ppm) as the Hf-105 capsule did.

Reactions (R in Fig. 4) other than the dissolution of oxygen in the α -Hf solid solution occurred in the untreated Hf-150 test pellet in the 2000- and 5800-h tests. After 5800 h, reactions also occurred in the treated and untreated Hf-105 test pellets and in the test capsules of both alloys. Three reaction products were observed in the test pieces. Electron microprobe results indicate that they were an oxide of hafnium, an oxide of hafnium and plutonium, and an oxide of hafnium, platinum, and palladium. The HfO_2 and the

$(\text{Hf,Pu})\text{O}_2$ reaction products usually occurred at the Hafn alloy/plutonia interface (Fig. 5), but in one sample (Fig. 6) the $(\text{Hf,Pu})\text{O}_2$ was distributed throughout the test piece. The Hf, Pt, Pd, O reaction product was observed only in the Hf-150 long-term test capsule, where it occurred across the entire cross section of the area adjacent to the plutonia pellet (Fig. 7).

The preoxidized surface layer on the Hafn alloy pieces acts to some extent as a barrier against further oxidation, but it also provides an additional source of

Fig. 2.

Hardness data for control pellets in their as-received state and after 2000 and 5800 h at 1000°C.

Fig. 3.

Hardness data for test pieces. Data for as-received pellets are shown on the ordinate, those for the control pellets are at lower right. R indicates beginning of some reaction other than the dissolution of oxygen in the α -Hf solid solution.

Fig. 4.

Oxidation behavior of test pieces. Oxygen content of as-received pellets is shown on the ordinate, that of control pellets is at lower right. R indicates beginning of some reaction other than dissolution of oxygen in the α -Hf solid solution.

oxygen contamination, as can be seen by comparing the as-received material (Fig. 8) with a control piece from the short-term test (Fig. 9). The oxide layer disappears after 2000 h at 1000°C.

The largest amount of hafnium or palladium detected in the plutonia was 100 ppm, and was found

Fig. 5.

Hafnialloy-150 test pellet (1) after 5800 h at 1000°C, showing hafnia (2) and $(\text{Hf}, \text{Pu})\text{O}_2$ (3) reaction products formed at Hafnialloy/plutonia interface. 200X.

Fig. 6.

Hafnialloy-105 test pellet after 5800 h at 1000°C, showing $(\text{Hf}, \text{Pu})\text{O}_2$ (1) distributed throughout the material. 500X.

in the long-term test pellets of both alloys. Because of the small sample size no analysis was made for platinum.

Fig. 7.

Hafnialloy-150 test capsule after 5800 h at 1000°C, showing the Hf-Pt-Pd-O reaction product (1). 500X.

Fig. 8.
As-received Hf-150 test pellet, showing the Haf-
nalloy/hafnia interface. 500X.

The plutonia pellets from the long-term tests dis-
integrated while being polished in water, although
plutonia is treated this way routinely at LASL without
such disintegration. X-ray analysis of the dis-

Fig. 9.
Hafnalloy-150 control pellet after 2000 h at
1000°C. The interface (1) between the preapplied
oxide coat and the Hafnalloy has disappeared and
the two layers have welded together. 500X.

integrated material revealed extremely fine-grained
plutonia.

Other changes that could make the Hafnalloys un-
desirable as containers for plutonia were some
agglomeration of the $\text{Hf}_2(\text{Pt,Pd})$ second phase and
considerable grain growth (Figs 10 and 11).

Both long-term test capsules were bulged (Fig.
12) when they were removed from the furnace, in
spite of the fact that the maximum internal pressure
of 483 kPa (70 psi) gives a circumferential stress of
2413 kPa (350 psi). In the long-term test, the Hf-
105 capsule was found to be cracked when it was
removed from the furnace (Fig. 13). Both long-term
test capsules cracked intergranularly (Fig. 14) while
they were being sectioned with the slow-speed dia-
mond saw, even though both had been pressure-
mounted previously in polyester resin, and both were
so brittle that they could be picked apart with
tweezers. In applications where Hafnalloy might be
used as a container for plutonia, the fuel-to-metal
ratio would be expected to be larger than the value
of 1 to 3 used in the present tests. In such applications
the tendency for oxygen pickup by the container
would be even greater.

The probable oxidation mechanism for Hafnalloys
in contact with plutonia involves oxygen adsorption
onto the alloy surface, followed by dissolution of oxy-
gen into the metal to form an interstitial solid solu-
tion. The oxygen molecules dissociate on the metal
surface, forming chemisorbed atomic oxygen that

Fig. 10.
Grain size of Hf-105 control pellet after 2000 h at
1000°C. 100X.

Fig. 11.

Grain size of Hf-105 control pellet after 5800 h at 1000°C. 100X.

diffuses into the alloy lattice by migrating from one interstitial site to the next empty one. Adsorption of oxygen is the most probable rate-determining step in the early stages, with diffusion gradually becoming rate-controlling as the oxygen gradient decreases. Oxygen transport away from the surface may finally become slow enough to permit formation of a hafnia scale on the alloy. The oxidation rate would then be governed by oxygen diffusion through the hafnia film, with oxygen migrating both by lattice diffusion and along low resistance paths, such as grain boundaries and dislocations. Similar interpretations have been made by Kofstad and Espevik¹ to explain their observations on the oxidation of hafnium.

Pretreatment of the Hafnialloy pellets with a hafnia layer would be expected to decrease the oxidation rate of the Hafnialloy. However, the hafnia layer gradually dissolves into the alloy and, in the presence of plutonia, the metal is exposed to oxidation by the fuel. In this study, dissolution of a 75-125- μ m-thick hafnia layer introduced 10 000-16 000 ppm of oxygen into the Hafnialloy pellets.

The oxidation behavior of the Hafnialloys may be approximated by examining the diffusion of oxygen into hafnium metal. The solubility of oxygen in hafnium² is almost temperature independent, varying from 20 at.% at 700°C to 22 at.% at 2000°C. The diffusion coefficients for oxygen in hafnium³ are $1.3 \times 10^{-9} \text{ cm}^2/\text{s}$ at 1000°C and $4.5 \times 10^{-11} \text{ cm}^2/\text{s}$ at 800°C.

Fig. 12.

Hafnialloy-150 test capsule after 5800 h at 1000°C. 10X.

The amount of oxygen diffusing into hafnium pellets of dimensions equivalent to those of the Hafnialloy samples of this study was calculated using Eq. (1) of Ref. 4.

$$M = \frac{2}{\sqrt{\pi}} (C_s - C_0) \sqrt{D t} \quad (1)$$

M is the total amount of oxygen that has diffused in time t across an area of the oxide-metal interface. C_s and C_0 are, respectively, the oxygen concentrations

Fig. 13.
Hafnialloy-105 test capsule after 5800 h at 1000°C.
4X.

at the surface and initially in the bulk (an initial bulk oxygen concentration of zero was assumed for this calculation). D is the diffusion coefficient. This treatment is based on the assumed formation of an oxygen-saturated surface layer on a semi-infinite solid and on the predominance of interstitial diffusion.

Application of Eq. (1) to the present experiments indicates that at 1000°C approximately 6000 ppm of oxygen would diffuse into the Hafnialloy pellet after

Fig. 14.
Hafnialloy test capsule after 5800 h at 1000°C,
showing intergranular cracks. 100X.

2000 h, and a level of 11 000 ppm would be attained after 5800 h (assuming that the Hafnialloys behave like hafnium metal). The amounts of oxygen measured after 2000 h in the untreated Hf-105 and the treated Hf-150 agreed with the calculated oxygen levels, indicating that interstitial diffusion is the predominant mechanism in these cases.

After 2000 h, the treated Hf-150 achieved an oxygen concentration over two times the calculated value, whereas the treated Hf-105 sample displayed one-third the calculated oxygen level, indicating that the oxide surface layer may have been effective in retarding oxidation. After 5800 h, the untreated samples attained saturation levels of oxygen, and diffusion along grain boundaries may have become significant in these longer term studies. Oxygen levels in the treated samples were considerably below saturation levels after 5800 h, showing that most of the oxygen diffusing into the alloys in these cases was probably obtained from the hafnia surface layer. Differences in the oxygen levels among the treated samples can be explained by variations in the oxide layer thickness and in the degree of reduction of the plutonia.

Partial molar free energies for atomic oxygen over plutonia and over hafnium-oxygen solid solutions were determined by Markin and Rand⁵ and by Silver et al.,⁶ respectively. Application of their results to the present experiments indicates that at equilibrium approximately 14 000 ppm of oxygen would have diffused into the untreated Hafnialloy pellet. Also, the composition of the plutonia pellet used in this study would have been reduced to about $^{238}\text{PuO}_{1.82}$ assuming that all of the oxygen released by the plutonia dissolved into the untreated Hafnialloy pellet. Additional oxygen from the plutonia dissolved into the capsule wall and into the treated Hafnialloy pellet; hence further reduction of the plutonia pellet took place.

Thermodynamic analysis indicates that applications involving plutonia-to-metal ratios of about 3 to 1 will result in complete saturation (20 at. % oxygen) of the metal following attainment of equilibrium at 1000°C. Similar calculations for plutonia-containment applications of the alloys at the lower temperature of 800°C indicate that equilibrium oxygen levels of about 10 at. % oxygen will be attained in the Hafnialloys at equilibrium. Theoretical calculations of the oxidation rate of hafnium metal at 800°C (using Eq. (1)) show that approximately 4000 ppm of oxygen will diffuse into the metal lattice in 20 000 h. Hardness data obtained from this study indicate that 4000 ppm of oxygen will cause the alloy to be brittle at room temperature.

IV. CONCLUSIONS

Hafnialloys Hf-105 and Hf-150 prove to be unacceptable as container materials for plutonia at 1000°C for periods of 2000 h or more. There is diffusion of oxygen and plutonium into the metal lattices, with resulting embrittlement of the alloys. Additional problems include agglomeration of a Hf-Pt-Pd second phase and the presence of considerable grain growth. Hafnialloy-105 oxidizes more slowly than Hf-150, but still becomes brittle when placed in contact with plutonia at 1000°C for 2000 h or more. Pretreatment of the alloys with a thin hafnia surface layer reduces the oxidation rate of the alloys, but does not prevent embrittlement over extended time periods.

Oxidation of the two Hafnialloys by plutonia is thermodynamically favorable at 1000°C. Calculations of the interstitial diffusion of oxygen into the alloys correlate well with experimental observations. Theoretical predictions indicate that even at 800°C the Hafnialloys will oxidize when in contact with plutonia.

ACKNOWLEDGMENTS

We express our appreciation to John Ogren of TRW Systems, Inc., for the Hafnialloy samples and containers, to E. A. Hakkila and Maynard Smith of LASL Group CMB-1 for performing electron

microprobe and oxygen chemical analyses, and to R. N. R. Mulford and S. E. Bronisz of Group CMB-5 for advice in the research and in manuscript review.

REFERENCES

1. P. Koistad and S. Espevik, "Kinetic Study of High-Temperature Oxidation of Hafnium," *J. Less Common Metals* 12, 382-394 (1967).
2. R. F. Domagala and R. Ruh, "The Hafnium-Oxygen System," *ASM Trans.* 58, 164-175 (1965).
3. J. P. Pemsler, "Diffusion of Oxygen in Hafnium," *J. Electrochem. Soc.* 111, 1185-1186 (1964).
4. L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals* (McGraw-Hill Book Co., NY, 1953), p. 445.
5. T. L. Markin and M. H. Rand in *Proc. Symposium on Thermodynamics with Emphasis on Nuclear Materials and Atomic Transport in Solids*, Vienna, July 22-27, 1965 (IAEA).
6. M. D. Silver, P. A. Farrar, and D. L. Komarek, "Thermodynamic Properties and Lattice Parameters of Hafnium-Oxygen Alloys," *AIME Trans.* 227, 876-884 (1963).