The Compatibility of $^{238}\text{PuO}_2$ With Various Nickel and Cobalt Base Alloys

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ABSTRACT

Results from a compatibility study between production grade $^{238}\text{PuO}_2$ with various nickel- and cobalt-base alloys are presented and discussed. The alloys are Hastelloy N, Hastelloy X, Haynes 25, Haynes 188, Inconel 625, and TD nickel. Test temperatures were 800 and 1000°C with thermal exposures up to 360 days. Suggested interpretation of the data and resultant mechanisms are given.

INTRODUCTION

As part of a general research and development project in support of the Radioisotopic Heat Source Program, a study of $^{238}\text{PuO}_2$ with various nickel- and cobalt-base alloys was initiated. Similar efforts with platinum, platinum-rhodium alloys, and various refractory metals and alloys have been published in two interim reports^{1,2} and will result in two subsequent final reports.

The intent of this effort is to determine, if possible, the mechanisms of the reactions, the rate of the reactions, and the possible effects of these reactions on the integrity of the liner material. As much of these data generated as possible are presented so that the reader may analyze the data and reach his own conclusions, which may or may not agree with those presented. Not all of the photomicrographs and electron microprobe data obtained are presented in this report. However, a serious attempt has been made to present as much information as possible without being redundant.

Relevant literature concerning $^{238}\text{PuO}_2$ compatibility is rare. Appendix A summarizes pertinent information and is taken primarily from a compilation on PuO_2 compatibility by Selle.³

Comparison of these data with the results of the present tests will conclude this report.

Materials Production grade fuel, produced in accordance with the SNAP-27 specifications, was used in this program. According to these specifications, the fuel may contain up to 2.0% of nonactinide cation impurities. Fuel produced to these specifications was used for several reasons. The most important of these is that it is desirable to know what reactions, if any, would take place in an actual heat source capsule in service. At the time these tests were initiated the reference fuel form was PuO_2 microspheres produced according to the SNAP-27 specifications. Secondly, production grade fuel is much more readily available than special purity fuel. In view of the large amounts of fuel needed for the entire program, this is an important consideration. All of the $^{238}\text{PuO}_2$ used in a given test series was from the same batch of fuel. Chemical analysis of the fuel used in each of the two series of tests is given in Appendix B.

Each of the test alloys examined were from one lot of material. Analyses of the test alloys are given in Appendix C.

Procedure Data were obtained at 800 and 1000°C. A total test matrix is shown in Appendix D. Capsule designs used in each case are indicated and are summarized in Appendix E. These capsule designs leave something to be desired. Their design was motivated primarily by a desire to obtain the maximum amount of test data in the shortest period of time for the lowest cost. This meant starting many of the tests with materials already on hand or using an easily obtainable mill product. In some cases the proper tubing was not available or delivery time was extremely long which necessitated the use of discs of one material embedded in the fuel which, in turn, was contained in a different liner material. A design of this type often leads to complications. This point was discussed in the interim reports on platinum and platinum alloys¹ and refractory metals and alloys² and will be demonstrated in this report as well. The effects of the interrelations between the liner and embedded discs that were observed are indicated in the report. Undetected influences are possible but will have to be resolved by separate testing of materials. However, useful information was obtained from the interaction among test alloys.

In both series of tests the $^{238}\text{PuO}_2$ was doubly encapsulated. The inner capsule used to contain the fuel was TIG welded closed. The TIG welds were made in an argon atmosphere using high purity argon as a cover gas. This container was then decontaminated and electron beam welded into a Haynes 25 secondary capsule used to protect the inner capsule from oxidation at the annealing temperature. Test coupons of metal were embedded in the fuel with care taken to avoid contact with the capsule wall or with each other. Retaining cups were placed in the inner capsules to restrict the movement of fuel and disks during decontamination and handling prior to annealing. Radiographs of the capsules were made prior to loading into the furnace in order to ensure that there was no contact between test materials.

All inner capsules, end caps, and retaining cups were machined from bar stock. The Haynes 25 outer capsules were machined from tubing, and end caps were machined from bar stock. The Hastelloy N and Haynes 188 test coupons were fabricated from sheet by electrical discharge machining, while the Inconel 625 and TD nickel coupons were cut from sheet by an abrasive cutoff wheel employing a 90 grit silicon carbide wheel.

All alloys were treated in a two-step acid pickle. The first step consisted of 4-6% potassium permanganate and 1-2% sodium hydroxide bath at 57-68°C for 15 min. The samples were then placed in a solution of 8-12% nitric acid and 2-3% hydrofluoric acid at 52-71°C for 15 min. After being rinsed in water, ethyl alcohol, and acetone, the capsules were assembled.

All capsules were annealed in muffle furnaces in an air atmosphere. Oxidation resistance was provided by the Haynes 25 outer container.

Metallographic sample preparation was done in a glovebox facility under a nitrogen atmosphere. Sectioning was done with an abrasive cutoff wheel employing 90 grit silicon carbide. The first specimens were mounted in a copper-filled diallyl phthalate to provide a conductive mount for electron microprobe analysis. Later samples were mounted in amber Bakelite for better retention of the edge and reaction product. In order to retain as much of the brittle reaction product as possible, the last group of samples were mounted in plastic epoxide cured in a vacuum/pressure mounting chamber. This technique involved first evacuating the samples in the uncured epoxide to about 25 mm Hg to remove any air from between the sample and epoxide. The chamber is then pressurized with about 500 psi of nitrogen to force intimate contact between the sample and mounting material and to keep bubbles from being formed in the epoxide by the $^{238}\text{PuO}_2$. The samples are then cured under pressure for 3 hr at 60°C.

Coarse grinding of the metallographic mount was done with 180-320 grit silicon carbide paper, and final grinding was done with 600 grit silicon carbide paper. Carbon tetrachloride was used as a lubricant in the grinding steps as well as in the ultrasonic cleaner between the various steps in grinding and polishing. The copper-filled diallyl phthalate and amber Bakelite mounts were rough polished on Texmet* or Politex-pre-PS** paper with 6- μm diamond paste with olive oil as a lubricant. An intermediate step of 3- μm diamond paste using Texmet or Politex-pre-PS paper was used. Final polishing was done on microcloth on a vibratory polisher with 0.3- μm alumina and water as a lubricant. Polishing of the epoxide mounts was a two-step process using 6- μm and 0.05- μm alumina on Texmet paper on vibratory polishers with water as a lubricant. All photomicrographs were taken with a Leitz MM5 metallograph.

Electron microprobe analyses were performed on Applied Research Laboratories and Hatachi instruments. Two types of analyses were done. In the first type, the electron beam scanning unit of the instrument was used to scan the specimen, and photographs were taken of the distribution of various elements using the signal from the characteristic x-ray to modulate the beam of the cathode ray tube. In this mode of operation the beam is scanned across an area of the sample so that a distribution of that particular element can be obtained. Also, by this technique, photomicrographs were taken with the backscattered electrons from the sample. The photomicrographs obtained in this manner yield a density distribution across the area scanned.

The second type of analysis was done using a finely focused static beam to indicate compositional changes as the specimen was moved under the beam. Analysis was made by driving the stage translation over a selected part of the specimen and feeding the signal from the characteristic x-ray through a rate meter to a strip chart. The resulting

*Texmet is a napless polishing paper supplied by A. B. Buehler, Ltd.

**Politex-pre-PS is a napless paper supplied by Geoscience.

trace gives a rough quantitative description for each of the elements sought as a function of the distance across the face of the sample. The data in this report are presented in the form of traces of these strip chart plots superimposed upon each other. The relative vertical displacement of each curve with respect to the others should not be considered as a quantitative comparison of the amount of one element with another. This relative displacement is a function of the counting rate and, hence, is a variable. However, for a given element, the changes in displacement of the curve, excluding electronic noise, can be used to indicate changes in composition. The number adjacent to the identification of each curve is the counting rate used for that particular element. Different counting rates were used in an attempt to obtain maximum sensitivity and still keep the trace on scale. The higher the counting rate for a given percent of scale, of one element with respect to another, the greater is the actual relative amount of that element with respect to the other. At the same time, decreasing the counting rate necessitates an increase in amplification, resulting in an increase in the noise-to-signal ratio. In order to obtain a more accurate comparison of one element with respect to another, the curves must be normalized with respect to one of the elements. If element B is to be compared with element A the following relationship is used:

$$\frac{\text{Counting rate B}}{\text{Counting rate A}} \times \frac{\% \text{ of scale of element B}}{\% \text{ of scale of element A}} = \text{relative amount of B with respect to A.} \quad (1)$$

It should be emphasized that this equation will give only a relative amount of B compared to A. No quantitative comparisons are implied. A further clarification of this point may be obtained from Figure 1, which shows the relative displacements of chromium at three different counting rates in a nickel-base alloy. The relative displacement equivalent to about 23 wt % chromium in this alloy is plotted for each of the three counting rates. The counting rate (10^5 , 5×10^5 , and 10^6) merely indicates the counting rate, in counts/min, that will produce the given displacement. In effect, the lower the counting rate the greater is the displacement for a given amount of the element under consideration. The background displacement must also be considered. This background is the zero wt % reading and is caused primarily by the continuous x-ray spectrum of all the elements being excited by the electron beam and electronic noise of the counting system. In order to make the comparison quantitative, other corrections must be made to compensate for differences in wavelength, peak intensities, absorption, density, etc. At the same time a standard of known composition must be used for comparison.

Because of the small size of the reaction products, consideration of the beam size and response of the microprobe is important. Figure 2 gives an x-ray strip chart showing the effect of the electron beam spot size and the instrument response of the Hatachi microprobe when going from a chromium to nickel standard. Figure 2 should be compared to the included x-ray strip chart analyses of the test samples when determining whether interdiffusion occurred between adjacent phases. The traces in Figure 2 do not account for edge rounding or detection of subsurface material which could effect the observed response for the real samples.

In addition to these tests, an attempt was made to determine the lattice parameters of the fuel after each test to determine whether any changes in stoichiometry or structure occurred as a result of the tests. Samples of the fuel powder were loaded into quartz capillaries with an inside diameter of 0.3 mm and a wall thickness of 0.02-0.03 mm. A standard Debye-Scherrer powder camera was used. Filtered copper K α radiation from a high intensity GE x-ray tube was used with exposure times of 2-4 hr. The film was covered with aluminum foil in order to minimize the effects of secondary radiation.

Physical and Thermodynamic Considerations Some of the thermodynamic and physical property data of metals and oxides that are of interest in this investigation are given in Table 1 and Figures 3 and 4. Table 1 gives the values for the change in free energy. Values used in these determinations are taken from Glassner's¹⁴ compilation and Oetting's¹⁵ data for plutonium oxides, which assume unit activities and must therefore be adjusted for each alloy.

The partial molar free energy of oxygen, $\Delta\bar{G}_{O_2}$, is plotted as a function of temperature for the $PuO_{2.00}$ - $PuO_{1.95}$ region in Figures 3A and 3B.¹⁶ These figures illustrate the increased stability of plutonium oxide with decreasing oxygen content. Values of $\Delta\bar{G}_{O_2}$ for the metal/oxide systems of interest in this portion of the compatibility program are also shown in the figures. Since a more negative $\Delta\bar{G}_{O_2}$ indicates a more stable configuration of the system, Figures 3A and 3B may be used to predict which metals will react with $^{238}PuO_2$ by reducing the fuel to a lower stoichiometry. For example, if the container of $^{238}PuO_2$ is composed of chromium, a reaction product of Cr_2O_3 may form at 1000°C. The formation of Cr_2O_3 will continue until the stoichiometry of the fuel is reduced to between $PuO_{1.90}$ and $PuO_{1.95}$. At this point the fuel would be stable with respect to Cr_2O_3 and equilibrium would be established. Any further reduction of the fuel will result in the instability of the Cr_2O_3 . Figure 3A also indicates that Cr_2O_3 is in equilibrium with $PuO_{1.95}$ at 1220°K. At temperatures less than 1220°K, Cr_2O_3 will be less stable than $PuO_{1.95}$.

Because of the dominant role in the interaction possessed by the selective oxidation of chromium and manganese and to aid in the analysis of the results, the Mn_2O_3/Cr_2O_3 binary phase diagram reported by Speidel and Muan¹⁷ has been included in Figure 4.

Results Included in the results are suggested identifications of the reaction products based on compositional determinations and comparison with available literature. Proposed identities do not mean the absence of other elements, as solution of certain cations is expected. Although identification of these phases was not possible with the information presented, they are relied on in the final analysis and suggested explanation of the compatibility results.

The format of the report includes a discussion of each alloy at each temperature. The behavior at 800 and 1000°C for all alloys, except TD (thoria dispersed) nickel, is compared jointly following the summaries of the 800 and 1000°C results as their behavior is considered to be similar. TD nickel is considered separately since it does not contain any of the reactive elements (i.e., Cr, Mn, Si, and Ti) which are present in the other alloys.

Table 1

FREE ENERGY OF REACTION FOR THE REDUCTION OF $^{238}\text{PuO}_2$ TO $^{238}\text{Pu}_2\text{O}_3$ AND ^{238}Pu BY VARIOUS ELEMENTS

Reaction	ΔG_f° (kcal)			
	1000°K		1200°K	
	Oetting ¹⁵	Glassner ¹⁴	Oetting ¹⁵	Glassner ¹⁴
$2\text{Al} + 6\text{PuO}_2 \rightarrow \text{Al}_2\text{O}_3 + 3\text{PuO}_2$	- 94.5	- 71.8	- 93.8	- 71.1
$4\text{Al} + 3\text{PuO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Pu}$	- 16.6	- 29.6	- 14.6	- 26.4
$\text{C} + 2\text{PuO}_2 \rightarrow \text{CO} + \text{Pu}_2\text{O}_3$	+ 28.8	+ 36.3	+ 19.7	+ 27.8
$\text{Co} + 2\text{PuO}_2 \rightarrow \text{CoO} + \text{Pu}_2\text{O}_3$	+ 39.7	+ 47.3	+ 39.0	+ 47.2
$2\text{Cr} + 6\text{PuO}_2 \rightarrow \text{Cr}_2\text{O}_3 + 3\text{Pu}_2\text{O}_3$	+ 22.0	+ 44.7	+ 21.5	+ 44.2
$\text{Fe} + 2\text{PuO}_2 \rightarrow \text{FeO} + \text{Pu}_2\text{O}_3$	+ 29.5	+ 37.0	+ 28.0	+ 36.1
$3\text{Fe} + 8\text{PuO}_2 \rightarrow \text{Fe}_3\text{O}_4 + 4\text{Pu}_2\text{O}_3$	+115.6	+146.0	+112.6	+142.8
$2\text{La} + 6\text{PuO}_2 \rightarrow \text{La}_2\text{O}_3 + 3\text{Pu}_2\text{O}_3$	-138.2	-115.5	-138.5	-115.8
$4\text{La} + 3\text{PuO}_2 \rightarrow 2\text{La}_2\text{O}_3 + 3\text{Pu}$	-104.0	-117.0	-104.0	-115.8
$\text{Mn} + 2\text{PuO}_2 \rightarrow \text{MnO} + \text{Pu}_2\text{O}_3$	+ 1.8	+ 9.3	+ 0.5	+ 8.6
$3\text{Mn} + 8\text{PuO}_2 \rightarrow \text{Mn}_3\text{O}_4 + 4\text{Pu}_2\text{O}_3$	+ 57.7	+ 88.1	+ 57.9	+ 88.1
$\text{Mo} + 4\text{PuO}_2 \rightarrow \text{MoO}_2 + 2\text{Pu}_2\text{O}_3$	+ 61.0	+ 76.2	+ 60.1	+ 75.2
$\text{Mo} + 6\text{PuO}_2 \rightarrow \text{MoO}_3 + 3\text{Pu}_2\text{O}_3$	+109.0	+131.7	+106.1	+128.9
$\text{Nb} + 2\text{PuO}_2 \rightarrow \text{NbO} + \text{Pu}_2\text{O}_3$	- 1.0	+ 6.5	- 2.1	+ 6.0
$2\text{Nb} + \text{PuO}_2 \rightarrow 2\text{NbO} + \text{Pu}$	+ 55.3	+ 51.0	+ 54.6	+ 50.7
$2\text{Nb} + 10\text{PuO}_2 \rightarrow \text{Nb}_2\text{O}_5 + 5\text{Pu}_2\text{O}_3$	+ 27.2	+ 65.1	+ 25.7	+ 63.5
$\text{Ni} + 2\text{PuO}_2 \rightarrow \text{NiO} + \text{Pu}_2\text{O}_3$	+ 39.4	+ 46.9	+ 38.5	+ 46.6
$\text{Si} + 4\text{PuO}_2 \rightarrow \text{SiO}_2 + 2\text{Pu}_2\text{O}_3$	- 14.0	+ 1.2	- 13.8	+ 1.3
$\text{Si} + \text{PuO}_2 \rightarrow \text{SiO}_2 + \text{Pu}$	+ 43.5	+ 39.2	+ 43.8	+ 39.9
$\text{Ti} + 4\text{PuO}_2 \rightarrow \text{TiO}_2 + 2\text{Pu}_2\text{O}_3$	- 29.6	- 14.4	- 29.4	- 14.3
$\text{Ti} + \text{PuO}_2 \rightarrow \text{TiO}_2 + \text{Pu}$	+ 27.9	+ 23.6	+ 28.2	+ 24.3
$\text{V} + 2\text{PuO}_2 \rightarrow \text{VO} + \text{Pu}_2\text{O}_3$	- 2.7	+ 4.8	- 3.4	+ 4.7
$2\text{V} + \text{PuO}_2 \rightarrow 2\text{VO} + \text{Pu}$	+ 51.9	+ 47.6	+ 51.9	+ 48.0
$2\text{V} + 6\text{PuO}_2 \rightarrow \text{V}_2\text{O}_3 + 3\text{Pu}_2\text{O}_3$	- 6.5	+ 16.2	- 7.6	+ 15.1
$4\text{V} + 3\text{PuO}_2 \rightarrow 2\text{V}_2\text{O}_3 + 6\text{Pu}$	+159.4	+146.4	+157.8	+146.0
$\text{W} + 4\text{PuO}_2 \rightarrow \text{WO}_2 + 2\text{Pu}_2\text{O}_3$	+ 55.2	+ 70.4	+ 54.2	+ 69.3
$\text{W} + 6\text{PuO}_2 \rightarrow \text{WO}_3 + 3\text{Pu}_2\text{O}_3$	+ 86.5	+109.2	+ 85.3	+108.0

HASTELLOY N AT 800°C

Six coupons of Hastelloy N were examined after 30, 60, 90, 181, or 360 days of exposure to $^{238}\text{PuO}_2$ at 800°C. After thermal exposures of up to 181 days the degradation of Hastelloy N included the internal selective oxidation of chromium, manganese, and vanadium; formation of voids; and dissolution of carbides. After 360 days at temperature, the interaction appeared to change as only Pu-Cr-O and Pu-Si-O reaction products were found in a reaction zone which was visually different from the samples annealed for shorter times. Due to its seemingly different response to $^{238}\text{PuO}_2$, the results of the 360-day sample are presented separately after the results of the other samples.

30- To 181-Day Exposure

Internal Reaction The subsurface attack appeared fairly undulatory, varying in thickness from approximately 5 to 20 μm after 30 days and 5 to 35 μm after 60, 90, and 181 days. Figure 5 illustrates the much greater subsurface attack at the coupon ends relative to the long edges. Depths of attack at the ends normally reached 120 to 180 μm ; however, the attack on one of the 60-day samples reached 280 μm . This end effect could be due to one or more of the following reasons: greater availability of oxygen; outward diffusion of chromium and manganese and the inward diffusion of oxygen in three directions rather than from one; a corner effect if the specimen had not been ground down far enough during metallographic preparation; the sample had not been sectioned through the middle; influence of the other materials in the same test capsule; or a result of preferential grain orientation remaining from previous rolling operations. The end effect is assumed to be merely a magnification of the same reaction mechanism. Therefore, subsequent information concerning the compatibility of Hastelloy N will deal with the effects seen along the long edge rather than the ends of the coupons.

Plutonium-238 dioxide causes three optically different zones of internal oxidation in Hastelloy N at 800°C. Detection and partial characterization of these zones can be accomplished by comparing Figure 6 with Figures 7 through 15. Figures 7 through 15 are photomicrographs of the same area as Figure 6 but taken with backscattered electrons and characteristic x-rays of the elements present.

The outer zone, though sometimes absent presumably due to spalling, did not vary much in thickness but remained about 7 to 9 μm wide. Two oxide products were found in the outer zone. First are the particles indicated by B in Figure 6 which appear to occur where the outer metallic edge is absent. Electron microprobe analyses of these particles found in the 30-, 60-, and 90-day samples showed:

Time at 800°C (days)	Analysis ^a							Found in Figure	Reference Letter
	Al ^b	Cr	Fe ^c	Ni ^c	O	Pu	V		
30&60	T	major	PT	PT	major	T	T @ 30, small amount @ 60	6	B
90	T	9.1 wt %	PT	PT	major	major	ND	16	B

^a T = Trace; PT = Possible Trace; ND = Not Detected

^b Determination of aluminum in this and other reaction products on all the materials of this test could not be determined due to contamination by Al_2O_3 polishing compound, which was observed under polarized light. The presence of aluminum in the reaction product other than by residue polishing compound is possible since it was present in trace quantities in both the Hastelloy N and the $^{238}\text{PuO}_2$ fuel.

^c Detection of a trace amount of these elements could be all or partially due to averaging of the oxide composition with the matrix.

Possible identification of these oxides are the $(\text{Cr},\text{V})_2\text{O}_3$ solid solution on the 30- and 60-day samples, and the perovskite-type compound PuCrO_3 (which theoretically contains 15.4 wt % chromium) on the 90-day sample. It is suggested that the $(\text{Cr},\text{V})_2\text{O}_3$ is part or all of an initial surface oxidation of Hastelloy N and that the B particles are small penetrations of an oxide which nucleated at the surface. It is believed that the 7.3 wt % chromium in Hastelloy N was unable to support surface oxide formation so the oxidation became internal. After a period of time the $(\text{Cr},\text{V})_2\text{O}_3$ was converted into the PuCrO_3 and some possibly into the Cr-Mn-O underlying layer (subsequently discussed).

The second oxide reaction product found in the outer zone is a semi-continuous layer denoted by A in Figure 6. A comparison of Figure 6 with Figures 7 through 15 shows that this oxide layer can be determined to contain primarily chromium and manganese, with small amounts of zinc*

*Zinc is present as an impurity in the $^{238}\text{PuO}_2$.

and vanadium, and a trace of plutonium. Analysis of this oxide layer on the 90-day sample (phase A in Figure 16) found about 29.7 wt % chromium; 15.5 wt % manganese; trace amounts of vanadium, zinc, and aluminum; and possible trace amounts of nickel and iron. Possible identification of this oxide is the MnCr_2O_4 -type spinel. The reported composition is lower than theoretical for MnCr_2O_4 (46.6 wt % Cr and 24.7 wt % Mn) but the difference is believed due to the small size of the oxide causing an averaging of its composition with the surrounding matrix. Support for the formation of MnCr_2O_4 is the equality of the experimental and theoretical ratios of chromium to manganese (both about 1.9:1) and the absence of substantial amounts of other elements such as nickel or iron.

The middle zone varies in thickness from about 5 to 15 μm after 30 days to about 30 μm after 60, 90, or 181 days (except at the coupon ends where it is much greater as previously described). This zone can be divided into inner and outer regions which are defined visually by the different morphology of the precipitates as indicated by C and D in Figures 6 and 16. Included in the outer region are oxide precipitates enriched with chromium, manganese, and, to a lesser extent, zinc and vanadium, but depleted of nickel, iron, and molybdenum*. These precipitates could be the MnCr_2O_4 -type spinel whose morphology differs from the overlying MnCr_2O_4 layer because of restriction of the inward diffusion of oxygen by the layer; or, if nickel and/or iron is present, a mixed spinel. In the inner region (D in Figure 6 and 16) are acicular precipitates which contain chromium and a small amount of vanadium and are depleted of nickel, iron, and molybdenum.*,**

The third and innermost zone of the subsurface oxidation includes precipitates which appear to occur preferentially in the grain boundaries extending 10 to 15 μm below the middle zone. Analysis of the oxide denoted by E in Figure 6 determined it to contain chromium with a little vanadium and depleted of nickel, iron, and molybdenum.*,** These intergranular oxides, which indicate more rapid intergranular diffusion, can also be seen in Figures 16 and 17. Although intergranular oxides were found in all the samples, they were typical only in the 30-, one 60-, and the 90-day samples. Only rarely were they found in the second 60- and 181-day samples.

To clarify the above description of oxide compositions, the analyses of the reaction products are summarized in Table 2. The basic compositions of the internal oxide fall into two categories, depending on whether or not they contain manganese. The outer internal oxides (A and C in Figure 6) contain manganese whereas the inner oxides (D and E in Figure 6) do not. An exception to this is the particle on the 60-day sample designated

*The extent of depletion of these elements in the internal oxides could not be determined due to the small size of the oxides relative to the possible resolving power of the electron microprobe, thus the analysis of the oxide was compromised by the composition of the matrix.

**Possible identification includes $(\text{Cr},\text{V})_2\text{O}_3$ solid solution, $(\text{Cr},\text{V},\text{Fe})_2\text{O}_3$ solid solution, or the NiCr_2O_4 -type spinel depending on the extent of the nickel or iron concentration.

by B in Figure 6 and believed to be a solid solution of Cr_2O_3 and V_2O_3 . Since this particle was not observed on the samples annealed for longer periods of time, it indicates possibly initial formation of $(\text{Cr},\text{V})_2\text{O}_3$ and its conversion with increasing time into the manganese-rich spinel or the Pu-Cr-O compound discussed previously.

Compositional Changes Examination of the Hastelloy N with the electron microprobe determined variations in its composition which are summarized in Table 3. Depletions of chromium, manganese, and vanadium are expected due to the oxide formation. Enrichments of molybdenum and cobalt result from these depletions. The enrichment of iron and zinc is due to their presence as impurities in the $^{238}\text{PuO}_2$. Depletion of nickel is thought to be a result of the enrichment of iron and zinc rather than reaction with the $^{238}\text{PuO}_2$ environment.*

No change in depths of depletion or enrichment was observed between the 90- and 181-day samples complementary to the lack of visual difference.

Void Formation Included in the subsurface attack was void formation.** Voids were observed at the ends of all test coupons but were observed typically along the edge of only one of the 60-day samples, the 90-day sample, and infrequently along the 181-day sample. Figure 17 illustrates their intergranular nature. Maximum depth reached by the voids was 175 μm below the sample edge in both the 60- and 90-day test coupons. These intergranular voids indicate either rapid outward diffusion of chromium through the grain boundaries or that the grain boundaries are acting as nucleating sites for voids created by the bulk diffusion of chromium. Since the chromium depletion depth (75 μm) is less than the 175 μm void formation, the former explanation is believed correct. Intergranular penetration of the chromium-rich oxide also indicates faster intergranular diffusion.

Variation in Microstructure A thin zone denuded of carbides was noticed in all samples and is best exemplified in Figure 18. Thickness of the zone increases slightly with time as shown in the following table.

*Iron and zinc increased a total of 10.8 wt % at the Hastelloy N edge. This could account for the replacement of the 6.8 wt % chromium and manganese loss plus effectively cause the depletion of 4 wt % nickel. A theoretical 4 wt % depletion of nickel caused by iron and zinc matches closely the 4.6 wt % loss determined experimentally.

**Although the voids are believed real, it is possible that they were caused by pullout of a phase during metallographic preparation.

Annealing Time (days)	Thickness of denuded zone (μm)
30	0-8
60	4-12
60(duplicate)	5-15
90	5-20
181	5-20
360	30-50

Solution of the carbides is thought to be due to compositional changes at the edge. Lack of change between the 90- and 181-day samples agrees with their visual and compositional similarities. The 360-day results will be discussed in the following section.

360-Day Exposure

Figures 19 and 20 typify the reaction interface on the 360-day sample. Differences between this reaction zone and the samples annealed for shorter periods of time are obvious. Electron microprobe examination of the reaction product indicated by A in Figure 19 determined it to contain oxygen, plutonium, and 14.7 wt % chromium. Phase A is thus believed to be PuCrO_3 , which theoretically contains 15.4 wt % chromium. Figure 20 demonstrates the large amount of PuCrO_3 which was formed. Analysis of Phase B in Figure 19 was hampered by its small size but is believed to contain oxygen and plutonium as major constituents with a trace of silicon. Analysis of the sample edge (Table 3) determined the composition to be comparable with the other samples except for a slightly higher manganese content (~1 wt % in the 360-day sample and 0.2 and 0.3 wt % in the 90- and 181-day samples). Thickness of the zone denuded of carbides increased to about 30 to 50 μm .

Visual comparison of this sample with the samples annealed at 1000°C (see succeeding report) finds a close similarity (compare Figure 19 with Figures 23 and 24). The visual analogy along with an increase in the thickness of the denuded zone indicates that a temperature excursion occurred during heat treatment of the 360-day sample. However, the temperature of the annealing furnace was continually monitored by a recorder and no increase in the test temperature was observed. Thus, the observed change in the mode of reaction which occurred between 181 and 360 days of exposure to 800°C is believed real and will be subsequently discussed.

Summary and Discussion Figure 21 pictorially describes the observed interaction after the various heat treatments. After 181 days or less at 800°C, $^{238}\text{PuO}_2$ causes relatively extensive internal oxidation of Hastelloy N. The internal oxidation is characterized by precipitation of oxides enriched in chromium, manganese, and, to a much lesser extent, vanadium and zinc.* Nickel, iron, and molybdenum appeared depleted in

*Small quantities of zinc were sometimes detected; however, the zinc content is due to its presence as an impurity in the fuel.

the oxides relative to the matrix, but except for the oxides nearest the edge*, their absence or presence could not be determined since the oxides were too small to be resolved by the electron microprobe. A small amount of PuCrO_3 was observed at the edge after 90 days at temperature.

After 360 days of exposure to $^{238}\text{PuO}_2$ at 800°C , the internal oxides which had previously formed apparently decomposed, being replaced by a Pu-Si-O phase accompanied by a massive formation of PuCrO_3 .

The proposed explanation of the change in the reaction mechanism is based on the reduction of the partial pressure of oxygen below the level necessary for the stability of the chromium-, manganese-, and vanadium-enriched oxides which initially formed. It is believed that the first stage of interaction between $^{238}\text{PuO}_2$ and Hastelloy N is the drawing of oxygen from the $^{238}\text{PuO}_2$ by chromium and manganese, making the fuel sub-stoichiometric. Figure 21A displays the first stage and the oxide reaction products which form. Figure 3A gives some indication as to the degree of dissociation that these elements can cause. For example, at 800°C the formation of Cr_2O_3 will continue until the stoichiometry of the fuel reaches $^{238}\text{PuO}_{1.98-2.00}$. This stage results in the internal oxidation observed after heat treatments of 30 or 60 days. Initiation of the second stage begins with the formation of PuCrO_3 as indicated in Figure 21B. It is suggested that this phase is more stable than the oxide products which formed initially and can therefore cause further reduction of the activity of oxygen in the system. PuCrO_3 continues to form by drawing oxygen from the fuel until the activity of oxygen in the fuel is lowered to the oxygen activity in each of the initially occurring oxide reaction products. Continuing formation of the PuCrO_3 then causes dissociation of the internal oxides. Dissociation of the manganese-rich spinel and subsequent diffusion of manganese into the sample account for the noted manganese enrichment of the edge of the 360-day sample. When dissociation of the original oxides is complete, the resultant reaction interface is described by Figure 21C, and the third stage of the Hastelloy N/ $^{238}\text{PuO}_2$ interaction begins. This portion of the interaction includes continued formation of PuCrO_3 by the reduction of the fuel and the growth of a Pu-Si-O phase. Formation of the Pu-Si-O is possible because of its large negative free energy of formation and thus low equilibrium partial pressure of oxygen.

Two obvious assumptions made in the hypothesis are that the free energy of formation of the perovskite-type compound PuCrO_3 and the Pu-Si-O reaction product are more negative than the chromium-, manganese-, and vanadium-enriched oxides which formed initially. Supporting evidence comes from efforts by Alexander¹⁸ on NdZrO_3 , NdAlO_3 , and SrZrO_3 . He determined that these three perovskites similarly reduced the activity of oxygen by a factor of about 5×10^{-2} relative to the free metal. Since the activity of oxygen is reduced by a factor of about 10^{-1} by

* PuCrO_3 , $(\text{Cr},\text{V})_2\text{O}_3$, and MnCr_2O_4 contained a maximum of a trace amount of nickel and iron and did not contain molybdenum.

Cr_2O_3 ¹⁸ and assuming similarity between these perovskites and PuCrO_3 , the equilibrium partial pressure of oxygen over PuCrO_3 would be about half that over Cr_2O_3 . Thermodynamic data for MnCr_2O_4 could not be found but considering the fact that MnCr_2O_4 was always found overlying Cr_2O_3 when both were found as surface layers, the MnCr_2O_4 does not appear to be as stable as Cr_2O_3 . This is in agreement with a rough approximation of the free energy of a spinel by assuming it to be slightly more stable than a solution of, in this case, MnO and Cr_2O_3 .¹⁸ Since the free energy of formation of MnO is much less than for Cr_2O_3 , the free energy of their solution (assuming Raoult's law to apply) would be less than Cr_2O_3 . Thermodynamic data for the Pu-Si-O was not found. Possible indication of its stability are the $\Delta\bar{G}_{\text{O}_2}$ value for SiO_2 given in Figure 3B.

The above theory proposes that the observed similarity in the appearance of the 360-day, 800°C sample and the 1000°C samples (subsequently discussed) represents a time/temperature relationship rather than an anomaly caused by an inadvertent increase in the temperature.

Table 2

COMPOSITION OF REACTION PRODUCTS ON HASTELLOY N HEAT TREATED AT 800°C

Reaction Product	Region of Internal Oxidation	Figure	Reference Letter	Element ^a									
				Al ^c	Cr	Fe ^b	Mn	Mo ^b	Ni ^b	O ^c	Pu ^c	V	Zn
Reaction product on surface	-	12	B	T	9.1	T	ND	ND	T	Major	Major	ND	ND
Semicontinuous layer	outer	2	A	T	Major	T	Minor	ND	T	Major	T	Small Amount	Small Amount
Semicontinuous layer	outer	12	A	T	29.7	T	15.5	ND	T	Major	ND	T	T
Particle on outside edge of semicontinuous layer	outer	2	B	T	40.5	T	ND	ND	T	Major	T	Small Amount	ND
Particles	Outer portion of middle	2	C	ND	Major	DEP	Minor	DEP	DEP	Major	ND	Small Amount	Small Amount
Acicular precipitates	Inner portion of middle	2	D	ND	Major	DEP	ND	DEP	DEP	Major	ND	Small Amount	ND
Particles in grain boundaries	inner	2	E	ND	Major	DEP	ND	DEP	DEP	Major	ND	Small Amount	ND

^aT: trace; ND: not detected; DEP: depleted in concentration relative to metal matrix.

^bThe concentration of nickel, iron, and molybdenum in the oxides could not be determined except as noted in the table since the oxides were too small to resolve and interference with the composition of the surrounding matrix occurred.

^cDetection of aluminum is possibly due to the presence of residue polishing compound.

Table 3

EFFECT OF $^{238}\text{PuO}_2$ UPON THE COMPOSITION OF HASTELLOY N AT $800^\circ\text{C}^{a, b}$

Element	Concentration at Edge Relative to Interior			Depth of Depletion or Enrichment into Sample (μm)			Conc. at Edge/Conc. in Interior			Concentration at Edge (wt %)			Concentration in Interior (wt %)			Concentration in Bulk Prior to Test (wt %)
	90 days	181 days	360 days	90 days	181 days	360 days	90 days	181 days	360 days	90 days	181 days	360 days	90 days	181 days	360 days	
Al	ND	ND	ND	ND	ND	ND	-	-	-	ND	ND	ND	ND	ND	ND	0.06
Co	? ^a	E	ND	? ^c	60	ND	? ^d	0.63	-	T	1.0	ND	? ^d	0.16	ND	0.1
Cr	D	D	D	75	75	≥ 85	0.30	0.42	≤ 0.55	2.1	4.3	4.2	6.9	10.6	≥ 7.9	7.3
Fe	E	E	E	90	80	≥ 85	3.50	3.15	≥ 2.25	16.8	14.7	12.8	4.8	4.7	≤ 5.7	3.3
Mn	D	D	E	95	80	? ^d	0.33	0.38	? ^d	0.2	0.3	1.2	0.6	0.8	? ^d	0.68
Mo	N	E	? ^a	0	30	? ^d	0	1.07	? ^d	? ^c	7.7	8.1	? ^c	7.2	? ^c	16.5
Ni	D	D	? ^d	65	75	? ^d	? ^d	0.94	? ^d	? ^c	68.4	65.1	? ^c	73.0	? ^d	71.0
Pu	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.7
V	D	D	D	? ^d	55	50	? ^c	0	0	T	ND	ND	T	T	T	0.25
W	N	ND	ND	0	ND	ND	? ^d	ND	ND	? ^c	ND	ND	? ^c	ND	ND	ND
Zn	E	E	E	80	75	≥ 85	∞	∞	∞	T	0.8	T	ND	ND	ND	ND

^aAll values were obtained by the electron microprobe with the exception of the bulk analysis performed prior to the test.^bD: depleted; E: enriched; N: neither depleted or enriched; ND: not detected; T: trace.^cNo standard available.^dData nebulous

FIGURE 1 - Relative electron microprobe displacements for chromium in a nickel-base alloy at three different counting rates.

FIGURE 2a - Signal response for the Hatachi electron microprobe traversing across adjacent nickel and chromium standards. Traces give an indication of the effect of the beam size and instrument response when moving at 10 μm per min in trace A and 25 μm per min in trace B.

FIGURE 2b.

FIGURE 3A- Partial molal free energy of oxygen for PuO_{2.0} to PuO_{1.61} and various metal/oxide systems of interest as a function of temperature.

FIGURE 3B- (continued)

FIGURE 4 - Diagram showing phase relation in the system Mn_2O_3 - Cr_2O_3 in air. Taken from Speidel and Muan.¹⁷

FIGURE 5 - Photomicrograph of Hastelloy N after 90 days at 800°C. 56.4X, unetched

FIGURE 6 - Photomicrograph of Hastelloy N after 60 days at 800°C. 670X, unetched

FIGURE 7 - Photomicrograph of Hastelloy N after 60 days taken with backscattered electrons. 1760X

FIGURE 8 - Photomicrograph of Hastelloy N after 60 days taken with CrK α radiation. 1760X

FIGURE 9 - Photomicrograph of Hastelloy N after 60 days at 800°C taken with $Mn_{K\alpha}$ radiation. 1760X

FIGURE 10 - Photomicrograph of Hastelloy N after 60 days at 800°C taken with $V_{K\alpha}$ radiation. 1760X

FIGURE 11 - Photomicrograph of Hastelloy N after 60 days at 800°C taken with $Zn_{K\alpha}$ radiation. 1760X

FIGURE 12 - Photomicrograph of Hastelloy N after 60 days at 800°C taken with $Ni_{K\alpha}$ radiation. 1760X

FIGURE 13 - Photomicrograph of Hastelloy N after 60 days at 800°C taken with $\text{Fe}_{K\alpha}$ radiation. 1760X

FIGURE 14 - Photomicrograph of Hastelloy N after 60 days at 800°C taken with $\text{Mo}_{L\alpha}$ radiation. 1760X

FIGURE 15 - Photomicrograph of Hastelloy N after 60 days at 800°C taken with $\text{Pu}_{M\alpha}$ radiation. 1760X

FIGURE 16 - Photomicrograph of Hastelloy N after 90 days at 800°C.
1180X, unetched

FIGURE 17 - Photomicrograph of Hastelloy N after 90 days at 800°C.
575X, unetched

FIGURE 18 - Photomicrograph of Hastelloy N after 181 days at 800°C. A denotes zone denuded of carbides. 300X, unetched

FIGURE 19 - Photomicrograph of Hastelloy N after 360 days at 800°C. A indicates PuCrO_3 and B indicates a Pu-Si-O phase. 1180X, unetched

FIGURE 20 - Photomicrograph of Hastelloy N after 360 days at 800°C.
75X, unetched

FIGURE 21 - Sketches of the Hastelloy N/²³⁸PuO₂ interaction at 800°C.

HASTELLOY N AT 1000°C

Four samples of Hastelloy N were examined after exposures to $^{238}\text{PuO}_2$ at 1000°C for periods of 30, 60, or 90 days. Visual results of the contact include surface reactions with silicon and chromium, an internal reaction with silicon and possibly manganese, and a zone denuded of carbide precipitates. All of these effects can be seen in Figure 22.

Surface Reaction The surface reaction formed a 5- to 10- μm layer of reaction product indicated by B in Figures 22 and 23. Absence of this layer in Figure 24 indicates either a lack of tenacity or that the layer is not continuous. Figure 25 is a photomicrograph of pieces of this layer which have apparently separated from the substrate during metallographic preparation. Because of the evidence in Figure 25 and the partial separation seen in Figures 22, 23, and other photomicrographs, the reaction product is believed to be continuous.

Figures 26 through 31 are photomicrographs of the same area as Figure 23 but taken with characteristic radiations of the various elements. These figures indicate that the layer is enriched in plutonium and silicon. Point analysis of the layer on the 90-day sample determined it to contain 5 to 6 wt % silicon, oxygen, and plutonium. After 30 and 60 days at temperature, the layer contained only a small amount of what appears to be a second phase; but after 90 days the amount of second phase had grown until it represented about 50% of the layer. Examination of the areas A and B in Figure 32 with the electron microprobe found no variation in composition beyond possible instrumentation error. It is possible that this two-phase appearance is a phenomenon of grain orientation or an undetermined compositional difference.

In addition to the Pu-Si-O reaction product, a second oxide reaction product was observed at the Hastelloy N/ $^{238}\text{PuO}_2$ interface. This reaction product has a globular morphology and forms at the exterior edge of the Pu-Si-O layer as shown in Figure 22 and indicated by A in Figure 23. Analysis of this oxide with the electron microprobe (see Figures 26 through 31) determined it to contain plutonium, chromium, and a slight amount of vanadium. Unlike the 30- and 60-day samples, the Pu-Cr-O reaction product developed a multiphase appearance after 90 days at temperature as indicated by C, D, and E in Figure 33. Table 4 gives the compositions of C, D, and E in Figure 33; and although they appear to be different phases, their compositions are similar (containing only oxygen,

plutonium, and 10 to 11.5 wt % chromium). The slight variations in composition listed in Table 4 indicate that C, D, E is the order of increase of chromium and decrease of plutonium, and that trace amounts of vanadium were found in C and E. The multiphase appearance could be due to slight compositional variations or possibly just grain orientation.

Though the chromium content is low, possible identification of the Pu-Cr-O phase is the perovskite-type compound PuCrO_3 which theoretically contains 15.4 wt % chromium. This would account for the presence of vanadium which also forms a perovskite-type compound PuVO_3 . Since both structures are orthorhombic, a solid solution of PuCrO_3 and PuVO_3 seems possible.

Internal Reaction Typical samples of the internal reaction are shown in Figures 22, 23, 24, and 32. The internal reaction product is present as segregated particles at the ends of the test coupons (where the attack was greatest), but most of the particles along the longitudinal edge of the coupon tended to form a line at their deepest penetration. The composition of the internal reaction product indicated by C in Figure 24 appears similar to the Pu-Si-O layer formed at the $^{238}\text{PuO}_2$ /Hastelloy N interface but with less plutonium. As did the Pu-Si-O layer, the internal oxide developed a multiphase appearance indicated by A and D in Figure 24. The results of a spot analysis of these two points are given in Table 4. These analyses determined oxides A and B to have similar compositions.

Several particles of internal oxide found in the photomicrograph of Figure 24 contain silicon and manganese but not plutonium (analysis for oxygen could not be performed and its presence is assumed). They can be seen by comparing Figures 27, 29, and 30. One of these particles is also indicated by D in Figure 23. The only internal oxide found in the 90-day sample was the Pu-Si-O. Either the silicon, manganese-bearing oxide was not present in the areas examined but located elsewhere, or the manganese was replaced by plutonium forming the Pu-Si-O.

Compositional Changes Compositional changes at the edge of the Hastelloy N were found. The variations, which are listed in Table 5, are primarily depletions of chromium, silicon, and vanadium caused by their interaction with the $^{238}\text{PuO}_2$ environment. Iron and zinc are enriched because of their presence as impurities in the fuel. The very slight depletion of nickel in the 60-day test is believed a result of the iron and zinc enrichments. The tungsten enrichment suggests that its mass transport (possibly by a volatile oxide) occurred during the early stages of interaction. Differences between the 60- and 90-day analyses indicate either equilibration of the reactants or, in some cases, a difference in sensitivity in the two electron microprobes used.

Void Formation Voids were observed at a maximum depth of about 30 μm after 90 days along the sample edge, principally at the ends where the internal reaction was greatest. There is doubt as to whether the voids are real since most are partially filled with the Pu-Si-O reaction

product and probably created by pullout of reaction product during metallographic preparation. But since the voids are located in regions depleted of chromium and silicon, some could be Kirkendall voids formed by coalescence of vacancies created by chromium and silicon diffusing out of the sample.

Variation in Microstructure A zone denuded of the primary blocky and secondary grain boundary particles was found along the edge of the sample as seen in Figure 22. One of the particles found below the denuded zone consists of molybdenum, silicon, chromium, and nickel* which agrees with data reported by Gehlbach and McCoy.¹⁹ They concluded that $Ni_3(Cr,Mo)_3(Si,C)$ primary particles and $Ni_2(Cr,Mo)_4(Si,C)$ grain boundary particles are the only precipitates that will form in heats of Hastelloy N containing about 0.6% silicon (material used in this test contained 0.7% silicon). The following table summarizes the thicknesses of the denuded zones. The trends noted are: no observable increase in the thickness of the denuded zone during the test periods indicated; the thickness of the denuded zone in the weld-affected zone is equal to or greater than in the normal structure; and the zone thickness is different on opposite sides of the coupon indicating dependency upon the environment established by the other materials (Hastelloy X, Haynes 188, and Haynes 25) in the test capsule.

THICKNESS OF DENUDED ZONE FOUND IN HASTELLOY N
SAMPLES AFTER EXPOSURE TO $^{238}PuO_2$ AT $1000^{\circ}C(\mu m)$

Time of exposure (days)	Microstructure of sample prior to test			
	Weld-affected zone		As-received (annealed)	
	Side 1	Side 2	Side 1	Side 2
30 ^a	110-115	90	100-120	95
60	110-120	65-70	100	80-90
60	120-135	100-115	80	85-90
90	70-90	75	75-80	80

^a The 30-day sample was slanted in its mount effectively increasing the thickness of the denuded zone. The values reported for the 30-day sample were adjusted so that the thickness of the coupon was the same as the 60- and 90-day coupons.

*No carbon was detected but this does not necessarily mean the particle is not a carbide as the sensitivity of the electron microprobe for carbon is very low.

Summary and Discussion Figure 34 pictorially describes the interaction between Hastelloy N and $^{238}\text{PuO}_2$ at 1000°C . It appears to be primarily concerned with the formation of a Pu-Si-O surface layer and simultaneous formation of a Pu-Cr-O reaction product (possibly PuCrO_3) at the interface between the surface layer and the $^{238}\text{PuO}_2$. This depletes the alloy edge of chromium and silicon. After the depletion of the silicon reaches a significant level, the inward diffusion of oxygen and plutonium becomes important. When the inward diffusion of oxygen and plutonium and the outward diffusion of silicon provide concentrations in excess of those corresponding to the solubility product of the resulting oxide in the Hastelloy N matrix, nucleation of the internal oxide occurs. The products of internal oxidation are one or more phases of Pu-Si-O with minor amounts of a silicon- and manganese-bearing oxide also found in the 60-day sample.

The continuous layer of Pu-Si-O separating the Hastelloy N from the $^{238}\text{PuO}_2$ appears to be beneficial to compatibility. The 1000°C , Hastelloy N sample exhibited a 13% decrease in the chromium content at the edge after 90 days, whereas the 800°C sample had a 58% decrease in the chromium content after 90 days. Since it would be normally expected that the chromium loss would increase with temperature, it is believed that the Pu-Si-O layer acted as a diffusion barrier to chromium ions. Because isolation of chromium from $^{238}\text{PuO}_2$ is important to prevent the mass transport of chromium* and degradation of the capsule caused by chromium depletion, silicon appears to be beneficial to compatibility. But the silicon concentration used in this test (0.7 wt %) is detrimental to the mechanical properties of Hastelloy N;¹⁹ therefore, some compromise in the amount of silicon seems in order.

*Deposition of chromium on T.D. nickel was found after heat treatment at 1000°C in contact with $^{238}\text{PuO}_2$. The deposit is believed due to mass transport via a gaseous phase (e.g., Cr_V , CrO , CrO_2 , or CrO_3).

Table 4

COMPOSITION OF VARIOUS REGIONS IN A HASTELLOY N SAMPLE AFTER EXPOSURE TO $^{239}\text{PuO}_2$ FOR 90 DAYS AT 1000°C

Region	Figure Reference	Indicating Letter	Intensity of Plutonium ^b	Elemental Composition ^a (wt %)								
				O	Cr	Si	Mo	Mn	Fe	Ni	V	Zn
Internal Pu-Si-O reaction product; lighter of two phases	24	A	58 ^b	P	0.3	5.0	0	0	0	0	<0.1	-
Metallic layer separated from base metal by internal Pu-Si-O	24	B	0	0	6.7	0.5	9.5	0.5	5.7	67.1	0	-
Base metal	24	C	0	0	7.2	0	8.6	0.7	5.9	68.4	0.15	-
Internal Pu-Si-O reaction product; darker of two phases	24	D	62 ^b	P	0.07	5.5	0	0	0	0	0	-
Base metal at coupon corner	33	A	0	T	6.7	0	? ^c	? ^c	? ^c	? ^c	~0.15	0
Surface layer of Pu-Si-O reaction product	33	B	50 ^b	P	0.4	6.2	0	T	T	T	0	0
Multiphased Pu-Cr-O reaction product	33	C	72 ^b	P	9.8	0	0	0	0	0	~0.15	0
	33	D	69 ^b	P	10.7	0	0	0	0	0	0	0
	33	E	65 ^b	P	11.6	0	0	0	0	0	~0.15	0

^a -: analysis not performed; P: present; T: trace^b No plutonium standard was available, therefore values given are intensities rather than the weight percent of the other elements. Plutonium intensities of Figure 30 are not comparable with those of Figure 32.^c Standards were not obtained.

Table 5

EFFECT OF EXPOSURE TO $^{238}\text{PuO}_2$ AT 1000°C ON THE COMPOSITION OF HASTELLOY N^{a, b}

Element	Concentration at Edge Relative to Interior		Depth of Depletion or Enrichment into Sample (μm)		Conc. at Edge/Conc. in Interior		Concentration at Edge (wt %)		Concentration in Interior of Sample (wt %)		Concentration of Bulk Prior to Test (wt %)
	60 days at 1000°C	90 days at 1000°C	60 days at 1000°C	90 days at 1000°C	60 days at 1000°C	90 days at 1000°C	60 days at 1000°C	90 days at 1000°C	60 days at 1000°C	90 days at 1000°C	
Al	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.06
Co	E	ND	225	ND	~1.92	ND	T	ND	T	ND	0.1
Cr	D	D	>275	60	<0.87	0.87	? ^c	7.2	? ^c	8.3	7.3
Fe	E	N	325	0	~1.44	1.00	? ^c	5.9	? ^c	5.9	3.3
Mn	E	N	125	0	~1.11	1.00	T	0.7	T	0.7	0.68
Mo	N	N	0	0	0.00	1.00	? ^c	8.6	? ^c	8.6 ^d	16.5
Ni	D	N	250	0	~1.02	1.00	? ^c	68.4	? ^c	68.4	71.0
Pu	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	D	D	150	35	0.00	0.00	ND	ND	T	0.3	0.7
V	D	N	150	0	~0.91	1.00	T	0.4	T	0.4	0.25
W	E	ND	125	ND	=	ND	T	ND	ND	ND	ND
Zn	E	ND	150	ND	=	ND	T	ND	ND	ND	ND

^a All values were obtained by the electron microprobe with the exception of the bulk analysis performed prior to the test.^b T: trace; -: analysis not performed; E: enriched; D: depleted; N: no effect; ND: not detected.^c No determination of backgrounds or standard were made in the 60-day test; therefore, reportable information is limited.^d The small amount of molybdenum found relative to the bulk analysis is partially due to the molybdenum which precipitates out of solution in the M_{23}C_6 carbides. However, 8.6% is still lower than the reported 12.2% solubility limit of molybdenum in Hastelloy N. The low value of molybdenum found is thought to be due to low sensitivity of the electron microprobe for this particular element. This was substantiated when Hastelloy N in the as-received condition was found to contain 9.5 wt %. Low values for molybdenum were found in all the molybdenum-bearing alloys.

FIGURE 22 - Photomicrograph of Hastelloy N after 60 days at 1000°C. A is the Pu-Cr-O reaction product. B indicates the layer of Pu-Si-O. C denotes the internal reaction. D is the depth of the denuded zone. 135X, unetched

FIGURE 23 - Photomicrograph of Hastelloy N after 60 days at 1000°C. A indicates the Pu-Cr-O reaction product thought to be PuCrO_3 . B denotes the Pu-Si-O layer and C the internal Pu-Si-O. D is an oxide particle-containing Si and Mn. 950X, unetched

FIGURE 24 - Photomicrograph of Hastelloy N after 90 days at 1000°C. A and D indicate the two appearances of the internal Pu-Si-O. A, B, C, and D indicate points of analysis by electron microprobe. The results of these analyses are given in Table 4. 575X, unetched

FIGURE 25 - Pieces of the Pu-Si-O layer which have become separated from the Hastelloy N surface. The Hastelloy N had been exposed to $^{238}\text{PuO}_2$ for 90 days at 1000°C. 1180X, unetched

FIGURE 26 - Photomicrograph of Hastelloy N after 60 days at 1000°C taken with backscattered electrons. 1760X

FIGURE 27 - Photomicrograph of Hastelloy N after 60 days at 1000°C taken with $\text{Pu}_{M\alpha}$ radiation. 1760X

FIGURE 28 - Photomicrograph of Hastelloy N after 60 days at 1000°C taken with $\text{Cr}_{K\alpha}$ radiation. 1760X

FIGURE 29 - Photomicrograph of Hastelloy N after 60 days at 1000°C taken with $\text{Si}_{K\alpha}$ radiation. 1760X

FIGURE 30 - Photomicrograph of Hastelloy N after 60 days at 1000°C taken with $Mn_{K\alpha}$ radiation. 1760X

FIGURE 31 - Photomicrograph of Hastelloy N after 60 days at 1000°C taken with $V_{K\alpha}$ radiation. 1760X

FIGURE 32 - Photomicrograph of the reaction interface between Hastelloy N and $^{238}\text{PuO}_2$ after 90 days at 1000°C . A and B are the "primary" and "secondary" portions of the Pu-Si-O layer, respectively. C and D denote the Pu-Cr-O reaction product. 575X, unetched

FIGURE 33 - Photomicrograph of the reaction interface between Hastelloy N and $^{238}\text{PuO}_2$ after 90 days at 1000°C . A represents the base metal. B is the Pu-Si-O layer. C, D, and E are all the Pu-Cr-O reaction product. C Composition for these points are listed in Table 4. 2000X, unetched

FIGURE 34 - Sketches of the Hastelloy N/²³⁸PuO₂ interaction at 1000°C.

HASTELLOY X AT 800°C

Five Hastelloy X capsules were exposed to $^{238}\text{PuO}_2$ for 30, 60, 90, 181, or 360 days at 800°C. For heat treatments of 181 days or less the interaction included a multi-oxide surface layer due to the selective oxidation of chromium and manganese. Other effects included slight penetrations of the oxide into the metal substrate, compositional variations, void formation, and formation of molybdenum-enriched precipitates in or just below the oxide. After 360 days at temperature, the results of the interaction changed as evidenced by visual changes in the reaction zone and by the almost total absence of the Cr_2O_3 which was observed in the specimens annealed for shorter periods of time. Due to the seemingly different response to the $^{238}\text{PuO}_2$, the results of the 360-day sample are presented separately after the results of the other samples.

30- to 181-Day Exposure

Surface Reaction Characterization of the surface reaction was hindered by spallation of the reaction product. Figure 35 is a photomicrograph of the capsule bottom after 60 days at 800°C, but also represents all the heat treatments except for the 30-day sample. There is no surface reaction product; only the small oxide penetrations into the metal substrate are observed. Discussion of the surface reaction is based on segments of the reaction product found remaining primarily on the capsule walls and on portions of the layer that were removed from the capsule but retained by the mounting material.

Three layers were observed to occur in the interfacial reaction product on Hastelloy X. The two inner layers were found on all the samples while the outer layer was detected only on the 90-day sample. The thickness of the two inner layers did not seem to be greatly effected by increasing the annealing time but varied from about 5 to 11 μm . Addition of the third layer to the reaction product increased its thickness to about 30 μm . An individual description of the layers is given in the following paragraphs.

The inner layer, as described by A in Figures 36, 37, and 38, is believed to be continuous. Portions of the layer missing in Figures 37 and 38 are thought to have been mechanically removed. Trace analyses of this layer seen in Figures 37 and 38 determined that the inner oxide was composed of approximately 64 wt % chromium plus trace amounts of other cations (nickel, iron, and possibly molybdenum); however, their presence could be due to

the small metallic particles dispersed in the oxide. Suggested identification of this layer is Cr_2O_3 on the basis of fairly equivalent experimental and theoretical (68.4 wt %) values for the chromium content.

The second layer is denoted by B in Figures 36, 37, and 38. This layer was found to be fairly continuous as shown in Figure 36 on the 30-, 60-, and 181-day samples. Only small deposits of the second layer were observed on the 90-day sample (see photomicrographs of Figures 37 and 38). Electron microprobe analyses determined that the layer contains oxygen, chromium, manganese, and zinc in the 30-day sample and a small amount of plutonium in the 90-day sample. Trace analysis of the layer in Figure 38 found chromium and 6.9 wt % manganese. If the 6.9 wt % manganese is a correct determination, it would correspond to about 10 wt % Mn_2O_3 . According to Speidel and Muan,¹⁷ there is about 11 to 12 wt % solubility of Mn_2O_3 in Cr_2O_3 at 800°C (see Figure 4). Thus, possible identification of this oxide is Cr_2O_3 with 10 wt % Mn_2O_3 in solid solution. However, a determination of 6.9 wt % manganese is probably below the true value due to errors inherent in analyzing a phase of approximately the same size as the electron beam of the microprobe. Thus, a more realistic composition of this oxide could indicate MnCr_2O_4 or fall in the two-phase region of the spinel and the $(\text{Cr,Mn})_2\text{O}_3$ solid solution.

The massive, outermost layer denoted by C in Figures 37 and 38 was determined to be an oxide containing plutonium and about 10.8 wt % chromium. Compound formation is suggested by uniform distribution of the elements. Possible identification is the perovskite-type compound, PuCrO_3 , whose theoretical chromium content (15.4 wt %) is higher than that determined experimentally. This Pu-Cr-O reaction product was not found on any other sample annealed for 181 days or less. Its absence could be due to spalling or its presence correlated with the decreased amount of the Cr-Mn-O. A more continuous layer of Cr-Mn-O could act as a diffusion barrier to chromium ions thus possibly retarding the formation of the Pu-Cr-O phase. Cr-Mn-O acting as a diffusion barrier is not thought responsible for this anomaly because it did not appear completely continuous on any of the samples* and the Pu-Cr-O phase was observed outside continuous Cr-Mn-O layers on other alloys. Subsequent discussion of the 30-day sample proposes that PuCrO_3 forms at the expense of the initially occurring oxides. Application of this theory to the 90-day sample could suggest earlier initiation of the PuCrO_3 in this one sample thus causing the reduced amount of Cr-Mn-O.

Internal Reaction Oxide penetration of less than 10 μm into all the samples created an irregular interface. Electron microprobe examination indicated that the oxide which penetrates the substrate is the same as the inner layer or Cr_2O_3 . Either these penetrations are caused by the

* Possible spalling of the Cr-Mn-O layer could account for the discontinuity.

depletion of chromium in these areas and subsequent inward diffusion of oxygen or caused by some unknown minor element.*

Compositional Changes Compositions of the Hastelloy X edge after 30 and 90 days of exposure to $^{238}\text{PuO}_2$ at 800°C are listed in Table 6. Variation in the composition at the edge was primarily the depletion of chromium and manganese due to their reaction with the capsule environment. The enrichment of nickel is a result of the chromium and manganese depletions. Zinc enrichment is due to its presence as an impurity in the $^{238}\text{PuO}_2$. The absence of zinc in the 30-day sample and enrichment in the 90-day sample correspond with the presence of zinc in the multi-oxide reaction product on the 30-day sample and absence in the reaction product on the 90-day sample. It thus appears the zinc is leached out of the $^{238}\text{PuO}_2$ as it takes part in the oxide formation, but then diffuses into the base metal with longer annealing times. Iron enrichment is believed a result of the chromium and manganese depletions; it is originally present as an impurity in the $^{238}\text{PuO}_2$. Molybdenum would be expected to be enriched since it did not appear to take part in the formation of surface oxides. The unexpected behavior of molybdenum is discussed in the following section.

Carbide Precipitation Precipitation of a molybdenum-enriched phase occurred in conjunction with the oxide formation. These particles were seen in or just below the oxide reaction product (depicted in Figures 35, 37, 38, and 39) and appear inert to the $^{238}\text{PuO}_2$ environment relative to the matrix. In the 90-day sample (Figures 37, 38, and 39) this precipitate occurred to a greater extent and appears as a layer with inter-dispersed oxide assumed to be Cr_2O_3 . An analysis of this precipitate, indicated by D in Figure 37, as determined from the x-ray strip chart analysis showed:

Cr:	43.8 wt %
Ni:	22.1 wt %
Mo:	14.5 wt %
Fe:	3.4 wt %
Co:	Trace
W:	Trace
Zn:	Trace

The analysis was hindered by the small size of the precipitate and Cr_2O_3 inclusions which would account for at least part of the 43.8 wt % chromium. Although the analysis is crude, it does indicate the enrichment of molybdenum in these particles relative to the 5.4 wt % found in the matrix adjacent to the oxide reaction product (see Table 7). It is believed that these precipitates could be M_6C carbides. Intermetallics do form in Hastelloy X²⁰ but their reported morphology differs from that observed here.

* Out of all the elements examined for (Al, Co, Cr, Fe, Mn, Mo, Ni, P, Si, and W) only chromium, oxygen, and aluminum were found. Since aluminum was absent in the Hastelloy X prior to the test (see Appendix C), its presence is due to residue Al_2O_3 polishing compound.

Void Formation Voids formed in one of the two 60-day samples and in the 90-day and 181-day samples.* Although the voids can be seen in Figures 35, 36, and 39, their preferential location in grain boundaries is best demonstrated in Figure 35. In all three of the samples the voids occurred primarily in the first 30 μm , with the maximum depth of about 100 μm occurring in the 90-day sample. Assuming the voids are real, intergranular void formation suggests either faster outward diffusion of chromium and/or manganese through the grain boundaries, or that the grain boundaries are acting as preferential sites for nucleation of voids. Since the voids were found deeper than the detected depletion of chromium or manganese (see Table 7), grain boundary diffusion is presumed responsible.

Variation in Microstructure A change in the microstructure was observed in the Hastelloy X along the reaction interface. Figure 40 displays the edge denuded of carbide precipitates. The thickness of the denuded zone was about 30 to 45 μm and 40 to 45 μm after 90 and 181 days at 800°C, respectively.

360-Day Exposure

Figures 41, 42, and 43 represent typical portions of the reaction zone after 360 days of exposure to $^{238}\text{PuO}_2$ at 800°C. Visual differences between it and the 800°C specimens annealed for shorter periods of time are obvious. Figure 44 is a photomicrograph of a onetime occurrence of the reaction product indicated by C. Results from an electron microprobe examination of designated reaction products in Figures 41-44 are given below.

Figure	Reference Letter	Composition (wt %) ^a										
		Co	Cr	Fe	Mn	Mo	Ni	O	Pu	Si	W	Zn
41	A	ND	39.4	1.7 ^b	20.1	ND	5.1	M	ND	ND	ND	ND
42	A	ND	42-46	T	18.9	ND	ND	M	T	ND	ND	ND
43	B	ND	12.6	T	T	ND	ND	M	M	ND	ND	ND
44	C	-	64	-	-	-	-	M	ND	-	-	-

^aND = Not Detected M = Major T = Trace - = analysis not performed

^bPossibly due to interference by the metallic matrix.

Suggested identifications of phases A, B, and C are the MnCr_2O_4 -type spinel, PuCrO_3 , and Cr_2O_3 , respectively.

The single occurrence of Cr_2O_3 appears contradictory to the reaction zone seen in Figures 41 and 42. In these two figures MnCr_2O_4 is seen in direct contact with or below the edge of the Hastelloy X. This indicates complete absence of Cr_2O_3 which occurred as a layer underlying the MnCr_2O_4 in the specimens annealed for shorter times. Since Cr_2O_3 is not attached to the base metal but entrapped in mounting material it could have spalled

* Although the voids are believed real, it is possible that they were caused by pullout of a phase during metallographic preparation.

off of a different section of the Hastelloy X capsule. This would indicate that the capsule environment is subject to localized changes.

Results from an analysis of the Hastelloy X after 360-day heat treatment are summarized in Table 6. Except for manganese, the elemental enrichments and depletions appear similar to the 30- and 90-day specimens but larger in magnitude. Manganese was enriched at the edge of the 360-day sample but completely depleted at the edge of the 30- and 90-day samples. This indicates an alteration in the behavior of manganese.

Summary and Discussion Figure 45 pictorially summarizes the 800°C, Hastelloy X/ $^{238}\text{PuO}_2$ interaction. The compatibility of $^{238}\text{PuO}_2$ with Hastelloy X at 800°C for periods of 181 days or less is characterized by the selective oxidation of chromium and manganese forming three oxide layers. The outer layer was observed only on the 90-day sample. Suggested identification of the inner, middle, and outer layers are Cr_2O_3 , the MnCr_2O_4 -type spinel or its mixture with $(\text{Cr,Mn})_2\text{O}_3$, and PuCrO_3 , respectively. The formation of an inner layer of Cr_2O_3 overgrown by a layer of MnCr_2O_4 is in agreement with the oxidation of Hastelloy X as reported by Clarke and Titus²⁰ but disagrees with Wasielewski²¹ and Wlodek²² who concluded that the NiCr_2O_4 -spinel and Cr_2O_3 or $(\text{Cr,Mn})_2\text{O}_3$ form. Oxide formation at the $^{238}\text{PuO}_2$ /Hastelloy X interface depletes the sample edge of chromium and manganese. Depletion of one or both of these elements is thought to cause shallow penetrations of the oxide into the metal, void formation, and enrichment of nickel, molybdenum, and iron. Enrichment of these elements possibly causes precipitation of a molybdenum-enriched phase possibly being the M_6C carbide.

After 360 days at temperature, the observed interaction differed from the samples annealed for shorter periods of time by the almost total absence of Cr_2O_3 .

The proposed explanation for the change in the resultant appearance of the interaction is based on the reduction of the partial pressure of oxygen below the level necessary for the stability of Cr_2O_3 and MnCr_2O_4 . Reduction of the activity of oxygen is accomplished by the growth of PuCrO_3 as mentioned in the previous discussion of the 800°C, Hastelloy N compatibility test. This theory proposes that the observed similarity in the appearance of the 360-day, 800°C sample and the 1000°C samples (subsequently discussed) represents a time/temperature relationship rather than an anomaly caused by an inadvertent increase in the test temperature.

The presence of MnCr_2O_4 and the single observed occurrence of Cr_2O_3 distinguishes this specimen from the Haynes 188 and Hastelloy N which were present in the same capsule and thus supposedly exposed to the same partial pressure of oxygen. This difference is believed possibly due to a localized reduction of the oxygen activity around Hastelloy N and Haynes 188 by silicon* as it formed a Pu-Si-O phase on these alloys.

* Silicon content in Hastelloy X, Haynes 188, and Hastelloy N was 0.15, 0.60, and 0.70 wt % respectively.

The dissociation of Cr_2O_3 prior to MnCr_2O_4 noted in Figures 41 and 42 appears contradictory to the assumption that Cr_2O_3 has a more negative $\Delta\bar{G}_{\text{O}_2}$. This is thought to be explained by the more rapid loss of chromium than of manganese from the exterior MnCr_2O_4 and the resultant inward diffusion of the excess manganese. If the dissociation of MnCr_2O_4 takes on the form $\text{MnCr}_2\text{O}_4 \rightarrow \text{MnO} + 2\text{CrO}_x + (3-2x)\text{O}$ (where $x = 0, 1, 2$ or 3), the more rapid loss of chromium could be due to a greater volatility of the CrO_x relative to the MnO . Or the chromium loss could be explained by the following reaction: $2^{238}\text{PuO}_{2-x} + \text{MnCr}_2\text{O}_4 \rightarrow 2\text{PuCrO}_3 + \text{MnO}_{2(1+x)}$. In either case the remaining MnCr_2O_4 would become enriched in manganese which is relieved by the reaction of the excess MnO with the underlying Cr_2O_3 forming MnCr_2O_4 and possibly accounting for the slight enrichment of manganese at the alloy edge. Similar manganese enrichments were found in the 360-day, 800°C Hastelloy N and Haynes 188 samples.

Table 6

EFFECT OF $^{238}\text{PuO}_2$ ON THE COMPOSITION OF HASTELLOY X AT $800^\circ\text{C}^{a,b}$

Element	Concentration at Edge Relative to Interior			Depth of Depletion or Enrichment into Sample (μm)			Conc. at Edge/Conc. in Interior			Concentration at Edge (wt %)			Concentration in Interior (wt %)			Concentration in Bulk Prior to Test (wt %)
	30 days	90 days	360 days	30 days	90 days	360 days	30 days	90 days	360 days	30 days	90 days	360 days	30 days	90 days	360 days	
Al	ND	-	-	ND	-	-	ND	-	-	ND	-	-	ND	-	-	ND
Co	-	E	E	-	25	40	-	? ^c	? ^c	-	T	T	-	PT	PT	0.9
Cr	D	D	D	40	35	95	0.76	0.73	0.41	18.5	17.2	10.9	24.4	23.7	26.7	22.1
Fe	-	E	E	-	30	80	-	1.12	1.13	-	20.7	24.8	-	18.4	22.0	17.3
Mn	-	D	E	-	35	60	-	0.00	7.50	ND	ND	1.2	-	T	T	0.4
Mo	-	N	E	-	0	75	-	1.00	2.02	-	5.4	7.5	-	5.4	3.7	8.9
Ni	E	E	E	40	35	100	1.10	1.13	1.18	-	47.3	63.0	-	42.0	53.2	49.5
Pu	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.15
W	-	N	N	-	0	0	-	1.00	1.00	-	T	T	-	T	T	0.6
Zn	ND	E	E	ND	45	70	ND	∞	∞	ND	T	T	ND	ND	ND	ND

^aAll values were obtained by the electron microprobe with the exception of the bulk analysis performed prior to the test.^bN: not detected; E: enriched; D: depleted; N: neither enriched or depleted; -: analysis not performed; T: trace; PT: possible trace^cDue to the small quantities of cobalt involved a ratio could not be determined.

FIGURE 35 - Photomicrograph of Hastelloy X after 60 days at 800°C. Absence of surface oxide is typical. 1870X, unetched

FIGURE 36 - Photomicrograph of Hastelloy X after 60 days at 800°C. The inner oxide indicated by A is thought to be Cr_2O_3 . The outer layer, B, contains Cr, Mn, and possibly Zn. 1870X, unetched

FIGURE 37 - Photomicrograph and x-ray strip chart analysis of reaction product removed from the Hastelloy X capsule but retained in the mounting material. 90 days at 800°C .

FIGURE 38 - Photomicrograph and x-ray strip chart analysis of reaction product removed from the Hastelloy X capsule but retained in the mounting material. Determinations for Ni, Fe, Mo, W, Co, and Zn have been omitted to avoid confusion. Their behavior is similar to that observed in Figure 37. 90 days at 800°C.

FIGURE 39 - Photomicrograph of Hastelloy X after 90 days at 800°C. Layer at the edge was determined to be rich in molybdenum. 1870X, unetched

FIGURE 40 - Photomicrograph of Hastelloy X after 90 days at 800°C. Note change in microstructure at the edge. This photomicrograph was taken with a differential phase interference contrast attachment to enable observation of the microstructure. 272X, unetched

FIGURE 41 - Photomicrograph of the Hastelloy X capsule wall after 360 days at 800°C. A is believed to be a manganese rich spinel. 275X, unetched

FIGURE 42 - Photomicrograph of the Hastelloy X capsule wall after 360 days at 800°C. A is thought to be a manganese rich spinel and B is PuCrO_3 . 1180X, unetched

FIGURE 43 - Photomicrograph of the bottom of the Hastelloy X capsule after 360 days at 800°C. B is thought to be PuCrO_3 . 1180X, unetched

FIGURE 44 - Photomicrograph of the bottom of the Hastelloy X capsule after 360 days at 800°C. C is believed to be Cr_2O_3 . 720X, unetched

FIGURE 45 - Sketches summarizing the Hastelloy X/ $^{238}PuO_2$ interaction after exposure to 800°C.

HASTELLOY X AT 1000°C

Three Hastelloy X capsules were examined after 30 or 60 days of exposure to $^{238}\text{PuO}_2$ at 1000°C. Figures 46 and 47 are photomicrographs of one of the 60-day samples and are similar to the 30-day sample. Figure 48 is a photomicrograph of a duplicate 60-day sample. Differences between the reaction interfaces of the 60-day samples are obvious and remain unexplained. It was thought that localized deviations in composition were responsible. However, analysis of each capsule found no difference in composition. Examination of the radiographs of the test capsules found no differences in contact with the $^{238}\text{PuO}_2$ or the other materials in the test capsule. The following discussion will be primarily concerned with the reaction seen in Figures 46 and 47; but, since examination of the capsules indicated that the differences were in magnitude rather than mechanism, the discussion also applies to the reaction seen in Figure 48.

In the compatibility of Hastelloy X with $^{238}\text{PuO}_2$ at 1000°C, the most predominant reaction involves silicon which is present as a minority element (0.15 wt %) in the Hastelloy X. A dark-colored reaction product is formed at the edge of the Hastelloy X (indicated by A in Figure 47) and proceeds to penetrate into the alloy preferentially at grain boundaries. Depth of penetration is about 15 μm after 30 days and 40 μm after 60 days. Partial characterization of this oxide can be accomplished by Figures 49 through 55. Figure 49 is an x-ray strip chart analysis which indicates that the reaction product is basically plutonium and oxygen with about 1.5 wt % silicon and a possible trace of manganese near the metallic substrate and aluminum.* Figures 51 through 55 are photomicrographs taken with specific radiations to show the elemental distribution in the reaction zone of Figure 50.

In a zone between 10 and 35 μm and 30 to 75 μm below the edge of the Hastelloy X after 30 and 60 days, respectively, the reaction product in the grain boundaries appears to have a different morphology from the Pu-Si-O; that is, the oxide phase becomes thinner. This effect is seen by comparing phases A and B in Figure 47. Examination of this reaction

* Residue alumina polishing compound was observed along the edge of the sample when it was viewed under polarized light. Aluminum could also result from its presence as an impurity in the fuel (see Appendix B).

product found enrichment of only plutonium, oxygen, and aluminum.* Since no aluminum was present in the Hastelloy X prior to the test, its presence may be due to the alumina polishing compound.** No identification of this phase could be made due to the masking effect of the alumina and its narrow width in respect to the electron beam of the electron microprobe.

A subsurface reaction created a fine internal reaction product best seen in the region denoted by C in Figure 47. These numerous minute precipitates were found as deep as 35 μm after 30 days and 75 μm after 60 days though most were located nearer the edge. Occasional occurrence of a rodlike oxide was noted associated with a grain or twin boundary (see Figure 48). Identification of the precipitates could not be made as they were too small to be resolved by the electron microprobe but appeared to contain plutonium, oxygen, and possibly aluminum.**

Besides its reaction with silicon, $^{238}\text{PuO}_2$ appears to interact with chromium from the Hastelloy X forming a Pu-Cr-O reaction product. Analysis of the light-colored Pu-Cr-O seen in Figures 50, 51, 53, and 55 showed uniform concentrations of plutonium and about 12.4 wt % chromium, along with a trace amount of iron and a possible trace quantity of manganese (oxygen content is assumed). The homogeneity and chromium content suggest possible formation of the perovskite-type compound PuCrO_3 . The Pu-Cr-O was observed in only one of the three capsules where it was not bound to the Hastelloy X or to the Pu-Si-O reaction product. It is thought that most of this phase was lost by spalling or during metallographic preparation.

Variation in Microstructure Figure 56 displays the zone denuded of carbides which is typical after exposure to $^{238}\text{PuO}_2$ at 1000°C. Thickness of this zone was about 100 μm after 30 days and 140 μm after 60 days. A rate curve for the depth of the denuded zone is shown in Figure 57. The two points can be fitted to the following parabolic rate equation:

$$\Delta x^2 = 13t + 400$$

where t is time in hours and Δx is the thickness of the denuded zone in μm . Solution of the carbides is believed due to the compositional variation at the edge of the Hastelloy X.

Compositional Changes Changes in the composition are listed in Table 7 and can basically be described as the depletion of chromium and the

* Cr, Fe, Mo, Ni, W, Mn, and Co appeared depleted and silicon was not in this oxide, but the concentration of these elements in the oxide could not be determined since the electron microprobe could not resolve the oxide and averaging of its composition with the metallic matrix occurred.

** Residue alumina polishing compound was observed along the edge of the sample when it was viewed under polarized light. Aluminum could also result from its presence as an impurity in the fuel (see Appendix B).

corresponding enrichment of the remaining elements. Depletion of silicon is also expected but its concentration was below the detectable limit as deep as 500 μm into the capsule. Chromium depletion is thought to be caused by the formation of the Pu-Cr-O reaction product and possibly by the evaporation of a chromium-bearing species.

Summary and Discussion Figure 58 presents a sketch of the observed Hastelloy X/ $^{238}\text{PuO}_2$ interaction to help clarify the results. At 1000°C, $^{238}\text{PuO}_2$ causes intergranular penetration of Hastelloy X to depths of up to 75 μm after 60 days. Penetration, or at least the initial penetration at the edge, is a result of a reaction with the silicon present as a minor constituent in the Hastelloy X. The $^{238}\text{PuO}_2$ also reacts with chromium causing its depletion in the Hastelloy X edge. This reaction creates a Pu-Cr-O product (thought to be PuCrO_3) at the Hastelloy X/ $^{238}\text{PuO}_2$ interface.

The effect of $^{238}\text{PuO}_2$ on Hastelloy X was analogous in some ways to the normal mode of oxidation of the alloy. That is, the subsurface oxidation of Hastelloy X involves the formation of relatively large particles of SiO_2 , a fine dispersion of oxide, and a zone denuded of carbides. The thick penetration of the Pu-Si-O (indicated by A in Figure 47) is similar to oxidation data reported by Clarke and Titus,²⁰ Sannier, Dominget, and Dairas,²³ and Wlodek,²² all concluding the oxide was SiO_2 . Figure 59 compares the depths of oxide penetration observed in the present test with those reported by Clarke and Titus for normal oxidation. Fair agreement exists between the oxidation data and the depth of penetration of the thick oxide. Penetration of the thin phase (indicated by B in Figure 47), which was not observed by any of the above authors during oxidation, is deeper than penetration reported by Clarke and Titus.

Hastelloy X/ $^{238}\text{PuO}_2$ interaction was not similar to the surface oxidation of Hastelloy X as reported by Clarke and Titus and by Wlodek. They observed Cr_2O_3 and spinel surface scales on oxidized Hastelloy X that were not detected when the Hastelloy X was exposed to $^{238}\text{PuO}_2$ at 1000°C. These scales were observed to occur on the samples heat treated at 800°C for 181 days or less. Their absence at 1000°C is believed due to a reduction of the partial pressure of oxygen below their equilibrium value and thus they are unstable. This hypothesis is explained in more detail in a later discussion comparing the 800 and 1000°C behavior of all the alloys.

Table 7

EFFECT OF EXPOSURE TO $^{238}\text{PuO}_2$ AT 1000°C FOR 60 DAYS UPON THE COMPOSITION OF HASTELLOY X^{a, b}

Element	Concentration at Edge Relative to Interior	Depth of Depletion or Enrichment into Sample (μm)	Conc. at Edge/ Conc. in Interior	Concentration at Edge (wt %)	Concentration in Interior (wt %)	Concentration of Bulk Prior to Test (wt %)
Al	ND	ND	ND	ND	ND	ND
Co	E	30-40	1.12	1.00	0.89	0.9
Cr	D	~250	0.59	13.5	23.1	22.1
Fe	E	~250	1.11	21.4	19.3	17.3
Mn	E	~150	2.92	0.38	0.13	0.4
Mo	E	~150	1.34	7.1	5.3	8.9
Ni	E	~250	1.08	50.9	47.2	49.5
Pu	ND	ND	ND	ND	ND	ND
Si	ND	ND	ND	ND	ND	0.15
W	E	25	1.34	0.63	0.47	0.6

^aAll values were obtained by the electron microprobe with the exception of the bulk analysis performed prior to test.^bE: enriched; D: depleted; N: no effect; ND: not detected.

FIGURE 46 - Photomicrograph of Hastelloy X after 60 days at 1000°C. 250X, unetched

FIGURE 47 - Photomicrograph of Hastelloy X after 60 days at 1000°C. A indicates the penetration by the Pu-Si-O reaction product which are preferentially intergranular. The narrow intergranular penetration indicated by B was found to contain only Pu and O, however, its thinness limited the effectiveness of its analysis. The fine precipitation of an internal reaction product are in focus in the arcs designated by C. 670X, unetched

FIGURE 48 - Photomicrograph of Hastelloy X after 60 days at 1000°C.
250X, unetched

FIGURE 49 - X-ray strip chart analysis and accompanying photomicrograph of Hastelloy X after 60 days at 1000°C . The line on the photomicrograph indicates the position of the one-dimensional scan. The arrow on the photomicrograph designates the internal oxide was too small to completely resolve but appeared to contain Pu, O, and Al. The Al could possibly be due to residue alumina polishing compound.

FIGURE 50 - Photomicrograph of Hastelloy X after 60 days at 1000°C. 670X, unetched

FIGURE 51 - Photomicrograph of Hastelloy X after 60 days at 1000°C taken with backscattered electrons. 880X

FIGURE 52 - Photomicrograph of Hastelloy X after 60 days at 1000°C taken with NiK_α radiation. 880X

FIGURE 53 - Photomicrograph of Hastelloy X after 60 days at 1000°C taken with $\text{Pu}_{M\alpha}$ radiation. 880X

FIGURE 54 - Photomicrograph of Hastelloy X after 60 days at 1000°C taken with $\text{Si}_{K\alpha}$ radiation. 880X

FIGURE 55 - Photomicrograph of Hastelloy X after 60 days at 1000°C taken with $\text{Cr}_{K\alpha}$ radiation. 880X

FIGURE 56 - Photomicrograph of Hastelloy X after 60 days at 1000°C. Note intergranular nature of the penetration and the zone denuded of carbide. 274X, etched

FIGURE 57 - Thickness of the zone denuded of carbides in Hastelloy X after 1000°C exposure to $^{238}\text{PuO}_2$ as a function of time.

FIGURE 58 - Sketch of the Hastelloy X/ $^{238}\text{PuO}_2$ interaction after 60 days at 1000°C.

FIGURE 59 - Comparison of the penetration data for normal oxidation of Hastelloy X with penetration observed in the Hastelloy X exposed to $^{238}\text{PuO}_2$ at 1000°C.

HAYNES 25 (L-605) AT 800°C

Five Haynes 25 capsules were examined after 30, 59, 91, and 179 days of exposure to $^{238}\text{PuO}_2$ at 800°C. Their interaction is characterized by selective surface and subsurface reactions with chromium and manganese, although reactions with cobalt, nickel, and iron are possible. A slight change in composition of Haynes 25 resulted from the reaction with chromium and manganese. Interpretation of the interaction was complicated by the small size of the reaction product and the absence of the reaction product either from spalling or from mechanical removal during the metallographic preparation.

Surface Reaction As a result of the interfacial reaction between Haynes 25 and $^{238}\text{PuO}_2$, a surface product was formed. The product appeared noncontinuous on the 30- and 59-day samples (see Figure 60) while portions were continuous on the 91- and 179-day samples (see Figures 61 and 62). Maximum thickness of the reaction product increased from about 1 μm after 30 days annealing to about 4 μm after 179 days. Only one phase could be distinguished in the reaction product of the 30-, 59-, and 91-day samples; however, a second outer phase was detected on the 179-day sample.

Examination of the surface oxide on the 91-day sample found chromium and manganese in the approximate concentrations given below:

<u>Element</u>	<u>wt %</u>	<u>wt % normalized^a</u>	<u>at. % normalized^a</u>
Cr	25.9	46.6	26.6
Mn	10.8	19.4	10.2
O	18.9	34.0	63.2
Total	55.6	100	100

^aNormalization assumes that only chromium, manganese, and oxygen are present. The presence or absence of the remaining matrix constituents of Haynes 25 could not be determined due to the small size of the oxide being examined; however, their depletion is known.

Figure 62 is a photomicrograph and x-ray strip chart analysis of the interfacial reaction product found on the 179-day sample. This analysis of the inner oxide found approximately 38 wt % chromium and 15.8 wt % manganese (these values are not normalized). Small amounts of plutonium (at the outer edge), cobalt, and tungsten and trace amounts of nickel and

iron are also present as gradients. At least part of the cobalt, tungsten, nickel, and iron concentration is due to the metallic particles distributed through the oxide but concentrated at the outer edge. The higher concentration of cobalt and tungsten relative to nickel and iron might suggest that these particles consist predominantly of the Laves phase.

The inner oxide on the 179-day sample appears to contain more chromium and manganese than the oxide on the 91-day sample; the difference is not believed to be real but due to the increased thickness of the oxide on the 179-day sample which allows a more accurate determination. Support for their being analogous is their similar ratio of chromium to manganese (2.40:1 for the oxide on the 91-day sample and 2.41:1 for the inner oxide on the 179-day sample). The ratio of chromium to manganese in the oxide on Haynes 25 is less than in the chromium, manganese oxides on Haynes 188 and Hastelloy N; yet the manganese content of Haynes 25 is nearly twice that of Haynes 188 or Hastelloy N. The presence of cobalt and possibly nickel and iron in the surface oxide could account for the high chromium-to-manganese ratio if they replace manganese in the spinel as +2 cations. If the inaccuracy inherent in analyzing a phase 2 or 3 μm wide is taken into account, then the approximate composition of this surface oxide could indicate the formation of a mixed spinel containing chromium, manganese, cobalt, and possibly nickel and iron. If the presence of metallic particles in the oxide accounts for all of the insoluble nickel, cobalt, iron, and tungsten, the oxide could also be the MnCr_2O_4 spinel or the spinel plus Cr_2O_3 solid solution to account for the high ratio of chromium to manganese.

The second oxide reaction product, found only on the 179-day sample, is indicated by A in Figures 62 and 63. Maximum observed thickness was about 3 μm . During preparation of this sample for electron microprobe examination, most of the outer phase was lost. This phase was observed only twice: as a 0.8- μm layer and as a particle recessed below the sampling surface (B in Figure 62). Examination of both with the electron microprobe gave similar results, but their accuracy is in question due to the size and position of the oxides examined. The results of the analysis of the subsurface particle are recorded in the x-ray strip chart of Figure 62. The particle was determined to be an oxide containing plutonium as a major constituent, about 10 to 13 wt % chromium, manganese as a gradient, a trace of cobalt, and a possible trace of tungsten (detection of cobalt and tungsten could be due to the presence of metallic particles in the oxide, or in the case of tungsten a background shift). Visually, this oxide appears to be the Pu-Cr-O reaction product found on other superalloys, and the 10 to 13 wt % chromium content supports this identification. However, the possible presence of manganese in this oxide distinguishes it from previously observed Pu-Cr-O. It has been suggested that the Pu-Cr-O is the perovskite-type compound PuCrO_3 . Manganese also forms a perovskite-type compound of PuMnO_3 ; however, it is reported as being cubic while PuCrO_3 is orthorhombic.⁷ Mutual solubilities are not known.

The lack of tenacity of the outer oxide on the 179-day sample is demonstrated by its removal during sample preparation and also indicated by

its separation from the sample seen in Figure 62. Removal of this oxide from the other samples could have occurred without being detected. Thus this oxide could have formed on samples heat treated for shorter periods of time.

The interfacial reaction between the $^{238}\text{PuO}_2$ environment and Haynes 25 also provides for the mass transfer of manganese and chromium to the T.D. nickel and possibly the Inconel 625*. It is suggested that transport is due to dissociative evaporation of the surface oxides (i.e., formation of vaporous Cr, CrO, CrO_2 , CrO_3 , and MnO).

Internal Reaction A subsurface reaction was observed in the 91- and 179-day specimens. This reaction is described by Figure 64 as being intergranular in nature reaching a maximum depth of penetration of about 22 μm after 179 days. This reaction was observed only two or three times in each of the 90- and 179-day samples and cannot be described as a typical event. Analysis of the subsurface oxides seen in Figure 64 found only concentrations of manganese and chromium as indicated in the following table:

Analysis at Point Indicated by	Element	wt %	wt % Normalized ^a	at. % Normalized ^a
A	Cr	30	66.4	53.3
	Mn	10	22.1	16.7
	O	5.2	11.5	29.7
	Total	45.2	100	99.9
B	Cr	30	50.7	27.1
	Mn	6.2	10.5	5.3
	O	23	38.9	67.6
	Total	59.3	100.1	100

^aNormalization assumes that only chromium, manganese, and oxygen are present. This is not necessarily true as explained in the succeeding paragraph.

Cobalt, nickel, and iron appeared depleted in these subsurface oxides but their presence or absence could not be determined due to the small size of the oxide. Their presence could be accounted for by either averaging of the composition of the oxide with that of the metallic matrix or their real presence in a basically chromium, manganese oxide. The only detectable difference between the subsurface oxide and the chromium, manganese surface oxide was a high ratio of chromium to manganese in the subsurface oxide. A higher chromium content indicates a higher percentage of Cr_2O_3 in a mixture with the manganese rich spinel; replacement of manganese by cobalt, nickel, and/or iron in the formation of a mixed spinel; or a result of averaging of the composition of the oxide with a matrix rich in chromium (about 20 wt %) while practically void of manganese (about 0.5 wt %).

* See the sections covering the compatibility of T.D. nickel and Inconel 625 with $^{238}\text{PuO}_2$ at 800°C.

Compositional Changes Compositional variations in the edge of the Haynes 25 after 91 and 179 days of exposure are listed in Table 8. Depletions of chromium and manganese were caused by their reaction with the capsule environment. The slight enrichment of cobalt in the 91-day sample is caused by the depletion of chromium and manganese. Enrichment of iron is believed due to its presence as an impurity in the $^{238}\text{PuO}_2$ but could partially be due to the chromium and manganese depletions.

Absence of cobalt and iron enrichment in the 179-day sample and nickel enrichment in both samples could be due to their interaction with $^{238}\text{PuO}_2$. However, the total chromium and manganese depletion was only about 2.2 wt % and 2.5 wt % for the 91 and 179 day samples, respectively. This small depletion could cause enrichment of cobalt, nickel, or iron which would be below the sensitivity of one (in the case of cobalt and iron) or both (in the case of nickel) of the electron microprobes used in the determinations. Absence of iron enrichment could also mean depletion of iron in the $^{238}\text{PuO}_2$.

Haynes 25 exhibited the least change in composition (with the possible exception of manganese) of all the chromium-bearing nickel- and cobalt-base alloys tested. This nobility suggests that the surface oxide is continuous and protective.

Variation in Microstructure Figure 65 displays the slight change in microstructure at the edge. After 179 days at temperature the variation was observed to occur 25 to 35 μm into the edge.

Summary and Discussion Figure 66 contains sketches which summarize the Haynes 25/ $^{238}\text{PuO}_2$ interaction after thermal exposures of up to 179 days. The interaction involves the selective oxidation of chromium and manganese resulting in the formation of two surface oxides. The inner oxide is rich in chromium and manganese, but might also contain cobalt and trace amounts of tungsten, nickel, and iron. Possible identification might include a mixed spinel containing principally chromium, manganese, and cobalt; the MnCr_2O_4 -type spinel; or a mixture of the MnCr_2O_4 -type spinel with Cr_2O_3 . The outer oxide is composed of plutonium and chromium, with possibly some manganese. Possible identification includes PuCrO_3 , a mixture of PuCrO_3 and PuMnO_3 , or their solid solution.

Also included in the surface reaction is a mechanism which accounts for the mass transport of manganese and chromium. The mechanism is believed to be the formation of volatile oxides by the decomposition of the surface oxides.

Subsurface oxidation occurred but was observed only infrequently. The internal oxide was enriched in chromium and manganese and appeared similar to the inner surface oxide but containing less manganese.

The reaction of the $^{238}\text{PuO}_2$ with chromium and manganese depleted the metal substrate of these elements. However, Haynes 25 demonstrated the least depletion of chromium of all the chromium-bearing nickel- and cobalt-base

alloys tested. This indicates that the interfacial reaction product was continuous and retarded the outward diffusion of chromium.

The oxidation of Haynes 25 at 1100°C and extrapolated to 1000°C was investigated by Wolf and Sandrock.²⁴ For parabolic oxidation they reported a single-layered external scale rich in both chromium and manganese, which is in agreement with the inner layer created by the $^{238}\text{PuO}_2$ environment on Haynes 25. They identified the layer as Cr_2O_3 and a high lattice parameter spinel.

An investigation of the oxidation of Haynes 25 at 871°C to 1093°C by Wlodek²⁵ gave results which differed from the effect noted here by $^{238}\text{PuO}_2$. He identified the inner layer of a two-layer scale as either Cr_2O_3 or the CoCr_2O_4 spinel. This disagrees with the results of the present test as manganese was associated with all oxide formation. Wlodek reported that the outer layer was the $\text{Co}(\text{Cr},\text{Mn})\text{O}_4$ -type spinel on the 871°C sample and a complex spinel approximating $(\text{Co},\text{Ni})(\text{Co},\text{Cr},\text{Mn})_2\text{O}_4$ on the 982°C sample. The manganese content of this outer layer (5 to 15 wt % and 10 to 25 wt % after 400 hr at 871° and 982°C, respectively) is in agreement with the inner scale formed by the $^{238}\text{PuO}_2$ environment (11 to 16 wt % at 800°C); however, the cobalt content determined by Wlodek is larger.*

* Wlodek's data indicate that the cobalt concentration in the outer oxide relative to the matrix as being 0 to 20% depleted at 871°C, and 20% enriched to 50% depleted at 982°C; while in the scale produced by $^{238}\text{PuO}_2$ cobalt appeared as a gradient from about 35 to 90% depleted (see Figure 62).

Table 8

EFFECT OF EXPOSURE TO $^{238}\text{PuO}_2$ at 800°C ON THE COMPOSITION OF HAYNES 25^{a, b}

Element	Concentration at Edge Relative to Interior		Depth of Depletion or Enrichment into Sample (μm)		Conc. at Edge/Conc. in Interior		Concentration at Edge (wt %)		Concentration in Interior (wt %)		Concentration in Bulk Prior to Test (wt %)
	91 days	179 days	91 days	179 days	91 days	179 days	91 days	179 days	91 days	179 days	
Co	E	N	30-40	0	1.06	1.00	52.3	48.0	49.4	48.0	51.3
Cr	D	D	30-40	40	0.96	0.94	24.1	20.8	25.1	22.2	20.1
Fe	E	N	30-40	0	1.28	1.00	2.3	1.62	1.8	1.62	1.9
Mn	D	D	30-40	40	0.25	0.35	0.4	0.6	1.6	1.7	1.4
Ni	N	N	0	0	1.00	1.00	10.7	10.3	10.7	10.3	10.1
Pu	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.04
W ^c	?	N	?	0	?	1.00	11.4	?	11.4	?	15.1
Zn	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

^aAll values were obtained by the electron microprobe by comparison with the appropriate standard and correcting for background with the exception of the bulk analysis performed prior to the test.

^bE: enriched; D: depleted; N: neither enriched or depleted; ND: not detected.

^cDue to the large concentration of tungsten-bearing precipitates, its concentration or change in concentration could not be determined.

FIGURE 60 - Photomicrograph of Haynes 25 after 30 days at 800°C. 2000X, unetched

FIGURE 61 - Photomicrograph of Haynes 25 after 91 days at 800°C. 2000X, unetched

FIGURE 62 - Photomicrograph and x-ray strip chart analysis of the inter-
face reaction product found on the specimen annealed for 179 days at 800°C.

FIGURE 63 - Photomicrograph of Haynes 25 after 179 days at 800°C. 1120X, unetched

FIGURE 64 - Photomicrograph of Haynes 25 after 91 days at 800°C. 1140X, unetched

FIGURE 65 - Photomicrograph of Haynes 25 after 179 days at 800°C. This photomicrograph was taken with a differential phase interference contrast attachment to enable observation of the microstructure. 272X, unetched

Symbol	Major Constituents	Minor or Trace Constituents ^a	Possible Identification
	O, Cr, Mn	Co, W, Ni, Fe	Mn,Cr ₂ O ₄ , MnCr ₂ O ₄ + Cr ₂ O ₄ S.S., or Mixed Spinel
	O, Pu, Cr	Co, W, Mn	PuCrO ₃ or PuCrO ₃ + PuMnO ₃

^aSmall size of the oxide phases prohibited accurate qualitative compositional determination. The presence of these elements is therefore questionable.

FIGURE 66 - Sketches depicting the Haynes 25/²³⁸PuO₂ interaction after various exposure to 800°C. Portions of the 90 and 179 day samples appeared like those heated for only 30 or 59 days. Absence of the surface oxide could be explained by spalling or removal during metallographic preparation.

HAYNES 25 (L-605) AT 1000°C

Test capsules of Haynes 25 were examined after 30, 60, 90, or 181 days of exposure to $^{238}\text{PuO}_2$ at 1000°C. Results indicate that $^{238}\text{PuO}_2$ causes scale formation at the reaction interface, with compositional changes and void formation in the sample edge.

Surface Reaction Figures 67 through 70 portray the development of the surface layer. The influence of spallation of the reaction product upon the observed development is unknown. Nucleation of the reaction product seems to occur as separate particles which extend over the sample edge with time, becoming a continuous layer on portions of the edge after about 90 days. The metallic peninsulas noted in Figures 68 and 69 consist primarily of precipitates, indicating their superior resistance to the $^{238}\text{PuO}_2$ environment relative to the base metal. Analysis of one of the particles determined it to be enriched in cobalt and tungsten and depleted of nickel suggesting the Laves-type Co_2W^* . Thickening of the oxide scale coincides with its extension over the surface of the sample. A slight tendency for the oxide scale to penetrate the metal substrate was noted after 181 days at temperature (see Figure 70), but penetrations were shallow ($<25\text{ }\mu\text{m}$) and occurrence was infrequent.

Degradation of the capsules was greater along the base than along the walls. The formation of the surface oxide, the number of voids, and the thickness of a zone denuded of carbides decreased with increasing wall height. This phenomenon is possibly due to a temperature gradient or poorer contact between the capsule and the $^{238}\text{PuO}_2$.

Average scale thicknesses along the base of the 30-, 60-, 90- and 181-day specimens are 1.0, 2.5, 6.5, and 8.5 μm , respectively. Thickness values would be useless if spalling of the surface oxide occurs. Evidence indicating that spalling has occurred can be seen in Figures 71, 72, and 73. The evidence consists of a onetime occurrence of a 30- μm thick segment of the scale in Figure 71, cracks in the scale in Figures 71 and 72, and separation of a portion of the layer in Figure 73.

A lighter-colored second phase was detected in the oxide layer of the 90- and 180-day test specimens (see Figures 72 and 73). Results of an

* Cobalt to nickel content was 15:1 indicating that the particle is not the M_6C carbide whose ratio is 1:2. Since only one particle was analyzed, identification of the other particles is not known.

analysis of both phases in the surface layer is given in Figure 72 as an x-ray strip chart analysis. This analysis found only plutonium, oxygen, and trace amounts of cobalt, iron, and nickel with the plutonium and oxygen concentration differing in the two phases. The ratio of the weight percents of oxygen and plutonium in the light-to-dark phases are about 1:2 and 10:9.5, respectively.

Since the scale consists of just plutonium and oxygen, it might seem that the layer is sintered $^{238}\text{PuO}_2$. However, the homogeneity of the scale, the formation of a second phase, wetting of the surface, and deterioration of the Haynes 25 edge indicate that the scale is a reaction product. But if the second phase is $^{238}\text{Pu}_2\text{O}_3$ and if the irregular edge of Haynes 25 is caused by evaporation of chromium and manganese, the scale could be a sintered form of $^{238}\text{PuO}_2$ not previously observed.*

Compositional Changes Compositional changes at the edge of the Haynes 25 are summarized in Table 9. Alteration of the composition is basically the depletion of chromium and manganese and the resulting enrichment of the remaining elements. The loss of chromium and manganese at least in part is believed to be by the formation of gaseous species (e.g., CrO , CrO_2 , CrO_3 , and MnO) at the oxide scale/ $^{238}\text{PuO}_2$ interface or in the absence of the scale possibly at the Haynes 25/ $^{238}\text{PuO}_2$ interface. Data which suggest this theory are based on the deposit of chromium and manganese found on the T.D. nickel coupon present in the Haynes 25 capsule.**

Observations of the standard capsule supported the theory that transport of manganese was due to the presence of $^{238}\text{PuO}_2$. The edge of this unfueled capsule was depleted of chromium*** but enriched in manganese, but in the fueled capsule both chromium and manganese were depleted.

Since manganese seems to require the $^{238}\text{PuO}_2$ environment for mass transport, transport by $\text{Mn}_{(v)}$ appears rejected. A possible mechanism for the movement of manganese involves the formation of $\text{MnO}_{(g)}$ as a result of the reaction of manganese with the partial pressure of oxygen made available by the change in stoichiometry of PuO_2 going to PuO_{2-x} .

Void Formation The outward diffusion of chromium and manganese created vacancies in the lattice which coalesced into Kirkendall-type voids near

* Figures 137 and 138 depict the normal appearance of $^{238}\text{PuO}_2$.

** Deposition of chromium and manganese onto the T.D. nickel is more thoroughly discussed in the section of this report concerning the compatibility of T.D. nickel.

*** Chromium depletion in the standard capsule could have been due to direct contact of the Haynes 25 with the T.D. nickel or due to the small amount of oxygen remaining in the capsule after welding (material deposit on the T.D. nickel standard was found).

the specimen edge as seen in Figure 74.* The number of voids decreased with increasing wall height. Maximum depth of void formation in the capsule base is listed below.

<u>Time at 1000°C</u> <u>(days)</u>	<u>Maximum Depth of Void Formation</u> <u>(μm)</u>
30	50-85
60	85-155
90	140-220
181	230-300

A rate curve for the above data is shown in Figure 75. The data can be fitted to the following parabolic rate equation:

$$\Delta X^2 = 18.5 t - 8000$$

where t is time in hours and ΔX is the depth of void formation in μm . Parabolic rate dependence supports the assumption that the voids are caused by the outward diffusion of chromium and manganese.

Variation in Microstructure Figure 76 displays the observed change in microstructure at the sample edge. Below is a table giving the thickness of the zone denuded of carbides as a function of temperature.

<u>Time at 1000°C</u> <u>(days)</u>	<u>Thickness of Denuded Zone</u> <u>(μm)</u>
30	35-60
60	65-90
90	95-100
181	95-110

The above data are plotted in Figure 77 as the square of the thickness as a function of time. A decrease in the growth of the denuded zone is observed after 90 days.

Summary and Discussion The compatibility of Haynes 25 with $^{238}\text{PuO}_2$ at 1000°C is characterized by the formation of an oxide scale at the reaction interface which developed a second phase after 90 days at temperature. Sketches depicting the observed evolution of the scale are presented in Figure 78. Only plutonium, oxygen, and a trace of cobalt were detected in the scale by the electron microprobe with the only observed difference between the two phases being a variation in the plutonium and oxygen

* The voids observed in the Haynes 25 are assumed to be a resulting phenomenon of the compatibility study and not due to the pullout of a reaction product or a phase normally present in the Haynes 25. Complete assurance that this assumption is correct is not possible.

contents. Depletion of chromium and manganese in the Haynes 25 edge indicates that the surface layer is not an effective diffusion barrier.

The reaction mechanism at the Haynes 25/ $^{238}\text{PuO}_2$ interface remains undetermined as the surface scale has not been identified. However, depletions of chromium and manganese suggest their reaction with the capsule environment. It is proposed that chromium and manganese form volatile oxides (e.g., CrO , CrO_2 , CrO_3 , MnO) allowing mass transport of these elements. Oxygen is made available for the oxidation of chromium and manganese by $^{238}\text{PuO}_2$ as it becomes substoichiometric.

Table 9

EFFECT OF EXPOSURE TO $^{238}\text{PuO}_2$ FOR 181 DAYS AT 1000°C UPON THE COMPOSITION OF HAYNES 25^{a, b, c}

Element	Concentration at Edge Relative to Interior	Depth of Depletion or Enrichment into Sample (μm)	Conc. at Edge/ Conc. in Interior	Concentration at Edge (wt %)	Concentration In Interior (wt %)	Concentration in Bulk Prior to Test (wt %)
Co	E	145	1.04	53.5	51.5	51.3
Cr	D	175	0.67	13.8	20.6	20.1
Fe	N	0	1.00	1.4	1.4	1.9
Mn	D	135	0.50	0.49	0.98	1.4
Ni	E	140	1.15	9.3	8.1	10.1
Pu	ND	ND	ND	ND	ND	ND
Si	ND	ND	ND	ND	ND	0.04
W	E	140	1.41	12.7	9.0	15.1
Zn	ND	ND	ND	ND	ND	ND

^aAll values were obtained by the electron microprobe with the exception of the bulk analysis performed prior to the test.^bDepth of void formation in this area was 140 μm .^cE: enrichment; D: depletion; N: neither enrichment or depletion; ND: not detected.

FIGURE 67 - Photomicrograph of the bottom edge of the Haynes 25 capsule after 30 days at 1000°C. Note 1 to 1.5 μm scale at the interface. 2000X, unetched

FIGURE 68 - Photomicrograph of the bottom edge of the Haynes 25 capsule after 60 days at 1000°C. 2000X, unetched

FIGURE 69 - Photomicrograph of the bottom edge of the Haynes 25 capsule after 90 days at 1000°C. Arrows indicate precipitates which appear more inert than the matrix. Analysis of one such particle indicated it was the Laves-type Co_2W . Areas were found where the surface oxide was continuous. 2000X, unetched

FIGURE 70 - Photomicrograph of the bottom edge of the Haynes 25 capsule after 180 days at 1000°C. 275X, unetched

FIGURE 71 - Photomicrograph of Haynes 25 after 90 days at 1000°C. This is a single occurrence of a 30 μm thick oxide layer, found to contain only Pu, O, and a trace of Co. Its thickness suggests partial spalling of the oxide layer has occurred. 1140X, unetched

FIGURE 72 - Photomicrograph and x-ray strip chart analysis of the surface layer found on Haynes 25 after 180 days at 1000°C. Phase A appears slightly higher in Pu and lower in O than the darker portion of the layer. Analyses for Si and Zn were omitted as they were not detected in either the Haynes 25 or the surface layer.

FIGURE 73 - Photomicrograph of bottom edge of the Haynes 25 capsule after 180 days at 1000°C. A indicates a piece of the surface layer which has bulk of the layer. 1120X, unetched

FIGURE 74 - Photomicrograph of the bottom edge of the Haynes 25 capsule after 180 days at 1000°C. 70.5X, unetched

FIGURE 75 - Square of the depth of void formation in Haynes 25 as a function of exposure time at 1000°C.

FIGURE 76 - Photomicrograph of Haynes 25 after 181 days at 1000°C. Note zone denuded of carbide at the edge. 148X, etched

FIGURE 77 - Square of the thickness of the denuded zone in Haynes 25 as a function of exposure time at 1000°C.

^aBased on analysis of only one particle.

FIGURE 78 - Sketches summarizing the development of the Haynes 25/²³⁸PuO₂ interaction at 1000°C.

HAYNES 188 AT 800°C

Six Haynes 188 coupons were examined after 30, 60, 90, 181, and 360 days of exposure to $^{238}\text{PuO}_2$ at 800°C. Interaction resulted in a multi-oxide reaction product due primarily to the selective oxidation of chromium and manganese. Subsurface effects included internal oxidation, void formation, and compositional changes. Plutonium did not appear to participate in the degradation of Haynes 188 annealed for 181 days or less. After 360 days at temperature, the reaction mode changed as only Pu-Cr-O and Pu-Si-O reaction products were formed in the reaction zone which was visually different from the samples annealed for shorter times. Due to the seemingly different response to the $^{238}\text{PuO}_2$, the results of the 360-day sample are presented separately after the results of the other samples.

30- to 181-Day Exposure

Surface Reaction The typical surface reaction product found on unwelded Haynes 188 differs from that sometimes found on the weld affected zone. Figures 79 and 80 are typical of the unwelded material and the weld-affected zone, respectively. Since the two oxides which make up the reaction product on the weld-affected zone seen in Figure 80 were also observed* in the reaction product of the unwelded material, the differences in morphology are thought to be due to variations in spalling tendencies and microstructure of the Haynes 188 rather than from differences in reaction mechanism. The weld bead seemed the preferential location for the oxide morphology of Figure 80. This suggests that compression stresses develop in the oxide layer due to its larger volume relative to the metal and that the curvature of the weld bead accounts for the larger oxide volume, thus reducing the internal stresses. In both morphologies the oxide creates an irregular surface by penetrating and removing portions of the metallic substrate. Maximum thickness of the oxide including base metal penetration was 38 μm after 181 days.

Haynes 188 coupons were close to or touching Haynes 25 on one side (see Appendix C). The morphologies indicated by Figures 79 and 80 were observed on both sides of the Haynes 188 coupon indicating that the Haynes 25 did not effect the interaction between the $^{238}\text{PuO}_2$ and Haynes 188.

*Identified by electron microprobe.

Electron microprobe analysis of the reaction product seen in Figure 79 determined it to be an oxide containing primarily chromium. Spot analysis of the particle indicated by the arrow found oxygen, 61.7 wt % chromium, 1.6 wt % manganese, and 1.2 wt % cobalt. Analysis of the underlying phase creating the irregular edge on the substrate found oxygen, 44 to 46 wt % chromium, and about 1 wt % manganese at its outer edge. There is no visual difference between the two oxides and they are believed to be the same phase. The difference in chromium content is believed due to the small size of the surface oxide relative to the resolving power of the electron microprobe. The determination of 61.7 wt % chromium suggests the formation of Cr_2O_3 solid solution which theoretically contains 68.4 wt % chromium.

Results from an electron microprobe analysis of the reaction product seen in Figure 80 are given in Figures 81 through 87 in the form of photomicrographs taken with backscattered electrons and characteristic x-rays. Comparison of these figures determines that two layers of oxide are present. The outer layer is enriched in chromium, manganese, and zinc; and the inner appears to be enriched only in chromium. Electron microprobe analysis of these same two layers in an area similar to that seen in Figures 88 and 89 is listed below.

Element Concentration ^a (wt %)										
Layer	Co ^b	Cr	Fe ^b	La	Mn	Ni	O	Ti	W	Zn
Inner	T	58.4	T	ND	ND	ND	P	ND	ND	ND
Outer	T to 5	47.0	T	ND	22.4	ND	P	ND	ND	ND

^a ND = Not Detected; P = Present; T = Trace.

^b Small amounts of cobalt and iron could be due to the metallic particles found distributed in the oxides.

Possible identification of the inner layer is Cr_2O_3 . The chromium content of the inner layer does not agree with the theoretical content of Cr_2O_3 (68.4 wt % Cr), but the difference is believed due to error in the determination because of the presence of metallic particles in a relatively thin layer (about 3 μm wide where examined). Absence of a substantial quantity of any other element in the oxide restricts the choice of possible identifications. The outer oxide layer is thought to be the MnCr_2O_4 -type spinel with possibly a small amount of cobalt and in the 60-day sample, zinc. Considering the relatively crude determination, the experimental composition is a good match for the theoretical composition of MnCr_2O_4 (46.4 wt % Cr and 24.7 wt % Mn).

Although the outer layer consists basically of the MnCr_2O_4 -type spinel, the spinel did not always appear continuous but frequently appeared mixed with Cr_2O_3 . The mixture of the darker spinel and the lighter Cr_2O_3 can best be seen in Figure 89. Oxide particles consisting of both the Cr_2O_3 and spinel were also found in and outside the outer layer of reaction product as indicated by the arrows in Figures 88 and 89.

Internal Reaction Figure 89 illustrates the internal precipitates observed in all the specimens. They appear as small, intergranular, rodlike oxides. Though concentrated in the first 100 μm in the 180-day coupon, they completely permeated the approximately 1000- μm thick coupon after 60 days. Analysis was performed on these precipitates with an electron microprobe for chromium, lanthanum, manganese, oxygen, plutonium, and silicon, none of which appeared to coincide with the precipitates. Their small size is believed to have prevented their identification.

Compositional Changes Compositional variations in the Haynes 188 edge after 60 and 181 days at 800°C are given in Table 10. Depletions of chromium and manganese are due to the oxide formation, and the enrichments of nickel and tungsten result from the chromium and manganese depletions. Cobalt is slightly enriched along the edge of the 60-day sample but slightly depleted or unaffected in the edge of the 181-day sample. The change in the behavior of cobalt could be explained by a more active participation in oxide formation. Enrichment of zinc and most of the iron enrichment is because of their presence as impurities in the $^{238}\text{PuO}_2$.

The metallic substrate below the oxides seen in Figures 79 and 80 were both analyzed and refer to the A and B determinations of the 181-day coupon in Table 10. Depletion of manganese is similar in both even though only a small amount of manganese was found at the outer edge of the oxide of Figure 79, while an oxide layer rich in manganese (thought to be MnCr_2O_4) was found in Figure 80. This supports the conclusion that the MnCr_2O_4 outer layer had formed, but spalled off the oxide seen in Figure 79; and that the reaction mechanism remains the same even though the oxide morphologies seem to differ.

Void Formation Void formation* became noticeable after 90 days at temperature and reached a maximum depth of 35 to 40 μm below the oxide scale in both the 90- and 181-day samples. The voids are believed to be Kirkendall voids formed by the coalescence of vacancies created by the outward diffusion of chromium and manganese.

*Voids nearest the edge in Figures 79, 88, and 89 appear to result from pullout of reaction product. Voids described in this section are those located farther from the edge and are indicated in Figures 79 and 89. Although these voids are assumed to be real, their creation by pullout of a phase cannot be eliminated.

Variation in Microstructure Figure 91 is a photomicrograph showing the change in microstructure at the edge. The thickness of the zone denuded of carbides was 20 to 50 μm after all heat treatments.

360-Day Exposure Figures 92, 93, and 94 typify the reaction interface on the 360-day sample. Visual comparison of the reaction zone of the 360-day sample with the other 800°C samples discloses obvious differences. Electron microprobe examination of the reaction product indicated by A in Figures 92 and 94 found plutonium and oxygen as major constituents with about 12 wt % chromium*. These oxides (along with A in Figure 93) are believed to be PuCrO_3 which theoretically contains 15.4 wt % chromium. Analysis of phase B in Figure 94 found plutonium, oxygen, and a trace of silicon. Composition of the edge (see Table 10) seemed compatible with the other 800°C samples except for the presence of about 0.4 wt % manganese which was absent in the other samples. Maximum depth of void formation was about 35 μm and thus similar to the other 800°C samples.

Comparison of this sample with the samples annealed at 1000°C (see succeeding report) finds similarities in their visual appearance (compare Figures 92 and 93 with 109) and in the reaction products formed. This indicates that a temperature excursion occurred during heat treatment of the 360-day specimen. However, the temperature of the annealing furnace was continually monitored by a recorder and no increase in the test temperature was observed. Thus a change in the reaction mechanism appears to have occurred between 181 and 360 days of exposure to 800°C and will be subsequently discussed.

Summary and Discussion The Haynes 188/ $^{238}\text{PuO}_2$ interaction is summarized in the sketches presented in Figure 95. Thermal exposures to 800°C for times of 181 days or less causes the formation of a multi-oxide reaction product on the Haynes 188 at 800°C which was primarily the result of the selective oxidation of chromium and manganese. Two oxide layers are created: the outer consists of chromium and manganese and is thought to be primarily the MnCr_2O_4 spinel but mixed with some Cr_2O_3 ; the inner is basically composed of chromium and is thought to be a solid solution of Cr_2O_3 . The process of oxidation depleted the metallic substrate of chromium causing the Cr_2O_3 to penetrate or precipitate internally and to separate chunks of the base metal from the Haynes 188 substrate. Maximum depth of attack was approximately 20 μm after 90 and 181 days. Plutonium was observed at the outside edge but not associated with the oxide reaction product.

After 360 days at 800°C the Cr_2O_3 and MnCr_2O_4 apparently decomposed and were replaced by the formation of the PuCrO_3 and Pu-Si-O phases.

*A trace amount of lanthanum and possibly aluminum were also found in the portion of the reaction product indicated by B in Figure 92. They appeared to partially replace the plutonium.

The proposed explanation for the change in the resultant appearance of the interaction is based on the reduction of the partial pressure of oxygen below the level necessary for the stability of Cr_2O_3 and MnCr_2O_4 . Reduction of the activity of oxygen is accomplished by the growth of PuCrO_3 and Pu-Si-O as mentioned in the previous discussion of the 800°C , Hastelloy N compatibility test (see page 19). This theory proposes that the observed similarity in the appearance of the 360-day, 800°C sample and the 1000°C samples (subsequently discussed) represents a time/temperature relationship rather than an anomaly caused by an inadvertent increase in the test temperature.

Table 10

EFFECT OF $^{238}\text{PuO}_2$ ON THE COMPOSITION OF HAYNES 188 AT 800°C^{*}

Element	Concentration at Edge Relative to Interior				Depth of Depletion or Enrichment into Sample (μm) (includes oxide layer)				Conc. at Edge/ Conc. in Interior				Concentration at Edge (wt %)			Concentration in Interior (wt %)			Concentration in Bulk Prior to Test (wt %)
	181 days				181 days				181 days				181 days			181 days			
	360 days				360 days				360 days				360 days			360 days			
	60 days	A	B	360 days	60 days	A	B	360 days	60 days	A	B	360 days	A	B	360 days	A	B	360 days	
Al	-	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.2
Co	E	D	N	E	110	70	0	≥ 50	1.10	0.95	1.00	≥ 1.12	34.5	43.7	44.8	36.4	43.7	≤ 40.0	40.9
Cr	D	D	D	D	95	60	95	≥ 60	0.77	0.66	0.51	≤ 0.38	15.4	13.0	9.1	23.2	25.4	≥ 23.9	21.5
Fe	E	E	E	E	100	65	70	≥ 75	5.00	5.58	4.92	≥ 2.60	9.5	6.4	8.6	1.7	1.3	≤ 3.3	1.46
La	-	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.15
Mn	D	D	D	D	65	80	75	≥ 50	< 0.84	0.00	0.00	≤ 0.50	ND	ND	0.4	0.7	0.6	≥ 0.8	0.76
Ni	E	E	E	E	100	60	45	≥ 60	1.19	1.06	1.17	≥ 1.18	20.4	24.3	22.6	19.3	20.8	≤ 19.2	20.6
Pu	-	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	-	ND	ND	ND	-	ND	ND	ND	-	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.6
W ^c	N	E	E	E	0	60	40	35	1.00	1.21	1.21	1.38	7.4	13.4	13.1	6.1	11.1	9.5	13.5
Zn	E	E	E	E	75	75	40	50	-	∞	∞	∞	T	T	T	ND	ND	ND	ND

* All values were obtained by the electron microprobe with the exception of the bulk analysis performed prior to the test.

^b E: enriched; D: depleted; N: neither enriched or depleted; ND: not detected; T: trace.

^c Values obtained for tungsten are very approximate because of large compositional variations. These variations are caused by the presence of tungsten-rich precipitates in the Haynes 188.

FIGURE 79 - Photomicrograph of Haynes 188 after 181 days at 800°C. Arrow indicates particle found to contain 61.7 wt % Cr. Void formation occurred in the base metal below the indicating line. 1180X, unetched

↑ Edge
retainer

FIGURE 80 - Photomicrograph of welded zone of Haynes 188 after 60 days at 800°C. 670X, unetched

FIGURE 81 - Photomicrograph of Haynes 188 after 60 days at 800°C taken with backscattered electrons. 1760X

FIGURE 82 - Photomicrograph of Haynes 188 after 60 days at 800°C taken with CoK_{α} radiation. 1760X

FIGURE 83 - Photomicrograph of Haynes 188 after 60 days at 800°C taken with NiK_{α} radiation. 1760X

FIGURE 84 - Photomicrograph of Haynes 188 after 60 days at 800°C taken with WL_{α} radiation. 1760X

FIGURE 85 - Photomicrograph of Haynes 188 after 60 days at 800°C taken with $\text{Cr}_{K\alpha}$ radiation. 1760X

FIGURE 86 - Photomicrograph of Haynes 188 after 60 days at 800°C taken with $\text{Mn}_{K\alpha}$ radiation. 1760X

FIGURE 87 - Photomicrograph of Haynes 188 after 60 days at 800°C taken with $\text{Zn}_{K\alpha}$ radiation. 1760X

FIGURE 88 - Photomicrograph of Haynes 188 after 181 days at 800°C. Arrow indicates particle containing a mixture of light Cr_2O_3 and darker MnCr_2O_4 1180X, unetched

FIGURE 89 - Photomicrograph of Haynes 188 after 181 days at 800°C. Arrow indicates particle consisting of a mixture of light Cr_2O_3 and darker MnCr_2O_4 . Void formation occurred in region below line. 1180X, unetched

FIGURE 90 - Photomicrograph of Haynes 188 after 181 days at 800°C. Note intergranular precipitates. 575X, unetched

FIGURE 91 - Photomicrograph of Haynes 188 after 90 days at 800°C. Note change in microstructure at the edge. 275X, etched

FIGURE 92 - Photomicrograph of Haynes 188 after 360 days at 800°C. A is thought to be PuCrO_3 . B also contained Pu, O, and Cr, but also contained trace amounts of La and possibly Al (detection of Al could be due to residue Al_2O_3 polishing compound). 1180X, unetched

FIGURE 93 - Photomicrograph of Haynes 188 after 360 days at 800°C. A is thought to be PuCrO_3 . B denotes a Pu-Si-O phase. 1180X, unetched

FIGURE 94 - Photomicrograph of Haynes 188 after 360 days at 800°C. A is thought to be PuCrO_3 . 1180X, unetched

FIGURE 95 - Sketches summarizing the Haynes 188/²³⁸PuO₂ interaction at 800°C.

HAYNES 188 AT 1000°C

Four coupons of Haynes 188 were examined after 30, 60, or 90 days of exposure to $^{238}\text{PuO}_2$ at 1000°C. The compatibility is characterized by surface reactions with chromium and silicon; internal reactions with silicon, lanthanum, manganese, and possibly aluminum*; compositional changes at the exterior edge of the sample; and void formation. Results of the surface and internal reactions can be seen in Figures 96 through 98.

Surface Reaction As a consequence of the surface interaction, two reaction products were detected. The reaction product occurring in major proportions is the light phase indicated by A in the photomicrographs of Figures 96 through 98. This phase is also located between points a and b, and c and d in the accompanying x-ray strip chart analysis of Figure 98. From the strip chart, this reaction product was determined to be about 73 wt % plutonium and 13 wt % chromium (analysis for oxygen could not be performed). If the remainder of the weight percent is assumed to be oxygen, the composition could be 21 at.% plutonium, 13 at.% chromium, and 61 at.% oxygen which approximates PuCrO_3 .

Unlike the Pu-Cr-O reaction product found on the 30- and 60-day samples, after 90 days it developed a multiphase appearance and contained some silicon. Figure 99 displays three visually different reaction products while their respective approximate compositions are listed below:

Approximate Composition of Phases A, B,
and C in Figure 99 (wt %)

<u>Phase</u>	<u>Plutonium^a Intensity</u>	<u>Cr</u>	<u>O</u>	<u>Si</u>
A	46	14.5	present	4.4
B	44	12	present	4.1
C ^b	51	4	present	4.4

^a No plutonium standard was available; therefore, intensity values are given for purpose of comparison.

^b C is small enough that its composition is compromised by its surroundings.

*Though aluminum appears to take part in the subsurface reaction, its presence, at least in part, is due to residue alumina polishing compound.

B is the most prevalent phase while A has the same light color as the Pu-Cr-O found on the 30- and 60-day samples. The visual difference between A and B could be due to their slight compositional differences or merely to grain orientation. C in Figure 99 was found only rarely and appeared depleted in chromium. It seems possible that C is the Pu-Si-O reaction product mentioned in the following paragraph.

The second reaction product occurring at the Haynes 188/²³⁸PuO₂ interface is the darker phase indicated by B in the photomicrographs of Figures 96 through 98. After 30 days at temperature, this phase occurs as scattered segments of a coating or layer on the Haynes 188 edge. After 60 and 90 days the layer became semicontinuous. The layer is found in the x-ray strip chart of Figure 98 between points d and e. Along with the x-ray strip chart, Figures 100 through 107 help determine that the oxide layer contains plutonium and silicon.

Internal Reaction The internal reaction observed in Figures 96 through 98 occurs primarily in the grain boundaries as indicated in Figure 108. Depth of intergranular penetration in the grain boundaries is given below.

<u>Time at temperature (days)</u>	<u>Depth of grain boundary penetration (μm)</u>
30	65-95
60	80-100
60(duplicate)	35-65
90	70-100

The oxide in the grain boundaries at or very close to the sample edge contains plutonium and silicon. Electron microprobe analysis of point C in Figure 109 found about 9 wt % silicon, oxygen, and plutonium. No compositional variation was detected across C, which appears multiphased. Its varying appearance could be due to subtle changes in composition or to grain orientation. Various oxides in Figure 110 were investigated with the electron microprobe and Table 11 lists the results. Relating the data in Table 11 and Figures 98 and 100 through 107 shows that several oxides occupy the grain boundaries just below the edge. Different oxides containing plutonium and aluminum*; plutonium, aluminum*, and lanthanum; plutonium, aluminum*, and chromium; and aluminum* and manganese seemed to occur.**

*Possible residue Al₂O₃ polishing compound.

**Partial identification of all internal oxides is a conjecture based on elements found enriched relative to the base metal.

Besides the grain boundary attack, the internal reaction possibly precipitated two oxides in a rod morphology. Oxides containing aluminum* and aluminum* with plutonium can be observed with the use of Figures 4, 100, 103, and 106. Approximate analysis of the rod denoted by B in Figure 109 is given in Table 11, but identification is impossible as it was too small to resolve.

Compositional Changes The composition of the edge of Haynes 188 changed as a result of the exposure to the $^{238}\text{PuO}_2$. Table 12 lists the changes in concentration, if any, for the various elements thought to be present. The variation in composition can be summarized as the depletion of chromium and the effect of this depletion upon the remaining constituents.

Void Formation Associated with the change in composition is the formation of voids** which appear more prevalent near the sample edge than in the bulk of the sample. These voids are probably due to the coalescence of voids created by the outward diffusion of chromium. Most voids were within 100 μm of the sample edge.

Variation in Microstructure Microstructural changes were observed at the edge as seen in Figure 110. Below is a list of thicknesses of the denuded zones of the various heat treatments.

Thickness of denuded zone found in Haynes 188 samples
after exposure to $^{238}\text{PuO}_2$ at 1000°C (μm)

Time of exposure (days)	Microstructure of sample prior to test	
	Weld-affected zone	As received (annealed)
30	105-110	105-115
60	130	145-155
60(duplicate)	110	100
90	110-150	110-150

No correlation can be made between the thickness of the denuded zone and the time at temperature.

Summary and Discussion The compatibility of Haynes 188 with $^{238}\text{PuO}_2$ at 1000°C appears concerned with reactions between the $^{238}\text{PuO}_2$ and chromium and certain minority constituents (e.g., Si, Mn, La, and possibly Al*). Figure 111 contains sketches which are meant to summarize and clarify this interaction. Silicon reacts with the $^{238}\text{PuO}_2$ to give a Pu-Si-O reaction product which is present as a noncontinuous layer on the Haynes 188 edge and as a subsurface oxide in the grain boundaries near the edge.

*Possible residue Al_2O_3 polishing compound.

**The voids or some of the voids may have been a result of inadvertent pullout of a phase during metallographic preparation.

Deeper into the sample, the grain boundary attack appears to be promoted by manganese, lanthanum, and possibly aluminum*. Although the internal reaction was primarily in the grain boundaries, intergranular precipitation of oxides in rod morphology occurred. Some rods appeared to contain plutonium, aluminum*, and oxygen, while others contained only aluminum and oxygen.

*Possible residue Al_2O_3 polishing compound.

Table 11

COMPOSITION OF VARIOUS INTERNAL OXIDE REACTION PRODUCTS FOUND IN HAYNES 188 AFTER EXPOSURE TO $^{238}\text{PuO}_2$ FOR 90 DAYS AT 1000°C AS SEEN IN FIGURE 109

Region	Indicating Letter	Composition (wt %) ^a												
		Al	Co	Cr	Fe	La	Mn	Mo	Ni	O	Pu ^b	Si	W	Zn ^c
Oxide in grain boundary	A	3.0	T	1.9	0	0	0	-	T	P	P	0	0	2.0 ^e
Oxide rod ^d	B	4.6	22.1	9.0	2.8	0	T	-	14.8	P	P	0	8.6	1.2 ^e
Oxide in grain boundary	C	0	0	T	0	0	0	0	0	P	P	8.8	0	T ^e
Oxide in grain boundary ^d	D	2.3	-	-	-	1.6	-	-	-	P	P	0	-	-

^a-: analysis not performed; P: present; T: trace^bThe plutonium concentration could not be determined because no plutonium standard was available.^cZinc was present as an impurity in the $^{238}\text{PuO}_2$ but a possible explanation for the apparent zinc content is the interference of $\text{Pu}_{L\beta_2}$ (second order) line at $1.4389\text{\AA}$ with the $\text{Zn}_{K\alpha_1\&\alpha_2}$ at $1.4363\text{\AA}$.^dArea under examination is small enough that part of the base metal will be included in the beam; therefore, averaging of composition occurs.

Table 12

EFFECT OF EXPOSURE TO $^{23}\text{PuO}_2$ AT 1000°C UPON THE COMPOSITION OF HAYNES 188^{a, b}

Element	Concentration at Edge Relative to Interior		Depth of Depletion or Enrichment into Sample (μm)		Conc. at Edge/Conc. in Interior		Concentration at Edge After 90 days at 1000°C (wt %)	Concentration in Interior of Sample After 90 days at 1000°C (wt %)	Concentration of Bulk Prior to Test (wt %)
	60 days at 1000°C	90 days at 1000°C	60 days at 1000°C	90 days at 1000°C	60 days at 1000°C	90 days at 1000°C			
Al	ND	ND	ND	ND	ND	ND	ND	ND	0.2
Co	E	E	250	≥ 320	1.02	≥ 1.05	37.7 ^c	≤ 35.9 ^c	40.9
Cr	D	D	250	225	0.90	0.57	13.4	23.4	21.5
Cu	ND	-	ND	-	ND	-	-	-	0.06
Fe	E	E	225	200	2.50	3.31	5.3	1.6	1.46
La	ND	ND	ND	ND	ND	ND	ND	ND	0.15
Mn	N	N	0	0	1.00	1.00	T	T	0.76
Mo	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ni	D	E	130	160	0.96	1.05	22.4	21.4	20.6
Pu	ND	ND	ND	ND	ND	ND	ND	ND	ND
S	ND	-	ND	-	ND	-	-	-	ND
Si	ND	ND	ND	ND	ND	ND	ND	ND	0.6
W	E	E	200	90	1.11	1.20	12.2	10.2	13.5
Zn	E	N	175	0	2.00	1.00	T	T	ND

^a All values were obtained by the electron microprobe with the exception of the bulk analysis performed prior to the test.^b T: trace; -: analysis not performed; E: enrichment; D: depletion; N: neither depletion or enrichment but was detected; ND: not detected.^c Did not have cobalt standard; average of iron and nickel standards used to get an approximate cobalt standard.

FIGURE 96 - Photomicrograph of Haynes 188 after 30 days at 1000°C. 250X, unetched

FIGURE 97 - Photomicrograph of Haynes 188 after 60 days at 1000°C. 250X, unetched

575X, unetched

FIGURE 98 - X-ray trace analysis and accompanying photomicrograph of Haynes 188 after 60 days at 1000°C.

FIGURE 99 - Photomicrograph of the end of the Haynes 188 after 90 days at 1000°C. 575X, unetched

FIGURE 100 - Photomicrograph of Haynes 188 after 60 days at 1000°C taken with the sample current. 1760X

FIGURE 101 - Photomicrograph of Haynes 188 after 60 days at 1000°C taken with $\text{Co}_{K\alpha}$ radiation. 1760X

FIGURE 102 - Photomicrograph of Haynes 188 after 60 days at 1000°C taken with $\text{Ni}_{K\alpha}$ radiation. 1760X

FIGURE 103 - Photomicrograph of Haynes 188 after 60 days at 1000°C taken with $\text{Pu}_{M\alpha}$ radiation. 1760X

FIGURE 104 - Photomicrograph of Haynes 188 after 60 days at 1000°C taken with $\text{Cr}_{K\alpha}$ radiation. 1760X

FIGURE 105 - Photomicrograph of Haynes 188 after 60 days at 1000°C taken with $\text{Si}_{K\alpha}$ radiation. 1760X

FIGURE 106 - Photomicrograph of Haynes 188 after 60 days at 1000°C taken with $Al_{K\alpha}$ radiation. 1760X

FIGURE 107 - Photomicrograph of Haynes 188 after 60 days at 1000°C taken with $La_{L\alpha}$ radiation. 1760X

FIGURE 108 - Photomicrograph of Haynes 188 after 90 days at 1000°C. etched

FIGURE 109 - Photomicrograph of Haynes 188 after 90 days at 1000°C. Approximate compositions of internal oxides indicated by A through D are given in Table 11. Surface reaction is missing and assumed lost during metallographic preparation or due to spalling. 575X, unetched

FIGURE 110 - Photomicrograph of Haynes 188 after 90 days at 1000°C. Note zone denuded of carbides and intergranular attack. 149X, etched

Symbol	Constituents	Possible Identification	Comments
	Pu, O	$^{238}\text{PuO}_{2-x}$	
	Pu, Cr, O	PuCrO_3	Appears multi-phased in 90-day sample & thus represented by two symbols. Contains small amount of Si in 90-day sample
	Pu, O, Si	Pu-Si-O,	Appears multi-phased
	Pu, Al ^a , O, ?	?	
	Pu, La, Al ^a , O ^b , ?	?	
	Al ^a , O ^b , ?	?	
	Mn, Al ^a , O ^b , ?	?	
	Void	Void	

^aPossible residue Al_2O_3 polishing compound.

^bAssumed.

FIGURE 111 - Sketch summarizing Haynes 188/ $^{238}\text{PuO}_2$ interaction after exposure to 1000°C. Most of the surface reaction had been lost from the 90 day sample.

INCONEL 625 AT 800°C

Five Inconel 625 coupons were examined after 30, 59, 91, or 179 days at 800°C. The interaction was characterized by the selective reaction of the $^{238}\text{PuO}_2$ with chromium and manganese resulting in the formation of a multi-layered, interfacial reaction product. In conjunction with the surface reaction, compositional changes and slight microstructural changes were noted in the Inconel 625 edge.

Surface Reaction The products of the surface reaction appeared to change with increasing time at temperature. After 30 days at 800°C, a continuous, 1- to 2- μm thick layer was formed on the Inconel 625 edge (Figure 112). A second phase, denoted by B in Figure 112, was observed frequently on the outside edge of the continuous layer.

After heat treating for 59 days, three phases were detected in the reaction product and are indicated by A, B, and C in the photomicrographs and x-ray strip chart analyses of Figures 113 and 114. The inner phase, A, is a 1- to 2- μm continuous layer which appears visually to be analogous to the layer on the 30-day sample, except slight ($<9\text{ }\mu\text{m}$) penetrations into the metal substrate are now noted creating an irregular edge. Results from the x-ray strip charts of Figures 113 and 114 determined the layer to contain oxygen, 42 to 45 wt % chromium, a trace of titanium, and possible trace amounts of aluminum*, nickel, iron, and plutonium. If it is assumed that this value for chromium is low due to the small size of the oxide and distribution of metallic particles which are presumably depleted of chromium, possible identification of this oxide is Cr_2O_3 . Phase B appears as a semicontinuous layer, optically similar to the outer reaction product found on the 30-day sample (phase B in Figure 112). Analysis indicates this middle phase of the reaction product to contain oxygen, chromium, 11 to 13.5 wt % manganese, a trace of titanium, and possible trace amounts of aluminum, nickel, iron, and plutonium. The chromium and manganese content suggests the formation of a mixture of the MnCr_2O_4 -type spinel with Cr_2O_3 solid solution. The reported value for the manganese is probably below the true value due to the small thickness of the oxide. If the value for manganese is low compared to the true value, possibly the oxide is the MnCr_2O_4 -type spinel. The outermost reaction product, C, appears globular in some areas but elsewhere as a layer. Spalling or removal during metallographic preparation

*Possibly due to residue Al_2O_3 polishing compound.

is believed to have occurred, thus causing the apparent different morphologies of C along with the frequent absence of the Cr-Mn-O middle layer. Phase C, as identified in the x-ray strip chart of Figure 114, contains plutonium, approximately 11 wt % chromium, and oxygen. This oxide is thought to be the perovskite-type compound, PuCrO_3 , which theoretically contains 15.4 wt % chromium.

Figures 115, 116, and 117 are photomicrographs of the reaction zone after annealing for 91 and 179 days and appear similar to each other. The reaction products appear to consist of two phases and thus differ from the reaction product on the 59-day sample which contained three phases. The quantity of reaction product is less than that observed in the 59-day sample indicating spalling, mechanical removal, or oxide evaporation. A fairly continuous layer less than $5\text{ }\mu\text{m}$ thick covers the Inconel 625 making slight ($\sim 5\text{ }\mu\text{m}$) penetration into the alloy. Figure 117 is a photomicrograph of the reaction zone where the $^{238}\text{PuO}_2$ (indicated by C) has been retained, and thus the presence of all the reaction product is assured. A and B in Figure 117 (and in Figures 115 and 116) indicate the two reaction products which were found on the 91- and 179-day samples. The inner reaction product A was found to be rich in oxygen, chromium, and manganese and to contain a trace of titanium. Two analyses of A for chromium and manganese gave results of 32 and 44 wt %, and 10 and 11.8 wt %, respectively. It is probable that these values are low since the width of the oxide is only 1 to $2\text{ }\mu\text{m}$ and averaging of the composition with the matrix will occur. The oxide, assuming the above values are low, could be the MnCr_2O_4 -type spinel or a mixture of the spinel with Cr_2O_3 solid solution. Identification of the mixture is supported by the higher ratio of chromium to manganese (3.2:1 and 3.73:1 for the above two determinations) than the theoretical value for MnCr_2O_4 (1.89:1). Phase B contains oxygen, roughly 60.2 to 73.4 wt % plutonium*, and about 11 wt % chromium. Considering the crude method at which these compositions were determined, they are a fairly close match for the composition of PuCrO_3 which theoretically contains 67.3 wt % plutonium and 15.4 wt % chromium.

Figure 118 is a photomicrograph of a piece of $^{238}\text{PuO}_2$ which was retained at the sample edge. Surrounding the $^{238}\text{PuO}_2$ (except where spalling is assumed to have occurred) is the Pu-Cr-O reaction product previously identified as PuCrO_3 . The presence of a PuCrO_3 coating on the particle of fuel rather than just as a layer separating the $^{238}\text{PuO}_2$ from the Inconel 625 must indicate the presence of a gaseous form of chromium (e.g. vaporous Cr, CrO , CrO_2 , or CrO_3).

*These two values for plutonium were obtained by assuming Phase C in Figure 117 was $^{238}\text{PuO}_2$ and using it for a standard. The larger value for plutonium is more reliable as it was determined on a much larger particle which could contain the entire electron beam of the microprobe.

Compositional Changes Compositional changes found in the edge of the Inconel 625 after 59- and 189-day heat treatments are listed in Table 13. The $^{238}\text{PuO}_2$ environment depletes the edge of chromium by the formation of a surface oxide and gaseous phase which contains chromium and thus effectively enriches the alloy edge in nickel, molybdenum, and iron. Most of the iron enrichment is believed due to its presence as an impurity in the $^{238}\text{PuO}_2$. The decrease in the quantity of the iron enrichment is thought due to depletion of iron in the $^{238}\text{PuO}_2$.

Variation in Microstructure Figure 119 typifies the microstructure after 179 days at 800°C . Depth of the change in the microstructure was about 25 to 50 μm for heat treatments of 60-179 days.

Summary and Discussion The compatibility of $^{238}\text{PuO}_2$ with Inconel 625 at 800°C is described by the selective oxidation of chromium and manganese forming a multi-oxide surface product. The oxides found in the surface product appeared dependent on time-at-temperature. Figure 120 has been added to help clarify the reported identification of the interfacial reaction products after the various annealing times. Two possible explanations for the absence or decrease in the amount of Cr_2O_3 in the 91- and 179-day specimens involve transport of manganese and the selective removal of chromium. These mechanisms are discussed below.

Indications that manganese was transported to Inconel 625 are: 1) mass transport of manganese did occur in the test capsule as evidenced by the Cr-Mn-O layer on the T.D. nickel; 2) the slight enrichment of manganese in the 179-day edge conflicts with the 59-day specimen and the active participation of manganese in oxide formation; and 3) the predominant nature of manganese in oxide formation in an alloy containing only 0.05 wt % manganese.

A more rapid loss of chromium from the spinel relative to the removal of manganese would enrich the remaining oxide in manganese. This process could involve faster evaporation of a chromium-bearing species than $\text{MnO}(\text{g})$ or be caused by the formation of PuCrO_3 according to the following equation:

The resultant manganese enrichment in the remaining oxide could be relieved by the reaction of manganese with the underlying Cr_2O_3 to form MnCr_2O_4 and possibly cause the observed slight manganese enrichment at the edge of the base metal. Similar preferential loss of chromium was observed in the Hastelloy X sample annealed for 360 days at 800°C . It was postulated that a decrease in the partial pressure of oxygen in the system caused the change in oxide morphology on Hastelloy X.* This theory could also be applied to the manganese enrichment of Inconel 625.

*See Hastelloy X report on page 19 for details.

Table 13

EFFECT OF EXPOSURE TO $^{238}\text{PuO}_2$ AT 800°C ON THE COMPOSITION OF INCONEL 625^{a, b}

Element	Concentration at Edge Relative to Interior		Depth of Depletion or Enrichment into Sample (μm)		Conc. at Edge/Conc. in Interior		Concentration at Edge (wt %)		Concentration in Interior (wt %)		Concentration of Bulk Prior to Test (wt %)
	60 days at 800°C	180 days at 800°C	60 days at 800°C	180 days at 800°C	60 days at 800°C	180 days at 800°C	60 days at 800°C	180 days at 800°C	60 days at 800°C	180 days at 800°C	
Al	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.1
Co	ND	-	ND	-	ND	-	ND	-	ND	-	0.05
Cr	D	D	~150	200-300	0.83	0.89	20.7	21.2	24.8	23.8	20.8
Fe	E	E	25	75	1.13	1.10	4.4	3.4	3.9	3.1	2.7
Mn	ND	E	ND	15-25	ND	∞	ND	0.25	ND	ND	0.05
Mo	E	E	40	40	1.31	1.61	5.9	8.7	4.5	5.4	9.2
Nb	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1
Ni	E	E	70	175	1.03	1.06	66.9	62.4	64.9	58.9	75.2
Pu	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Si	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.3
Ti	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.2
V	ND	-	ND	-	ND	-	ND	-	ND	-	0.01
Zn	ND	-	ND	-	ND	-	ND	-	ND	-	ND

^aAll values were obtained by the electron microprobe with the exception of the bulk analysis performed prior to the test.^bND: Not detected; E: Enriched; D: Depleted; N: Neither enriched or depleted; -: Analysis not performed.

FIGURE 112 - Photomicrograph of Inconel 625 after 30 days at 800°C. A and B indicate inner and outer reaction products, respectively. 575X, unetched

1180X, unetched

FIGURE 113 - X-ray strip chart analysis and accompanying photomicrograph of Inconel 625 after 59 days at 800°C. Line on photomicrograph indicates position of one-dimensional scan.

FIGURE 114 - X-ray strip chart analysis and accompanying photomicrograph of Inconel 625 after 59 days at 800°C. Line on photomicrograph indicates position of one-dimensional scan.

FIGURE 115 - Photomicrograph of Inconel 625 after 91 days at 800°C. Oxides indicated by A and B contain Cr and Mn, and Pu and Mn, respectively. 575X, unetched

FIGURE 116 - Photomicrograph of Inconel 625 after 179 days at 800°C. Oxides indicated by A and B contain Cr and Mn, and Pu and Cr, respectively. 1870X, unetched

FIGURE 117 - Photomicrograph of Inconel 625 after 179 days at 800°C. A contains Cr, Mn, and O. B contains Pu, Cr, and O. C is fuel. 1870X, unetched

FIGURE 118 - Photomicrograph of Inconel 625 after 179 days at 800°C. Note particle of fuel coated with oxide containing Pu and Cr and thought to be PuCrO_3 . 720X, unetched

FIGURE 119 - Photomicrograph of Inconel 625 after 179 days at 800°C.
Note microstructural change at the edge. 275X, etched

FIGURE 120 Sketch summarizing the Inconel 625/ $^{238}\text{PuO}_2$ interaction at 800°C .

INCONEL 625 AT 1000°C

Five Inconel 625 coupons were examined after being heat treated in contact with $^{238}\text{PuO}_2$ at 1000°C for periods of 30, 60, 90, or 181 days. Their interaction resulted in a surface layer whose growth and penetration into the alloy was governed by the presence of precipitates which formed in the edge of the Inconel 625 substrate. Other effects were a subsurface reaction resulting in a precipitate with a rodlike morphology and a zone denuded of carbides.

Surface Reaction Figures 121 through 125 are photomicrographs of the reaction interface which typify the mode of surface attack. The interaction is described by the formation of a continuous reaction product and intergranular penetration. Infrequent penetration of the reaction product into the weld-affected zone is characteristic (see Figure 124) and is due to the large grains present and, therefore, fewer grain boundaries intersecting the sample edge. The thickness of the surface layer increased from 1.5-2.0 μm after 30 days to 3-4 μm after 181 days. No discernible increase in the depth of intergranular penetration by the reaction product was found. A common depth of 10 to 15 μm with a maximum at about 25 μm was observed at all heat treatments.

The surface layer appeared multiphased. Results from a point analysis of the two phases indicated by A and B in Figure 125 are given in the following table.

APPROXIMATE COMPOSITIONS OF LIGHT AND DARK REACTION
PRODUCTS FOUND ON INCONEL 625 AFTER 181 DAYS AT 1000°C^{a, b}

<u>Element</u>	Concentration in light reaction product at Point A in Figure 125 (wt %)		Concentration in dark reaction product at Point B in Figure 125 (wt %)	
	<u>normalized using 12% O</u>		<u>normalized using 12% O</u>	
Al	ND	ND	ND	ND
Cr	7.0	6.1	1.8	1.8
Fe	ND	ND	ND	ND
Mo	ND	ND	ND	ND
Nb	ND	ND	ND	ND
Ni	3.3	2.9	4.9	5.0
O	12 or 18 ^d	10.5	12 or 18 ^d	12.2
Pu	85 ^c	74.5	78 ^c	79.2
Si	ND	ND	T	T
Ti	6.8	6.0	1.8	1.8

^a ND = Not Detected; T = Trace

^b During this analysis, the electron beam tended to wander. The sample was treated with a 2% solution of detergent which stabilized the beam somewhat but not enough to ensure the accuracy of the values reported above.

^c Standard used for plutonium was a chunk of fuel entrapped on the surface of the T.D. nickel coupon which was assumed to be ²³⁸PuO₂. These values thus represent rough approximations.

^d 18 wt % oxygen was determined by comparison with a SiO₂ standard; and the 12 wt % oxygen was determined by using a chunk of fuel entrapped on the surface of the T.D. nickel coupon as a standard and assuming it to be ²³⁸PuO₂. When the SiO₂ standard was applied to the fuel, it indicated that it was ²³⁸PuO₄. Since this is impossible, the 12 wt % value for the oxygen content is considered more accurate.

Oxygen, plutonium, chromium, titanium, and nickel were found in both phases. The outer, darker phase contains less of all the metallic elements than the lighter phase except nickel which exhibits a small increase. A trace of silicon is also noted in the dark secondary phase.

A second mode of surface attack was observed when precipitates were found at the edge of the Inconel 625 as illustrated by Figures 126, 127, and 128*. A continuous oxide reaction product on the exterior edge of the precipitates is believed to have occurred but which spalled leaving the noncontinuous appearance seen in Figures 127 and 128. The edge seen in Figure 126 looks as if it is in the early stages of development of the edge seen in Figures 127 and 128. Figure 128 includes x-ray strip chart analysis of the area indicated by the line in the accompanying photomicrograph and the approximate compositions of phases A, B, and C and are listed in Table 14. The oxide phase indicated by A contained only plutonium and oxygen but its small size limits the accuracy of the analysis. Reaction product C in Figure 128 consists of plutonium, oxygen, chromium, nickel, some iron, and a trace of manganese. This oxide appears much higher in nickel than either oxides found in Figure 124. The difference in oxide composition could be real or due to erroneous results caused by wandering of the electron beam.**

Precipitate Formation Formation of precipitates was observed at the edge of all the samples but the sample heat treated for the shortest period of time (30 days). Phase B in the x-ray trace analysis of Figure 128 is one of these precipitates and its composition is given in Table 14. An opinion expressed by International Nickel Company, Inc.²⁶ was that these are M_6C carbides, rich in niobium, nickel, and molybdenum, which normally form at 1000°C. The preferential precipitation of these carbides at the edge is possibly due to enrichment of molybdenum and niobium since these elements were not observed to take part in the formation of the oxide reaction product. These carbides appear to be more inert to the $^{238}\text{PuO}_2$ environment than the matrix (see Figures 126, 127, and 128) and therefore change the appearance of the surface reaction.

The more predominant formation of these carbides in the areas seen in Figures 126, 127, and 128 relative to the area seen in Figures 121 through 125 could possibly be due to an influence by the other materials present in the same compatibility test (T.D. nickel, and Haynes 25). Since T.D. nickel acted as a getter for chromium it could have possibly increased the chromium depletion in the nearest Inconel 625 edge, effectively enriching it in the constituents of the M_6C carbides (Mo, Ni, and Nb).

*These precipitates can also be seen in Figures 121 through 124 but their occurrence is not as frequent; they are usually found deeper in the metal substrate and therefore do not affect the growth of the oxide as demonstrated in Figures 126 through 128.

**Wandering of the electron beam was a problem with this sample. The sample was treated with a 2% detergent solution which stabilized the beam somewhat but not enough to ensure accurate positioning of the beam and thus possibly the results were erroneous.

Internal Reaction Subsurface reaction resulted in rod and possibly particle formation. Maximum depth of their formation was about 35 μm after 30 days and roughly 60 μm after 180 days. Though they were assumed to be oxides, their composition is unknown as they were too small to be resolved by the electron microprobe.

Compositional Changes After 180 days at 1000°C, the composition at the edge of the Inconel 625 seen in Figure 123 had changed, but this alteration was less than experienced by any of the other superalloys after heat treatments at 800 or 1000°C. Results from a compositional analysis listed in Table 15 disclose that the relatively small depletion of chromium was the only detectable compositional variation. The small depletion of chromium relative to the other superalloys suggests that the layer of reaction product acts as a diffusion barrier.

Variation in Microstructure A zone denuded of carbides was found at the edge of the Inconel 625 below the precipitates thought to be M_6C carbides. The change in microstructure is best seen in Figure 129. Thickness of the denuded zone was about 150 μm after 181 days at 800°C.

Summary and Discussion Figure 130 contains sketches which summarize the Inconel 625/ $^{238}\text{PuO}_2$ interaction at 1000°C. A surface reaction creates a complex, multi-oxide reaction product composed primarily of plutonium, chromium, titanium, and possibly iron and manganese. A continuous layer of oxide occurs which penetrates the Inconel 625 intergranularly except where growth of the oxide is influenced by the presence of precipitates (thought to be M_6C carbides). These precipitates appear to be more noble than the matrix to the $^{238}\text{PuO}_2$ environment. Penetration of the substrate does occur in the presence of the precipitates but appears to be more solution of the surrounding matrix than intergranular penetration.

Inconel 625 had the least chromium depletion of all the chromium-bearing superalloys tested at either 800 or 1000°C. This suggests that the surface oxide is acting as a diffusion barrier.

Table 14

APPROXIMATE COMPOSITIONS FOR AREAS DESIGNATED IN FIGURE 128^b

Region	Approximate Concentration of Element Specified (wt %) ^a										
	Al	Cr	Fe	Mo	Mn	Nb	Ni	O	Pu	Si	Ti
A	ND	ND	ND	ND	ND	ND	ND	P	P	ND	ND
B	ND	11.7-14.2	0.8	34.1	0.2	10.7	51.3-31.6	ND	ND	1-2	ND
C	ND	10.4-14.2	1.8	PT	0.6	ND	51.3-33.2	P	P	ND	0.7
Edge of Substrate	ND	18.3	3.2	4.5	0.9	ND	69.4	ND	ND	ND	ND

^a PT: possible trace; P: present; ND: not detected

^b During this analysis, the electron beam tended to wander. The sample was treated with a 2% solution of detergent which stabilized the beam somewhat but not enough to ensure the accuracy of the values reported.

Table 15

EFFECT OF EXPOSURE TO $^{238}\text{PuO}_2$ FOR 181 DAYS AT 1000°C UPON THE COMPOSITION OF INCONEL 625^{a, b}

Element	Concentration at Edge Relative to Interior	Depth of Depletion or Enrichment into Sample (μm)	Conc. at Edge/ Conc. in Interior	Concentration at Edge (wt %)	Concentration in Interior (wt %)	Concentration in Bulk Prior to Test (wt %)
Al	ND	ND	ND	ND	ND	0.1
Cr	D	200	0.94	20.1	21.3	20.8
Fe	N	0	1.00	3.2	3.2	2.7
Mo	N	0	1.00	4.6	4.6	9.2
Mn	N	0	1.00	0.9	0.9	0.05
Nb	N	0	1.00	T	T	1.1
Ni	N	0	1.00	61.2	61.2	75.2
O	ND	ND	ND	ND	ND	0.002
Pu	ND	ND	ND	ND	ND	ND
Si	ND	ND	ND	ND	ND	0.3
Ti	ND	ND	ND	ND	ND	0.2

^a All values were obtained by the electron microprobe with the exception of the bulk analysis made prior to the test.^b E: Enrichment; D: Depletion; N: Neither Enrichment or Depletion; ND: Not detected; T: trace.

FIGURE 121 - Photomicrograph of Inconel 625 after 90 days at 1000°C.
575X, unetched

FIGURE 122 - Photomicrograph of Inconel 625 after 90 days at 1000°C.
575X, unetched

FIGURE 123 - Photomicrograph of Inconel 625 after 181 days at 1000°C.
275X, unetched

FIGURE 124 - Photomicrograph of Inconel 625 after 90 days at 1000°C,
typical position of weld affected zone. 575X, unetched

FIGURE 125 - Photomicrograph of Inconel 625 after 181 days at 1000°C.
1120X, unetched

FIGURE 126 - Photomicrograph of Inconel 625 after 90 days at 1000°C.
575X, unetched

FIGURE 127 - Photomicrograph of Inconel 625 after 90 days at 1000°C.
575X, unetched

FIGURE 128 - X-ray strip chart analysis and accompanying photomicrograph of Inconel 625 after 60 days at 1000°C. Composition of A, B, and C are given in Table 14.

FIGURE 129 - Photomicrograph of Inconel 625 after 181 days at 1000°C. Note change in microstructure of the base metal at the edge. 275X, etched

FIGURE 130 - Sketches depicting the Inconel 625/²³⁸PuO₂ interaction at 1000°C. B shows the interface where the precipitates (thought to be carbides) have influenced the attack.

T. D. NICKEL AT 800°C

Five coupons of T. D. (thoria dispersed) nickel were examined after 30, 59, 91, and 179 days of exposure to $^{238}\text{PuO}_2$ at 800°C. Except for void formation the T. D. nickel appeared unaffected in the 30-, 59-, and 91-day samples, but two surface oxides were detected on the 179-day sample. One of the oxides occurred as a result of the mass transport of chromium and manganese. As a consequence of the mass transport, this determination of the compatibility of T. D. nickel with $^{238}\text{PuO}_2$ is rendered ineffective.

Mass Transport of Chromium and Manganese Evidence of mass transport was found by electron microprobe examination of the edge of the 30-day specimens and of the surface oxides and edge of the 179-day specimen. The predominantly occurring oxide (indicated by A in Figures 131 and 132) was mostly observed in the mounting material although small pieces did remain on the metallic substrate as indicated in Figure 131. Analysis of this oxide found approximately 32.8 wt % chromium, 9.1 wt % manganese, and trace amounts of plutonium, silicon, and aluminum*. The edge of the T. D. nickel also contained trace amounts of chromium and manganese (see Table 16). Since the analysis of the T. D. nickel prior to the compatibility test did not show any chromium and only 0.001 wt % manganese, mass transport of these elements is evident. Transport of chromium and manganese is possibly due to the dissociative vaporization of the surface oxides** on Inconel 625 and Haynes 25 present in the same compatibility capsule.

Surface Reaction A second surface oxide was observed on the 179-day sample. It was found only once and this single occurrence is seen in Figure 132 where the oxide particle is denoted by B. Analysis of this particle found oxygen, plutonium, about 1.4 wt % silicon***, a small amount of thorium at the edge nearest the metallic substrate, trace amounts of chromium and manganese, and a possible trace of nickel. Since oxide B contains only trace amounts of chromium and manganese, its occurrence is probably independent of their mass transport. The presence of only a possible trace of nickel also indicates a formation independent of the nickel matrix. Its occurrence is possibly due to the presence of

*Possible residue Al_2O_3 polishing compound.

**Possible gaseous species are $\text{Cr}(\text{v})$, $\text{Mn}(\text{v})$, CrO , CrO_2 , CrO_3 , and MnO .

***T. D. Nickel contained 0.001 wt % silicon prior to the test.

a thorium agglomerate at the surface, or an anomaly caused by contamination of the sample prior to the test or by the $^{238}\text{PuO}_2$. If the oxide is not due to sample contamination, it would mean that $^{238}\text{PuO}_2$ would react with any thorium* at the surface of the T. D. nickel.

Compositional Changes Table 16 summarizes the analyses of the edges of the 30- and 179-day samples. Besides the slight enrichment of chromium and manganese, iron enriches the edge causing nickel to appear depleted. Enrichment of iron is due to its presence as an impurity in the $^{238}\text{PuO}_2$.

Void Formation Figures 133 through 136 are photomicrographs of the T. D. nickel samples annealed for 30, 59, 91, and 179 days, respectively. These figures portray the void formations which occur along the sample edge. The density of voids appears to reach a maximum in the 59-day sample and then they decrease in number until they are almost completely absent in the 179-day sample. Figure 133 includes an x-ray strip chart analysis of the 30-day specimen with the position of the voids indicated. Possible dependence on the iron content at the edge is suggested by location of the voids relative to the iron enrichment.

A possible explanation for the formation of voids is the removal of nickel from the sample edge at a rate which is faster than the deposition of iron, manganese, and chromium. The vacancies thus created coalesce into the observed voids. Since a nickel-bearing oxide was not found on the T. D. nickel, removal of the nickel could be by the formation of NiO(g) or by dissolution of the nickel by the $^{238}\text{PuO}_2$. The decrease in the density of the voids with time at temperature is possibly due to a decrease in the rate of removal of nickel**. This could be caused by the lowering of the partial pressure of oxygen in the system forcing a reduction in the rate of NiO(g) formation; or due to the Cr-Mn-O surface layer acting as a diffusion barrier to nickel.

Summary and Discussion The determination of the compatibility of T. D. nickel with $^{238}\text{PuO}_2$ was hindered by the mass transport of manganese and chromium to the sample edge causing the formation of a Cr-Mn-O surface layer. Other effects include the single observation of a Pu-Si-Th-O phase and the formation of voids.

Conclusions drawn from the above test are:

1. Possible interaction with the test environment was observed resulting in the formation of voids near the T. D. nickel edge. The process of void formation could be by removal of nickel by the formation of NiO(g) and appears to decrease with time at temperature.

* ThO_2 and PuO_2 reportedly form a solid solution.^{12,13}

**Since the rate at which Fe, Mn, and Cr are deposited decreases with time (see Table 16), the rate of nickel removal would have decreased even faster so that it becomes less than or equal to the rate of deposition of Fe, Mn, and Cr.

2. Thoria and $^{238}\text{PuO}_2$ appear to interact when in contact. The thoria dispersed in the nickel was unaffected by the compatibility test.

Table 16

EFFECT OF $^{238}\text{PuO}_2$ UPON THE COMPOSITION OF T.D. NICKEL AT 800°C ^{a, b}

Element	Concentration at Edge Relative to Interior		Depth of Depletion or Enrichment into Sample (μm)		Conc. at Edge/Conc. in Interior		Concentration at Edge (wt %)		Concentration in Interior (wt %)		Concentration in Bulk Prior to Test (wt %)
	30 days	179 days	30 days	179 days	30 days	179 days	30 days	179 days	30 days	179 days	
Al	-	ND	-	ND	-	ND	-	ND	-	ND	0.05
Cr	E	E	25	35	∞	∞	T	0.2	ND	ND	ND
Fe	E	E	55	85	∞	∞	3.9	~ 5	ND	ND	0.02
Mn	E	E	45	85	∞	∞	0.7	1.2	ND	ND	0.001
Mo	-	ND	-	ND	-	ND	-	ND	-	ND	ND
Ni	D	D	50	90	0.93	0.93	90.5	94.2	97.5	100.2	97.93
Pu	-	ND	-	ND	-	ND	-	ND	-	ND	ND
Si	-	ND	-	ND	-	ND	-	ND	-	ND	0.001
Th	N	N	0	0	1.00	1.00	T	T	T	T	1.9

^a All values were obtained by the electron microprobe with the exception of the bulk analysis prior to the test.^b D: depleted; E: enriched; N: neither depleted or enriched; ND: not detected; T: trace; -: analysis not performed.

FIGURE 131 - Photomicrograph of T.D. nickel after 179 days at 800°C. The oxide indicated by A is composed of Cr and Mn. 1950X, unetched

FIGURE 132 - Photomicrograph of T.D. nickel after 179 days at 800°C. 770X, unetched

FIGURE 133 - X-ray strip chart analysis and photomicrograph of T.D. nickel after 30 days at 800°C. Arrow on photomicrograph indicates traverse of the electron microprobe.

FIGURE 134 - Photomicrograph of T.D. nickel after 59 days at 800°C.
56.4X, unetched

FIGURE 135 - Photomicrograph of T.D. nickel after 91 days at 800°C.
56.4X, unetched

FIGURE 136 - Photomicrograph of T.D. nickel after 179 days at 800°C.
70.5X, unetched

T. D. NICKEL AT 1000°C

Five T.D. nickel coupons were examined after being exposed to $^{238}\text{PuO}_2$ at 1000°C for 30, 60, 90, or 181 days. Determination of the compatibility was masked by mass transport of chromium and manganese to the T.D. nickel. Besides the effect caused by the mass transport no other deterioration of the sample edge was observed.

Mass Transport of Chromium and Manganese The mass transport of chromium and manganese resulted in increased thickness of the coupon as noted in the following table.

EFFECT OF EXPOSURE TO THE CAPSULE ENVIRONMENT FOR VARIOUS TIMES AT 1000°C UPON THE THICKNESS OF THE T.D. NICKEL COUPONS^a

<u>Time at Temperature (days)</u>	<u>Thickness (cm)</u>
0	0.124 - 0.126
30	0.126
60	0.127
90	0.129 - 0.130
90	0.130 - 0.131
181	0.132

^a Measurements were made on photomicrographs of the samples, thus possible error is introduced by slanting of the specimens in the mounts.

The deposit of manganese and chromium also caused the formation of metallic protrusions at the coupon ends*. Figures 137 through 139 are photomicrographs of these projections which have entrapped particles of $^{238}\text{PuO}_2$.

* The end of the coupon refers to the 0.125-cm transverse edge of the sheet stock. For its relative position in the capsule see Appendix C-2.

Results of an electron microprobe examination of a typical portion of the sample edge after it had been exposed to the capsule environment for 181 days (a portion similar to that seen in Figure 140) are given in Table 17. The analysis determined that about 3.4 wt % chromium, 6.4 wt % manganese, and a trace of iron were found at the sample edge. Analysis of the metallic protrusions seen in Figure 138 found a similar amount of manganese but about a 75% increase in the chromium content. Diffusion depths of chromium and manganese could not be determined as its inward diffusion from both sides of the 0.130-cm coupon had completely permeated it. Prior to the test no chromium and only 0.001 wt % manganese were found in the T.D. nickel; however, after 180 days at 1000°C, 0.2 wt % chromium and 2.2 wt % manganese were found at the center of the sample.

Haynes 25, Inconel 625, and T.D. nickel were present in the same test capsule (see capsule design No. 2 in Appendix C). Depletions of chromium and manganese in Haynes 25 and the relatively small depletion of chromium in Inconel 625 (see Tables 9 and 15), indicate that these two materials are the probable source of these two contaminating elements. The small amount of iron found at the T.D. nickel edge is probably from the iron present as an impurity in the $^{238}\text{PuO}_2$.

Mass transport of chromium and manganese are thought to be due to the formation of volatile species at the $^{238}\text{PuO}_2$ /scale interface of the Haynes 25 and Inconel 625. Evidence supporting vapor deposition is the development of metallic protrusion enveloping the $^{238}\text{PuO}_2$ particles rather than uniform growth below the $^{238}\text{PuO}_2$. Possible gaseous species formed are MnO , $\text{Cr}(\text{v})$, CrO , CrO_2 , and CrO_3 . Observations on the standard capsule indicated that the $^{238}\text{PuO}_2$ environment is necessary for the manganese transport and thus suggests that manganese vapor is not responsible for its transport.

Compatibility of "Alloyed" T.D. Nickel No interaction between the "alloyed" T.D. nickel and the $^{238}\text{PuO}_2$ was detected. Figure 140 is a photomicrograph of a typical portion of the sample after exposure to the capsule environment for 181 days at 1000°C. The surfaces of this sample and of those with shorter heat treatments appear clean with no visual evidence of reaction with the $^{238}\text{PuO}_2$. Electron microprobe analysis of the portion of the end of the coupon seen in Figure 138 did not detect any reaction product between the $^{238}\text{PuO}_2$ and the "alloyed" T.D. nickel. No plutonium was found in the base metal; however, trace amounts of manganese, chromium, and nickel in the $^{238}\text{PuO}_2$ were indicated. Close examination of Figure 138 reveals small metallic particles in the $^{238}\text{PuO}_2$ where the trace amounts of manganese, chromium, and nickel were found. These particles could be part of a tiny metallic network running through the porous chunks of $^{238}\text{PuO}_2$ and ending at the base metal (which could account for their nickel content); or they could be isolated particles. If they are isolated particles it would mean that nickel was removed from the T.D. nickel possibly by either $\text{NiO}(\text{g})$ formation or by dissolution.

There was no observed effect of the $^{238}\text{PuO}_2$ on the thoria as thorium was detected in a trace amount throughout the coupon.

Summary and Discussion This experiment did not determine the compatibility of T.D. nickel with $^{238}\text{PuO}_2$ at 1000°C because of side reactions caused by the presence of Haynes 25 and Inconel 625 in the same test capsule as the T.D. nickel. These side reactions caused the deposition of manganese and chromium onto the surface of the T.D. nickel.

Although the compatibility remains undetermined, several conclusions can be made.

- Since a reaction product was not found below or mixed with the manganese and chromium deposit, rapid interaction between T.D. nickel and the fuel forming a stable* reaction product does not occur.
- A thoria-dispersed, nickel base alloy containing 3 to 6 wt % manganese appears unaffected by the fuel at 1000°C . Since this concentration represents a maximum reached after 181 days, lesser concentrations are assumed in the 30, 60, and 90 day samples. Because no interaction was seen with any of these other samples, the lower concentration of chromium and manganese are compatible at the shorter heat treatments.
- Slow removal of nickel is possible. The process of removal could be by formation of $\text{NiO}(\text{g})$ or by dissolution. It was also thought possible that nickel was drawn from the T.D. nickel heat treated at 800°C . No other evidence of nickel migration was observed.

* The partial pressure of oxygen is believed to be lowered during the early stages of the test (see next section on 800 and 1000°C T.D. nickel compatibility), thus possibly causing a phase which forms initially to become unstable and decompose.

Table 17

EFFECT OF EXPOSURE TO $^{238}\text{PuO}_2$ FOR 90 DAYS AT 1000°C UPON THE COMPOSITION OF T.D. NICKEL^{a, b}

Element	Concentration at Edge Relative to Interior	Depth of Depletion or Enrichment Into Sample (μm)	Concentration at Edge/Concentration at Interior	Concentration at Edge (wt %)	Concentration in Interior (wt %)	Concentration in Bulk Prior to Test (wt %)
Al	ND	ND	ND	ND	ND	0.35
Co	ND	ND	ND	ND	ND	0.1
Cr	E	To center of coupon, $650\mu\text{m}^d$	^c	3.4	0.2 ^d	ND
Fe	E	250	^c	T	ND	0.32
Mn	E	To center of coupon, $650\mu\text{m}^d$	^c	6.4	2.2 ^d	0.001
Mo	ND	ND	ND	ND	ND	ND
Nb	ND	ND	ND	ND	ND	ND
Ni	D	To center of coupon, $650\mu\text{m}^d$	0.92	85.7	92.9	97.8
Pu	ND	ND	ND	ND	ND	ND
Si	ND	ND	ND	ND	ND	0.001
Th	N	0	0	T	T	1.9
Ti	ND	ND	ND	ND	ND	ND
Zn	ND	ND	ND	ND	ND	ND

^a T: trace; E: enrichment; D: depletion; N: neither enrichment or depletion; ND: not detected.^b All values were obtained with the electron microprobe with exception of the bulk analysis performed prior to the test.^c Since these elements were not present initially, any amount found at the edge would give an infinite value to the change in weight percent.^d Result of complete permeation of the test coupon by these elements.

FIGURE 137 - Photomicrograph of the end of the T. D. nickel coupon after 181 days at 1000°C. 275X, unetched

FIGURE 138 - Photomicrograph of the end of the T.D. nickel coupon after 181 days at 1000°C. 1120X, unetched

FIGURE 139 - Photomicrograph of the end of the T.D. nickel coupon after 181 days at 1000°C. 275X, etched

FIGURE 140 - Photomicrograph of T.D. nickel after 181 days at 1000°C. 275X, unetched

DISCUSSION

800 and 1000°C T.D. Nickel Compatibility The presence of other alloys in the same test environment influenced the interaction between T.D. nickel and $^{238}\text{PuO}_2$ in two ways. Besides the contamination of the T.D. nickel with manganese and chromium which has been discussed previously, the presence of elements in the system which form stable oxides (i.e., Cr, Mn, Si, and Ti) is believed to have caused the $^{238}\text{PuO}_2$ to become substoichiometric. This would effectively reduce the partial pressure of oxygen in the system and possibly produce conditions in which a reaction product which would normally form on T.D. nickel (such as NiO which normally forms on T.D. nickel as a result of oxidation²⁷⁻²⁹) to be unstable.

Figure 3A gives a possible indication of the true compatibility of T.D. nickel with $^{238}\text{PuO}_2$. The respective positions of the lines representing the ΔG_{O_2} for NiO and PuO_2 indicate that nickel will not draw oxygen from $^{238}\text{PuO}_2$ in order to form NiO. Therefore, the only stable formation of NiO would have to result from the normal dissociation of $^{238}\text{PuO}_2$ when it is heated or from the oxygen in the system left from the atmosphere present during sample preparation.

One difference between the specimens heat treated at the two temperatures is the absence of the Cr-Mn-O layer on the 1000°C samples, even though a much larger deposit of chromium and manganese occurred. The proposed explanation for this phenomenon is based on a faster reduction of the partial pressure of oxygen in the samples annealed at 1000°C than at 800°C. Thus, prior to 30 days at 1000°C, the partial pressure of oxygen in the system is below the equilibrium pressure for the Cr-Mn-O phase and it decomposes. If the 800°C samples were to be heat treated for longer periods of time, it is probable that partial pressure of oxygen would be lowered enough so the Cr-Mn-O layer would dissociate*.

800°C Compatibility A summary of the 800°C compatibility of $^{238}\text{PuO}_2$ and each of the six nickel- and cobalt-base alloys is given in Table 19 as an aid for comparison. The observed interaction can be separated into two categories.** The first includes all of the alloys annealed for 181 days or less and the second covers the alloys (Hastelloy N, Haynes 188, and Hastelloy X) heat treated for 360 days. Interaction with the alloys annealed for 181 days or less was dominated by the selective oxidation

*Dissociation or partial dissociation of Cr_2O_3 and MnCr_2O_4 was observed on Hastelloy N, Haynes 188, and Hastelloy X after exposure to 800°C for 360 days.

**A proposed explanation for the two categories has been discussed in the individual discussions of Hastelloy N, Hastelloy X, and Haynes 188 and will also be included in a subsequent discussion comparing 800 and 1000°C.

of chromium and manganese forming a multioxide reaction product. Suggested identifications of these oxides* are Cr_2O_3 , an overlying layer of manganese-rich spinel (i.e., MnCr_2O_4), and an outer formation of the perovskite-type compound PuCrO_3 . The formation of PuCrO_3 is possibly delayed 60 or more days at temperature.

Interaction observed in the alloys annealed for 360 days was characterized by the decrease or absence of the manganese-rich spinel and Cr_2O_3 which had formed during shorter heat treatments. A more predominant formation of the PuCrO_3 and the occurrence of a Pu-Si-O phase appeared to replace the oxides which formed initially.

The behavior of each element which was considered will be described separately. The descriptions are meant to be general in order to be applicable to all the alloys. However, where it is felt necessary, the individual alloys are discussed. Determination of the role played by each element was hampered considerably by the small size of the oxides relative to the resolution of the electron microprobe and by small metallic particles which were distributed in many of the oxides. Both of these hinderances would exaggerate the detected concentration in the oxide of the elements that are present in the metal and decrease the detected concentration of elements enriched in the oxides.

When the behavior of each element is examined, consideration must be given to the activity of the element in the alloy, as a change in its activity could change its behavior. Also, each element is affected by the behavior of the other elements. This is exemplified in this test by chromium and manganese acting as sacrificial elements, thus protecting the other elements.

Aluminum Detected in trace amounts in the oxides of all the alloys tested including Hastelloy X and Haynes 25 which did not originally contain aluminum. Visual examination of the samples under polarized light found residue Al_2O_3 polishing compound. Therefore, the detection of aluminum could be due to Al_2O_3 polishing compound. The origin of the aluminum could also be from the aluminum impurity in the fuel. Even if aluminum does take part in forming some of the oxides it was never found in more than trace quantities, and thus could not be considered a controlling factor in the compatibility.

Cobalt The cobalt content of the oxides on the cobalt-base alloys is uncertain due to the presence of metallic particles (presumably

*Variations did occur in the oxides which formed. For deviations refer to Table 19 or the individual discussions of the alloys.

enriched in cobalt) in the oxides or due to the small size of the oxides making them impossible to resolve. Results obtained are listed below.

<u>Alloy</u>	<u>Heat Treatment (days)</u>	<u>Oxide</u>	<u>Cobalt Content</u>
Haynes 25	179 or less	Mn-rich spinel	depleted 35 to 90% as gradient away from base metal
	179 or less	PuCrO ₃	absent
Haynes 188	181 or less	Cr ₂ O ₃ ^a	trace
	181 or less	MnCr ₂ O ₄ ^a	trace to 5 wt %
	360	PuCrO ₃	absent
	360	Pu-Si-O	depleted

^a absent in 360-day sample

Chromium Chromium reacts readily with the ²³⁸PuO₂ environment. Several suggested mechanisms involving chromium are listed below.

1. Formation of Cr₂O₃ on all the chromium-bearing alloys annealed for 181 days or less except Haynes 25. Haynes 25 had the highest manganese content, possibly encouraging spinel formation rather than Cr₂O₃. Formation of Cr₂O₃ by the reduction of ²³⁸PuO₂ to ²³⁸Pu₂O₃ according to the reaction:

$$\Delta G_f = +22 \text{ kcal at } 1000^\circ\text{K}^{15}$$

gives a positive free energy change. Therefore, the Cr₂O₃ is believed a result of the partial reduction of ²³⁸PuO₂ by chromium-forming ²³⁸PuO_{2-x}. Figure 3A indicates that chromium will draw oxygen from ²³⁸PuO₂ at 800°C until its stoichiometry is between ²³⁸PuO_{1.986} and ²³⁸PuO_{2.00}. At that point the chemical potential of oxygen will be the same in each oxide and no further reduction will occur.

2. Formation of an oxide rich in chromium and manganese on all the alloys annealed for 181 days or less. See items 1, 2, and 3 describing the behavior of manganese.
3. Formation of a Pu-Cr-O compound containing 9 to 15 wt % chromium and, in the one determination possible, roughly 60 to 73 wt %

plutonium. It is proposed that it is the perovskite-type compound, PuCrO_3 . PuCrO_3 theoretically contains 15.4 wt % chromium and 67.3 wt % plutonium, a close match to the crude experimental determination. It was observed on Haynes 188 heat treated for 360 days, Inconel 625, Hastelloy X, and Hastelloy N. On Haynes 25 (highest in manganese) a similar oxide was observed but possibly contained some manganese (≤ 10 wt %) indicating a mixture of PuCrO_3 and PuMnO_3 (both perovskite-type compounds) or their solid solution. The PuCrO_3 was also observed as a coating on $^{238}\text{PuO}_2$ particles along the edge of Inconel 625 suggesting that it is (at least in this case) a product of a reaction between the $^{238}\text{PuO}_2$ and a gaseous chromium phase.

4. Production of a gaseous chromium-bearing phase possibly due to the sublimation of Cr_2O_3 or the manganese-rich spinel. Volatilization of Cr_2O_3 is well known and possibly involves the formation of CrO , CrO_2 , and CrO_3 .³⁰⁻³² Mass transport of chromium to T.D. nickel and formation of a PuCrO_3 coating on $^{238}\text{PuO}_2$ particles give evidence of a gaseous phase.
5. After initial formation of Cr_2O_3 at the reaction interface, chromium is internally oxidized in Hastelloy N. Except for possible formation of a manganese-rich spinel near the edge, the subsurface oxide particles were too small to resolve with the electron microscope and therefore remained unidentified.
6. After 360 days at 800°C all chromium-bearing oxides (Cr_2O_3 , MnCr_2O_4 , and the chromium-enriched suboxides in Hastelloy N) appeared to have totally dissociated on Haynes 188 and Hastelloy N, and partially dissociated on Hastelloy X.

As a result of the above reactions, the edge of the alloys became depleted of chromium. Chromium depletion led to the formation of Kirkendall voids in three alloys exhibiting the greatest depletion (Hastelloy N, Hastelloy X, and Haynes 188). The voids appeared to preferentially form in the grain boundaries indicating more rapid diffusion in the grain boundaries.

Iron The concentration of iron in any of the oxides (except in Hastelloy N*) is believed to be ≤ 1 wt %. Iron was also a major impurity in the $^{238}\text{PuO}_2$ but remained depleted in the oxides while enriching the metallic matrixes. It is thus considered a passive element.

* The internal oxides which formed in Hastelloy N, except for those nearest the edge, were too small to resolve with the electron microprobe. Consequently, their composition remains undetermined. Chromium, manganese, vanadium, and zinc were the only elements found enriched in these oxides; while nickel, iron, and molybdenum were depleted (concentrations of nickel, iron, and molybdenum were less than 50, 12, and 5 wt %, respectively).

Lanthanum Lanthanum was present only in Haynes 188. It was found associated with a reaction product only once, as a trace quantity in a basically Pu-Cr-O phase in the 360-day sample.

Manganese Manganese reacted with the $^{238}\text{PuO}_2$ environment. The manganese/ $^{238}\text{PuO}_2$ interaction took on the following characteristics:

1. Selective oxidation of manganese in nickel-base alloys containing about 20 wt % chromium and annealed for 181 days or less formed a Cr-Mn-O surface layer. The oxide is thought to be the MnCr_2O_4 -type spinel or its mixture with Cr_2O_3 . Promotion of spinel formation by manganese has been previously reported.³³ Table I indicates that pure manganese will not reduce $^{238}\text{PuO}_2$ to $^{238}\text{Pu}_2\text{O}_3$. According to the thermodynamic data for $\text{PuO}_{1.61}$ to $\text{PuO}_{2.00}$ reported by Markin et al.¹⁶ displayed in Figure 3A, manganese can reduce the stoichiometry of $^{238}\text{PuO}_2$ to about $^{238}\text{PuO}_{1.92}$ at 800°C by forming MnO. It is thus considered possible that MnO forms, but subsequently reacts with Cr_2O_3 to form MnCr_2O_4 . Also possible is the solution of MnO in Cr_2O_3 as shown in the phase diagram given in Figure 4. MnCr_2O_4 spinel then forms upon increasing MnO content.
2. Selective oxidation of manganese in nickel-base alloy containing 7.3 wt % chromium (Hastelloy N) and annealed for 181 days or less formed two morphologies of oxide enriched in chromium and manganese. The one closest to the edge was a semicontinuous layer thought to be the MnCr_2O_4 -type spinel. Below this layer oxide particles were formed but their composition (other than enrichment of chromium and manganese and depletion of nickel, iron, and molybdenum) could not be determined as the particles were too small to resolve.
3. Selective oxidation of manganese in cobalt-base alloys exposed to 800°C for 181 days or less formed the same manganese-rich spinel as on the nickel-base alloys but it possibly contained some cobalt (see previous discussion of cobalt), and thus a cobalt-bearing mixed spinel is considered possible. Also on Haynes 25 a Pu-Cr-Mn-O reaction product was observed. It is believed to be a mixture of the perovskite-type compounds PuCrO_3 or their solid solution.
4. Mass transport of manganese occurred as evidenced by the Mn-Cr-O scale and enrichment of manganese at the edges of T.D. nickel and possibly of Inconel 625 (T.D. nickel and Inconel 625 originally contained 0.001 and 0.05 wt % manganese, respectively). Possible explanation of the transport is dissociative vaporization of the manganese-rich spinel on Haynes 25 giving MnO(g) .
5. After 360 days at 800°C all manganese-bearing oxides (manganese-rich spinels and the manganese-enriched suboxides in Hastelloy N) appeared to have totally dissociated on Haynes 188 and Hastelloy N and partially dissociated on Hastelloy X. The dissociation caused the enrichment of manganese at the edge of the metallic substrate.

Due to the above reactions, all the alloys containing 0.4 wt % manganese became depleted of manganese at the edge when annealed for 181 days or less. The depletion possibly encouraged the formation of Kirkendall voids found in some of the alloys. Alloys containing 0.05 and 0.001 wt % manganese became slightly enriched in manganese at the edge due to its mass transport from other alloys in the system.

Molybdenum Molybdenum is thought to be inert to $^{238}\text{PuO}_2$.*

Niobium Niobium was present only in Inconel 625 as a minor constituent (1.1 wt %). It was not detected in the reaction product and therefore was considered inert.

Nickel Maximum nickel content detected in the oxide reaction products was 2 to 5 wt %.* The actual nickel content could not be determined due to resolution limitations of the electron microprobe. Void formation in T.D. nickel suggests possible removal of nickel. Removal of nickel could be by formation of $\text{NiO}_{(g)}$ or by dissolution.

Silicon Silicon was detected in a small amount (1.4 wt %) in the single occurrence of a Pu-Si-Th-O reaction product on T.D. nickel. It was not found in any other reaction product on any of the alloys which were annealed for 181 days or less. A trace amount of silicon was found associated with the reaction product composed primarily of plutonium and oxygen in Hastelloy N (0.70 wt % Si) and Haynes 188 (0.60 wt % Si) after 360 days at 800°C. This phase was absent in Hastelloy X (0.15 wt % Si) after the same heat treatment. Silicon is considered inactive during the initial stages of interaction but later forms a Pu-Si-O phase if its concentration is 0.60 wt % or greater.

Thorium (present as ThO_2) Thorium is present only in T.D. nickel. A trace of thorium was found associated with the single occurrence of a reaction product composed of plutonium, oxygen, and silicon. It appears possible that thorium will interact with $^{238}\text{PuO}_2$ if in contact.

Titanium Titanium is present only in Inconel 625 (0.2 wt %) and Haynes 188 (0.02 wt %). It was detected in trace amounts (≤ 1 wt %) in all oxides on Inconel 625 and was absent in the oxides of Haynes 188. Therefore, only solution of titanium by the oxides was observed.

Vanadium Vanadium was detected in trace quantities in some of the oxides of Hastelloy N; its presence coincides with chromium and the

* The internal oxides formed in Hastelloy N when annealed for 181 days or less, except for those nearest the edge, were too small to resolve with the electron microprobe. Consequently, their composition remains undetermined. Chromium, manganese, vanadium, and zinc were the only elements found enriched in these oxides; while nickel, iron, and molybdenum were depleted (concentration of nickel, iron, and molybdenum was less than 50, 12, and 5 wt % respectively).

absence of manganese. Possible formation of $(\text{Cr},\text{V})_2\text{O}_3$ solid solution occurs on samples annealed for 181 days or less.

Tungsten Trace amounts were seen in oxide on Haynes 25; however, its presence is thought due to the resolution limitations of the electron microprobe. Tungsten is thus considered inactive in the $^{238}\text{PuO}_2$ environment.

Zinc Present only as an impurity in the $^{238}\text{PuO}_2$, it was initially concentrated in the Cr-Mn-O reaction products, possibly in the form of $(\text{Mn},\text{Zn})\text{Cr}_2\text{O}_4$. Zinc was also found in trace quantities in Cr_2O_3 . With increasing time at temperature zinc appears to move into the base metals, remaining only in trace amounts in the oxides. This indicates zinc depletion of the $^{238}\text{PuO}_2$. The egression of zinc from the oxide suggests that it would not actively participate in oxide formation if initially in the alloy.

The following table can be used to compare the depletion of chromium with the surface scale of all the alloys containing about 20 wt % chromium.

Alloy	$\Delta\text{Wt } \% \text{ of Cr}$ at sample edge	Time at Temperature (days)	$\Delta\text{Wt } \%$ /day	Scale ^a
Haynes 25	4	91	0.044	Mn-rich spinel
	6	179	0.033	Mn-rich spinel
Inconel 625	17	60	0.28	Cr_2O_3 + overlying Mn-rich spinel
	11	179	0.062	Mn-rich spinel
Haynes 188	23	60	0.38	Cr_2O_3 + overlying Mn-rich spinel
	34	181	0.19	
	49	181	0.27	
	≥ 62	360	≥ 0.17	PuCrO_3
Hastelloy X	24	30	0.80	Cr_2O_3 + overlying Mn-rich spinel
	27	90	0.31	
	59	360	0.16	PuCrO_3

^aAll of the Cr_2O_3 scales were continuous while only the spinel scales on Haynes 25 and the 179-day Inconel 625 sample were continuous.

From the above table two general trends are noted. First is that the single continuous layer of the manganese-rich spinel found on Haynes 25 and the 179-day Inconel 625 sample appears more protective against chromium depletion than the double layer of Cr_2O_3 and noncontinuous spinel. Assuming similarities among MnCr_2O_4 , CoCr_2O_4 , and NiCr_2O_4 spinels, the suggested protective nature of MnCr_2O_4 agrees with data reported in Kofstad,³⁴ stating that the diffusion of chromium in CoCr_2O_4 and NiCr_2O_4 is slower than in Cr_2O_3 . Wlodek³⁵ and Wasielewski²¹ attribute the protective behavior of the manganese-rich spinel which covers Cr_2O_3 to the reduction in the formation of volatile chromium-bearing species. The second trend is that the change in weight percent per day decreases with time at temperature. This could be explained by secondary formation of a protective manganese-rich spinel or by the decrease in the partial pressure of oxygen in the system.

1000°C Compatibility The compatibility of these six nickel-and cobalt-base alloys was characterized by the reaction of chromium and the strong oxide-forming minor constituents (Si, Ti, Mn, V, La, and possibly Al) with $^{238}\text{PuO}_2$. Except for T.D. nickel, the interaction between the $^{238}\text{PuO}_2$ and the test materials resulted in a plutonium-bearing surface oxide. Subsurface reactions included intergranular oxidation and intragranular precipitation of small particles assumed to be oxides. Except for Inconel 625, the major elements (Ni, Co, and Fe) did not enter into the reaction with the capsule environment. The refractory metals (W and Mo) appeared completely inert to the $^{238}\text{PuO}_2$. These observations verify Figure 3A. Table 20 summarizes the effect of the $^{238}\text{PuO}_2$ environment upon each of the alloys tested as an aid for comparison.

Below is a description of the elemental behavior discussed collectively for all the superalloys. Individual alloys are mentioned; however, where possible their comparable behavior is presented. Since the behavior of each alloy is dependent upon the presence of other elements, a change in the compatibility with normal fluctuation in alloy composition must be considered.

Aluminum Aluminum was detected in the internal oxides of Haynes 188 and Hastelloy X. Since Hastelloy X did not originally contain aluminum and visual examination of the samples under polarized light found Al_2O_3 polishing compound, the detection of aluminum is possibly due to residue Al_2O_3 polishing compound. The detection of aluminum could also be due to its presence as an impurity in the fuel.

Cobalt Cobalt was detected only in the Haynes 25 surface scale but in a trace amount. It is thus considered fairly inert to $^{238}\text{PuO}_2$.

Chromium Chromium appears to react readily with the capsule environment. All of the chromium-bearing superalloys tested became depleted of chromium at their edge causing in some cases, formation of Kirkendall voids. Three reactions involving chromium have been proposed.

A Pu-Cr-O phase containing 10 to 14.5 wt % chromium was found on Hastelloy N, Haynes 188, and Hastelloy X. It is suggested that it is the perovskite-type compound PuCrO_3 , which contains 15.4 wt % chromium, a fair match to the relatively crude determination of 10 to 14.5 wt % chromium in the Pu-Cr-O reaction product.

The three superalloys on which the PuCrO_3 was found were all in the same test capsule, while the PuCrO_3 was not observed on any of the other superalloys in the other test capsule. If this is not a coincidence, it could indicate a difference in capsule environment, the contamination of the reaction product of one alloy with the reaction product of another, or spalling. Since the PuCrO_3 was observed on all the chromium bearing alloys annealed at 800°C , absence of this phase from Inconel 625 and Haynes 25 is believed due to exfoliation.

A second proposed reaction between chromium and the capsule environment involves the formation of volatile chromium-bearing species (i.e., CrO , CrO_2 , CrO_3). Evidence of this reaction is the deposit of chromium on the T.D. nickel. Although this supports the formation of a vapor phase on only one alloy (assumed to be Haynes 25, the alloy with the largest chromium depletion in the capsule), the reaction mechanism has been extended to all the chromium-bearing alloys to explain their depletion of chromium.

Chromium was also involved in the formation of the complex oxides also containing plutonium, oxygen, titanium, nickel, and possibly iron that make up the reaction product on Inconel 625. The reaction mechanism is undetermined but seems associated with the presence of titanium as all the constituents of the reaction product except titanium were present in other superalloys.

Iron Iron was present in trace amounts in the Pu-Si-O reaction product found associated with the Hastelloy N and Haynes 188 coupons. A small amount was possibly associated with the plutonium-bearing product on Inconel 625. Since no sizeable quantity of iron was coupled with a reaction product it is considered fairly inert to $^{238}\text{PuO}_2$.

Lanthanum Lanthanum was found in conjunction with a plutonium-bearing oxide located in a grain boundary of Haynes 188. Therefore, it appears to encourage grain boundary penetration.

Manganese Manganese reacted with $^{238}\text{PuO}_2$ as it was associated with the reaction product of all the superalloys in trace or small quantities. Below is a list of the superalloys and the role assumed by manganese in its compatibility with $^{238}\text{PuO}_2$.

<u>Superalloy</u>	<u>Base</u>	<u>Wt % Mn</u>	<u>Effect of Manganese</u>
T.D. Nickel	Ni	0.001	Large deposit (6.4 wt % at its edge) of manganese due to mass transport from Haynes 25. Mass transport is believed by formation of $MnO_{(\xi)}$.
Inconel 625	Ni	0.05	Trace amount in plutonium-bearing reaction product though possibly due to mass transport from Haynes 25.
Hastelloy X	Ni	0.4	Trace in intergranular Pu-Si-O reaction product.
Hastelloy N	Ni	0.68	Trace amount in Pu-Si-O surface layer.
Haynes 188	Co	0.78	Small amount in intergranular oxide.
Haynes 25	Co	1.4	Large depletion due to its transport to T.D. nickel. Mass transport of manganese is possibly due to the formation of $MnO_{(\xi)}$.

Molybdenum Molybdenum is inert to $^{238}PuO_2$.

Niobium Niobium is present only in the Inconel 625 as a minor constituent (1.1 wt %). It was not detected in the reaction product and is thus considered inert.

Nickel Nickel was found in trace quantities in the Pu-Si-O reaction product on Haynes 188 and Hastelloy N and was present in the plutonium-bearing reaction product on Inconel 625. The reaction of nickel in Inconel 625 is possibly associated with the presence of titanium as all the constituents of the Inconel 625 reaction product except titanium were present in other superalloys. Thus, nickel appears fairly inert to $^{238}PuO_2$ except in Inconel 625.

Silicon Silicon, present as a minority element, greatly affected the compatibility of $^{238}PuO_2$ with Hastelloy N, Hastelloy X, and Haynes 188 at 1000°C. Their reaction produces an unidentified Pu-Si-O phase containing 1 to 9 wt % silicon depending on the superalloy. Literature concerning the Pu-Si-O ternary mentions the substantial solid solubility of SiO_2 in $^{238}PuO_2$.¹¹ Thus, possibly the reaction product is a $^{238}PuO_2$ - SiO_2 solid solution.

Below is a list of the alloys tested, their silicon content, and the respective reaction, if any, between silicon and $^{238}\text{PuO}_2$.

<u>Alloy</u>	<u>Base</u>	<u>Wt % Si</u>	<u>Reaction</u>
Hastelloy N	Ni	0.70	Continuous layer plus semi-continuous subsurface layer
Haynes 188	Co	0.60	Semicontinuous layer plus intergranular penetration
Inconel 625	Ni	0.30	None
Hastelloy X	Ni	0.15-0.20	Intergranular penetration
Haynes 25	Co	0.04	None
T.D. Nickel	Ni	0.001	None

If it is possible to neglect the effect of completely different alloy compositions on the behavior of silicon, several conclusions may be reached from the above list.

1. The absence of reaction between the 0.30 wt % silicon in Inconel 625 is believed due to its 0.2 wt % titanium. It is thought that titanium forms a more stable plutonium-bearing oxide than does silicon*.
2. Unless a stronger oxide former (such as Ti) is present, it appears that silicon will react with $^{238}\text{PuO}_2$ if present in quantities of 0.15-0.20 wt % or greater.
3. As the silicon content of the alloy is increased the reaction converts from the subsurface to the surface. Such a transition from internal to external attack was discussed for the oxidation of Ag-In alloys by Rapp.³⁶ He states the change in mechanism is due to the increased outward flux of solute with increased solute content which effectively reduces the oxygen activity in the alloy due to the surface reaction.

A continuous layer of Pu-Si-O is beneficial to compatibility as it is thought to be a diffusion barrier to chromium ions (see Hastelloy N report).

*Assuming similarity with SiO_2 and TiO_2 ; this is substantiated by the more negative free energy of formation of TiO_2 (-170.4 kcal) than SiO_2 (-145.0 kcal).¹⁴

Interaction between silicon and $^{238}\text{PuO}_2$ was found on all the materials in one type of test capsule but was not detected in any of the alloys of the other type of capsule (similar to PuCrO_3). This could indicate a difference in capsule environment or vapor transport of silicon by $\text{SiO}(g)$. However, this behavior could be expected by comparing the silicon contents of the materials in each type of capsule and assuming the titanium-bearing oxide on Inconel 625 is more stable than the Pu-Si oxide. The internal formation of the Pu-Si-O reaction product on all three alloys also opposes the idea of an artificially imposed behavior.

Thorium (present as ThO_2) There was no observable reaction with $^{238}\text{PuO}_2$.

Titanium Titanium reacts with $^{238}\text{PuO}_2$ to form a complex oxide also containing plutonium, nickel, and chromium with small amounts of iron and manganese. The occurrence of this reaction product seems dependent upon the presence of titanium as all the other constituents were present in other superalloys but did not participate in any reaction. This reaction appears to be more energetically favorable than the Pu-Si-O reaction.

Vanadium A small amount was present in Pu-Cr-O reaction product (PuCrO_3). Reaction with $^{238}\text{PuO}_2$ appears to have formed a solid solution of the orthorhombic perovskite-type compounds PuCrO_3 and PuVO_3 .

Tungsten Tungsten was inert to $^{238}\text{PuO}_2$.

Zinc Present as an impurity in the $^{238}\text{PuO}_2$, zinc diffuses into the alloys initially enriching the edge. After becoming depleted in the fuel its concentration in the alloys levels out. It is possibly found in oxide reaction products in Haynes 188 in very small quantities. Diffusion into the metal substrate rather than concentration in the oxides indicates zinc will not enter into interaction with $^{238}\text{PuO}_2$ if initially present in the alloy.

Comparison of the 800 and 1000°C Compatibility and Suggested Explanation for the Results Heat treatments at 800°C for 180 days or less generally produced scales of Cr_2O_3 , a manganese-rich spinel, and PuCrO_3 , the PuCrO_3 forming after a delay of 60 or more days at temperature. The three alloys which were annealed for 360 days at 800°C* indicated that a change in the results of the interaction occurred between 180 and 360 days as exemplified by total or partial decomposition of the Cr_2O_3 and the manganese-rich spinel, and creation of a Pu-Si-O phase in the alloys containing 0.60 wt % Si or greater. The 360-day, 800°C reaction zone appeared similar to that observed at 1000°C which was typified by the formation of PuCrO_3 and either Pu-Si-O or a complex titanium-bearing oxide. Below is a suggested hypothesis which is believed in agreement with all experimental data. It has been previously discussed in the 800°C Hastelloy N, Hastelloy X, and Haynes 188 reports and in the comparison of the 800 and 1000°C behavior of T.D. nickel but is presented again because it is believed applicable to all the alloys.

*Heat treatment of these three alloys occurred in the same capsule.

A proposed explanation of the observed change in the results of the 800°C compatibility as time at temperature increased from 180 to 360 days and the difference between the 1000°C interaction and that noted initially at 800°C is based on the reduction of the partial pressure of oxygen existing in the closed system. It is proposed that the initial reaction between the chromium and manganese-bearing alloys with $^{238}\text{PuO}_2$ at 800 and possibly 1000°C is the selective oxidation of chromium and manganese generally forming Cr_2O_3 , a manganese-rich spinel, and later PuCrO_3 . These oxides form by the reduction of $^{238}\text{PuO}_2$ to $^{238}\text{PuO}_{2-x}$. As $^{238}\text{PuO}_2$ becomes more substoichiometric with respect to its oxygen content, its oxygen partial pressure decreases. This is demonstrated in Figure 3 where the partial molar free energy of oxygen, $\Delta\bar{G}_{\text{O}_2}$, is plotted as a function of temperature for $\text{PuO}_{2.00}$ - $\text{PuO}_{1.81}$. The formation of each oxide will continue until it has lowered (made more negative) the $\Delta\bar{G}_{\text{O}_2}$ of the fuel to the $\Delta\bar{G}_{\text{O}_2}$ of the oxide or until one of the components of the oxide has been consumed. For instance, if the chromium content of the alloy is sufficient, the formation of Cr_2O_3 will reduce $^{238}\text{PuO}_2$ to between $^{238}\text{PuO}_{1.98}$ and $^{238}\text{PuO}_{2.00}$ at 800°C and between $^{238}\text{PuO}_{1.90}$ and $^{238}\text{PuO}_{1.95}$ at 1000°C, or until the $\Delta\bar{G}_{\text{O}_2}$ is lowered to about -135 kcal at 800°C and -127 kcal at 1000°C. Since several oxides form simultaneously, continued formation of the most stable oxide will lower the $\Delta\bar{G}_{\text{O}_2}$ below the equilibrium value for the other oxides causing them to become unstable and decompose. This process is believed to have caused the observed variations in compatibility results. Continued formation of the more stable PuCrO_3 and the initiation of the silicon- and titanium-bearing oxides reduced the $\Delta\bar{G}_{\text{O}_2}$ below the equilibrium value for Cr_2O_3 and the manganese-rich spinel*. Thus, in the systems examined in the present study, decomposition of these two oxides is suggested to have occurred between 180 and 360 days at 800°C and prior to 30 days at 1000°C.

Variation in the behavior of silicon and titanium at 800°C versus 1000°C is thought to be due to the difference in their rate of diffusion at the two temperatures. An increase in the diffusion rate with temperature would provide a greater amount available for interaction at the edge. The absence of Cr_2O_3 and spinel in the 360-day, 800°C samples and in the 1000°C samples allows interaction between the silicon and plutonium resulting in the observed Pu-Si-O phase and the plutonium, titanium-bearing oxide rather than SiO_2 or TiO_2 .

Similar effects which differed only in magnitude at 800 and 1000°C were microstructural differences at the edge thought to be caused by compositional changes and mass transport of chromium and manganese. Mass transport of chromium and manganese was caused by their sublimation. Evaporation of Cr_2O_3 is well known^{30, 31, 32} with resultant species possibly being CrO , CrO_2 , and CrO_3 . Evaporation of the manganese-rich spinel might result in the above gaseous species for Cr_2O_3 and $\text{MnO}(\text{g})$.

* Justification for the relative stability of these oxides was previously presented in the results of the 800°C, Hastelloy N compatibility.

Possible evidence of evaporation of MnO is reported by Brewer and Mastick³⁸ who concluded that MnO_2 and Mn_2O_3 readily dissociate in the temperature range of 900 to 1000°C resulting in MnO(g) . Although evaporation is believed to explain the mass transport of chromium and manganese and thus reduction in the amount of surface oxide, complete absence of Cr_2O_3 and spinel which normally form at 1000°C must be explained by their instability resulting from a reduction in the partial pressure of oxygen.

Table 19

SUMMARY OF 800°C COMPATIBILITY

Alloy	Surface Reaction ^{a, b}	Subsurface Reaction ^a	Void Formation ^c
Hastelloy N	Initial formation of Cr_2O_3 particles which appear to transform into PuCrO_3	For heat treatments of 181 days or less, Cr, Mn, V, and Zn^d were internally oxidized to depths of 5 to $20\mu\text{m}$ except at coupon ends where maximum depth reached $280\mu\text{m}$. Intergranular precipitation of oxide enriched in Cr and V to maximum of $30\mu\text{m}$. After 360 days at temperature only a Pu-Si-O phase was detected as deep as $25\mu\text{m}$ into base metal.	Intergranular to maximum depth of $175\mu\text{m}$. Found in 60- and 90-day samples
Hastelloy X	Heat treatments for 181 days or less formed three layers: Inner: Continuous Cr_2O_3 Middle: noncontinuous MnCr_2O_4 or its mixture with $(\text{Cr}, \text{Mn})_2\text{O}_3$ Outer: noncontinuous PuCrO_3 (90-day sample only) After 360 days, PuCrO_3 is dominant phase with minor occurrence of MnCr_2O_3 and Cr_2O_3	After 181 days or less, Cr_2O_3 penetrated substrate $<10\mu\text{m}$. Precipitation of a Mo-enriched phase thought possibly to be carbides at the oxide/metal interface. After 360 days, deposit of MnCr_2O_4 was observed to occur rarely and to a maximum depth of $15\mu\text{m}$.	Intergranular to maximum depth of $100\mu\text{m}$
Haynes 25	Formation of a two-layer scale for annealing times of 179 days or less: Inner: Continuous MnCr_2O_4 + Cr_2O_3 solid solution or a mixed spinel consisting of Cr, Co, Mn, Ni, and Fe. Outer: Noncontinuous PuCrO_3 or its mixture with PuMnO_3 .	Heat treatments up to 179 days resulted in rare intergranular penetration by oxide enriched in Cr and Mn to maximum depth of $20\mu\text{m}$.	None
Haynes 188	After 181 days or less at temperature, a two-layer scale formed. Inner: Continuous Cr_2O_3 Outer: continuous, composed of mixture of MnCr_2O_4 and Cr_2O_3 . After 360 days only PuCrO_3 was detected.	For heat treatments of 181 days or less intergranular precipitation of rodlike phase was detected. Precipitation occurred primarily at the edge but permeated the $1000\mu\text{m}$ sample after 60 days. Penetration of the base metal by Cr_2O_3 was also observed reaching a maximum depth of $20\mu\text{m}$ after 90 and 181 days. After 360 days at temperature, PuCrO_3 penetrated the edge $<10\mu\text{m}$. Pu-Si-O was also found 7 to $15\mu\text{m}$ into the base metal.	Maximum depth of 35 to $40\mu\text{m}$
Inconel 625	After 59 days at temperature scale consisted of three layers: Inner: Continuous Cr_2O_3 Middle: noncontinuous MnCr_2O_4 or its mixture with Cr_2O_3 Outer: noncontinuous PuCrO_3 After 91 and 179 day anneals scale consisted of two layers: Inner: Continuous MnCr_2O_4 or its mixture with Cr_2O_3 Outer: noncontinuous PuCrO_3	$<10\mu\text{m}$ penetration by inner surface oxide creating irregular edge.	None
T.D. Nickel	Single layer of Cr-Mn-O due to mass transport of Cr and Mn. One time occurrence of Pu-Si-Th-O	None	None

Table 19 (continued)

Alloy	Original Si Content (wt %)	Original Cr Content (wt %)	Conc. of Cr at Edge/ Conc. Cr in Interior	Original Mn Content (wt %)	Conc. Mn at Edge/ Conc. Mn in Interior	Thickness of Microstructural Changes (μm)
Hastelloy N	0.70	7.3	0.42 after 181 days ≤ 0.55 after 360 days	0.68	0.38 after 181 days	5-20 after 181 30-50 after 360
Hastelloy X	0.15	22.1	0.73 after 90 days 0.41 after 360 days	0.4	1.12 after 90 days 1.13 after 360 days	30-45 after 90 40-45 after 181 45-55 after 360
Haynes 25	0.04	20.1	0.94 after 179 days	1.4	0.35 after 179 days	25-35 after 179
Haynes 188	0.60	21.5	0.51-0.66 after 181 days ≤ 0.38 after 360 days	0.76	0.00 after 181 days ≤ 0.50 after 360 days	25-70 after 181
Inconel 625	0.30	20.8	0.89 after 179 days	0.05	"after 179 days"	25-50 after 60- 179 days
T.D. Nickel	0.001	Not Detected	"	0.001	"	None

*Identification of the reaction products is based on composition only and therefore is tentative.

^bScales are indicated as either continuous or noncontinuous according to optical observation. Spalling of the scales did occur and thus their discontinuity could have been due to their removal.

^cSome of the voids could have been created as a result of pullout of a phase.

^dInitially present only as an impurity in the PuO_2 .

^eThis element was detected as a trace amount at the edge but was not detected in the interior, thus leading to an infinite enrichment at the edge.

Table 20

SUMMARY OF 1000°C COMPATIBILITY

Alloy	Surface Reaction ^a	Subsurface Reaction	Maximum Depth of Void Formation ^b
Hastelloy N	Continuous 5 to 10 μ m thick layer of Pu-Si-O underlying globular PuCrO ₃ .	Precipitation of Pu-Si-O as particles which tend to become a semicontinuous layer with time. Possible internal oxidation of Si and Mn.	Possible void formation whose maximum depth is about 30 μ m after 90 days.
Hastelloy X	Nucleation of Pu-Si-O at intersection of grain boundaries with edge. Formation of globular PuCrO ₃ .	Intergranular penetration reaching 30 to 75 μ m after 60 days. Initial penetration by Pu-Si-O, deeper penetration by unidentified Pu-bearing phase. Dispersion of minute particles and occasional rodlike precipitate associated with grain or twin boundary.	None
Haynes 25	Continuous layer of Pu-bearing oxide containing a trace of Co.	Intergranular penetration of surface oxide reaching <25 μ m after 181 days at temperature.	200-240 μ m after 181 days
Haynes 188	Continuous layer of Pu-Si-O with overlying PuCrO ₃ .	Intergranular penetration reaching 70-100 μ m after 90 days. Precipitation of rodlike phase believed to be an oxide possibly composed of Pu and Al and just Al.	100-125 μ m after 90 days
Inconel 625	Continuous layer of multiphased, complex oxide containing Pu, Ti, Ni, Cr, with a little Fe and Mn.	Intergranular penetration of maximum depth of 25 μ m after 30 to 181 days by surface oxide.	None
T.D. Nickel	Deposit of Cr and Mn due to mass transport from other alloys in same compatibility capsule.	None	None

Table 20 (continued)

<u>Alloy</u>	<u>Original Silicon Content (wt %)</u>	<u>Original Chromium Content (wt %)</u>	<u>Conc. Cr at Edge/Conc. Cr in Interior</u>	<u>Original Mn Content (wt %)</u>	<u>Conc. Mn at Edge/Conc. Mn in Interior</u>	<u>Depth of Microstructural Changes (μm)</u>
Hastelloy N	0.7	7.3	0.87 @ 90 days	0.68	1.11 after 60 days 1.00 after 90 days	70-135 at all times
Hastelloy X	0.15 to 0.20	22.1	0.59 after 60 days	0.4	2.92 after 60 days	140 after 60 days
Haynes 25	0.04	20.1	0.67 after 181 days	1.4	0.50 after 181 days	85-100 after 181 days
Haynes 188	0.60	21.5	0.57 after 90 days	0.76	1.00 after 90 days	110-150 after 90 days
Inconel 625	0.30	20.8	0.94 after 181 days	0.05	1.00 after 181 days	1.50 after 181 days
T.D. Nickel	0.001	Not detected	17.0 after 181 days	0.001	2.91 after 181 days	None

*Identification of reaction products are tentative based on composition only.

^bSome of the voids could have been created as result of pullout of a phase.

CONCLUSIONS

The compatibility of the nickel-and cobalt-base alloys as described in this report is dominated by the behavior of the constituents forming the reaction products with the most negative free energy of formation (i.e., Cr, Mn, Si, Ti). The interaction is believed dependent on the partial reduction of the $^{238}\text{PuO}_2$ by the reactive constituents as dictated by Figure 3A and 3B. This makes the fuel substoichiometric with respect to the oxygen. Thus, the extent of interaction is a function of the chemical potential of oxygen in the reaction product relative to the fuel. Since the present test was run in a closed system, the formation of any one oxide can draw oxygen from any other if its chemical potential for oxygen is more negative. Therefore, if the abundance of each of the constituents of the most stable oxide is great enough, the formation of the most stable oxide can reduce the partial pressure of oxygen below the equilibrium value for any simultaneously occurring oxide causing its instability and subsequent decomposition.

Compatibility at 800°C for annealing times of about 180 days or less was generally characterized by the selective oxidation of chromium and manganese forming Cr_2O_3 , a manganese-rich spinel, and the perovskite-type compound PuCrO_3 . After 360 days at 800°C the Cr_2O_3 and spinel appeared to have partially or wholly decomposed leaving PuCrO_3 and a newly initiated Pu-Si-O phase. After 30 to 180 days at 1000°C, the compatibility was depicted by the selective oxidation of chromium, manganese, and either silicon or titanium forming a Pu-Si-O phase or a complex plutonium, titanium-bearing oxide. Similarity was observed between the 360-day, 800°C samples and those annealed at 1000°C. Relating the above hypotheses to this interaction, the decomposition of Cr_2O_3 and spinel after 180 days at 800°C and conceivably prior to 30 days at 1000°C is caused by the continued formation of PuCrO_3 and possibly the oxides containing silicon and titanium.

The compatibility of alloys not containing chromium and manganese was not determined as they were contaminated with these elements by mass transport from neighboring alloys in the same system.

Superalloys normally contain about 20 wt % chromium for oxidation resistance. Present data indicate that the presence of chromium is primarily detrimental at 800 to 1000°C. Chromium reduces the $^{238}\text{PuO}_2$ to $^{238}\text{PuO}_{2-x}$ by forming or helping to form oxide layers between the containment material and the fuel. These layers could be beneficial if they act as a diffusion barrier or if chromium acted as a sacrificial element to prevent interaction with more noble elements. The disadvantages of chromium are: it forms a very stable PuCrO_3 compound whose continued formation causes reduction of the possibly protective Cr_2O_3 and manganese-rich spinel, it forms gaseous species allowing mass transport, and its depletion in the alloys is the source of void formation.

The 7.3 wt % chromium in a nickel-base alloy (Hastelloy N) will not sustain surface oxide formation in a $^{238}\text{PuO}_2$ environment when annealed for 180 days or less at 800°C, and internal oxidation of the chromium will result.

At 800°C, manganese in nickel- and cobalt-base alloys promotes the formation of an oxide scale believed to be a spinel. This scale was found overlying Cr_2O_3 on those alloys containing 0.001* to 0.76 wt % manganese. The spinel on Haynes 25 containing 1.46 wt % manganese was in direct contact with the metal substrate. The spinel appeared to reduce the depletion of chromium in the base metal. Mass transport of manganese was detected at both 800 and 1000°C and was believed to occur due to the formation of MnO(g) by the dissociative vaporization of the spinel.

Silicon forms a Pu-Si-O phase after 30 to 180 days at 1000°C and after 360 days at 800°C. The morphology of the oxide depends on the silicon content and annealing temperature. At 1000°C continuous surface scale formed on the alloy containing 0.7 wt % silicon (the maximum of all alloys tested). As the silicon content was reduced or the temperature decreased the Pu-Si-O becomes internal. No interaction was detected with 0.001 or 0.04 wt % silicon. The continuous layer of Pu-Si-O appeared to retard the chromium depletion in the base metal.

Titanium, present as 0.2 wt % in Inconel 625**, appeared to promote the formation of a continuous, plutonium-bearing oxide at 1000°C. These 1000°C Inconel 625 samples suffered the least chromium depletion of all alloys annealed at either 800 or 1000°C. Therefore, the titanium-bearing surface oxide seems to be the best diffusion barrier for chromium ions of all the scales that developed.

Minor amounts of elements that form stable oxides (i.e., La, Mn, and possibly Al) seem to encourage internal oxidation at 1000°C.

Nickel, cobalt, and iron appear fairly resistant at both 800 and 1000°C when accompanied by elements which form more stable oxides (i.e., Cr, Mn, Si, and Ti). Solution of these cations is possible in the Cr_2O_3 and manganese-rich spinel although their concentration could not be determined. Possible loss of nickel was detected from T.D. nickel at 800°C indicating formation of NiO(g) or solution by the fuel.

* The presence of manganese in this scale on T.D. nickel which contained 0.001 wt % manganese is due to mass transport of the manganese.

** Inconel 625 contained 0.3 wt % Si; therefore, the titanium-bearing oxide forms preferentially to the Pu-Si-O phase.

Additions of tungsten and molybdenum do not affect the compatibility of nickel- and cobalt-base alloys at 800 or 1000°C when elements which form more stable oxides (i.e., Cr, Mn, Si, and Ti) are present in the same system. Possible occurrence of mass transfer of tungsten was noted only once as a trace amount on the edge of Hastelloy N exposed to $^{238}\text{PuO}_2$ for 60 days at 1000°C.

The effect of rare earth addition to a cobalt-base alloy was undetermined. Rare earths are reported to increase the oxidation characteristics of alloys by promoting parabolic kinetics through the increase of scale adherence, reduction of chromium diffusion, and decrease in interfacial porosity. The lanthanum-containing Haynes 188 exhibited greater chromium depletion and generally less adherence of oxide than Haynes 25. However, the large difference in the role of silicon and manganese could have masked any benefit from the lanthanum addition.

Interaction did occur between materials present in the same test capsule in the form of mass transfer of elements which form volatile species. Future tests should be designed with only one material in the system; or, if more than one material is proposed for containment, designed to duplicate real situations. Information gained by the faulty design of the present test is the mass transport of chromium and manganese and the decomposition of an oxide on one material by the reduction of the oxygen partial pressure of the system by the formation of a more stable oxide on another material. In the absence of more stable oxides and thus in the presence of a higher oxygen partial pressure, mass transfer of other elements by such oxides as NiO^* , CoO , WO_3^* , MoO_2 , and MoO_3 should be considered possible.

Since the interaction between $^{238}\text{PuO}_2$ and nickel- and cobalt-base alloys appears dependent on the ability of $^{238}\text{PuO}_2$ to become substoichiometric, the initial use of substoichiometric fuel rather than $^{238}\text{PuO}_2$ would effect compatibility. Possible results of the use of substoichiometric fuel would be the inhibition of the Cr_2O_3 and spinel formation and reduction of mass transport by restricting the formation of volatile oxides. Published data subsequently discussed indicate that chromium will not interact with PuO_{2-x} if the stoichiometry is adequately reduced.^{5,8}

*Possible occurrence of these volatile oxides was detected as previously discussed.

COMPARISON OF PRESENT TEST WITH THE LITERATURE

The 800°C results for annealing times of 180 days or less of the present test are not analogous to the previously recorded data (see Appendix A). A compatibility test of a 80Ni/20Cr alloy was conducted at a similar temperature,⁵ but the use of a pretest hydrogen sinter of the fuel is believed responsible for dissimilar results. Hydrogen could cause the reduction of PuO_2 and thus lower the oxygen chemical potential of the system and make certain reaction products unstable. This phenomenon is thought to be similar to the dissociation of Cr_2O_3 and manganese-rich spinel after 360 days at 800°C observed in the present test.

Present 1000°C results are in fair agreement with the literature. Similar conclusions in alloy compatibility are the passivity of nickel and iron and dependence upon the silicon content for interaction. The basic difference is in the behavior of chromium. As suggested by Prichard, Johnson, and Leary,⁸ absence of chromium interaction in some previous experiments is due to the use of hydrogen in the tests. As already stated, hydrogen could have reduced the PuO_2 .

Molybdenum and tungsten were reported to form volatile oxides as low as 800 and 1200°C, respectively.^{1,2,4} No evidence of mass transfer of molybdenum was observed and only one possible occurrence of tungsten transport was detected.

X-RAY ANALYSIS OF FUEL

Attempts to correlate x-ray data in these samples with the interaction has met with little success. A summary of x-ray analysis data obtained is given in Table 21. While there are some variations in the lattice parameter, these variations are all within experimental error of the measurements. Therefore, it is not possible to say conclusively that the $^{238}\text{PuO}_2$ becomes substoichiometric. An explanation of the results might be that the samples were stored several months in an argon atmosphere prior to analysis. Whether this had any effect on the results is unknown.

Table 21

SUMMARY OF X-RAY ANALYSES PERFORMED

<u>Test Series^a</u>	<u>Temperature (°C)</u>	<u>Time (days)</u>	<u>Lattice Parameter^b (Å)</u>	<u>Phases Present</u>
A	800	60	5.4150 (4)	PuO _{1.96} -PuO _{2.00}
	800	181	5.4114 (2)	PuO _{1.96} -PuO _{2.00}
B	800	30	5.4136 (2)	PuO _{1.96} -PuO _{2.00}
	800	91	5.4134 (3)	PuO _{1.96} -PuO _{2.00}
	800	91	5.4136 (5)	PuO _{1.96} -PuO _{2.00}
A	1000	60	5.4129 (3)	PuO _{1.96} -PuO _{2.00}
B	1000	30	5.4135 (2)	PuO _{1.96} -PuO _{2.00}
	1000	60	5.4131 (4)	PuO _{1.96} -PuO _{2.00}
	1000	90	5.4137 (4)	PuO _{1.96} -PuO _{2.00}

^aA: Hastelloy N, Hastelloy X, Haynes 188 capsule; B: Haynes 25, Inconel 625, TD Nickel capsule.

^bNumber in parentheses is standard deviation.

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APPENDIX A

PREVIOUSLY EXISTING INFORMATION ON THE COMPATIBILITY
OF $^{238}\text{PuO}_2$ WITH NICKEL AND COBALT-BASE ALLOYS

Existing information on the compatibility of PuO_2 with pertinent alloys is limited to general observations on Inconel, Ni-Cr alloys, and various stainless steels and is subsequently discussed. The following information with only a few exceptions, is taken from a compilation by J. E. Selle.³

Duplex pellets consisting of Inconel (14 wt % Cr, 6 wt % Fe, balance Ni) and PuO_2 powders were sintered for 2 hr at 1038, 1093, or 1177°C (1900, 2000, or 2150°F) in a hydrogen environment.⁴ Metallographic and x-ray analyses found no indication of reaction.

No reaction was detected between various austenitic stainless steels (AISI types 304, 316, 318, and 347) and PuO_2 after 2-hr heat treatments at 1038, 1093, or 1177°C (1900, 2000, or 2150°F) in a hydrogen atmosphere.⁴ Type 302 stainless steel (0.48 wt % Si) was found compatible with PuO_2 at 1325°C for times up to 28 days; however, PuO_2 did react with type 302-B stainless steel (2.26 wt % Si). The resulting reaction product was composed of only silicon and plutonium. The authors concluded that the determining factor in whether or not type 302 stainless steel was compatible with PuO_2 was the silicon content.

An alloy of 80 Ni/20 Cr containing 0.85 wt % silicon was heated in contact with PuO_2 for 400 hr at 649 to 1093°C.⁵ The PuO_2 had decomposed to $\alpha\text{-Pu}_2\text{O}_3$ and PuO_{2-x} during a pretest sinter at 1200°C for 12 hr in hydrogen. No reaction was observed by metallographic, x-ray, and electron microprobe analyses. Interaction was found between the PuO_2 and the silicon present as an impurity in the 80 Ni/20 Cr.

Available data pertaining to the compatibility of $^{238}\text{PuO}_2$ with the constituents of the superalloys are summarized in the following table.

Element or Compound	Heat Treatment			Type of Analysis	Results	Reference
	Temperature (°C)	Time	Test Environment ^a			
Al	600	----	vacuum	A, B	Formation of interfacial layer of Al ₂ O ₃	6
Al ₂ O ₃	1593	4 hr	hydrogen	B	With impurities, formation of perovskite-type compound PuAlO ₃ . With high purity Al ₂ O ₃ , no reaction.	4
	1500	2 hr	hydrogen	B	CrO ₃ and PuO ₂ powders reacted in alumina crucible gives formation of perovskite-type compound PuAlO ₃ .	7
Al(OH) ₃	1500	2 hr	argon	B	Reactants PuO ₂ , Al ₂ O ₃ , and C in alumina container resulted in perovskite-type compound PuAlO ₃ .	7
	1500	2 hr	air	B	Reactants PuO ₂ and Al(OH) ₃ in alumina container resulted in PuO ₂ only.	7
	1500	2 hr	hydrogen	B	Reactants PuO ₂ and Al(OH) ₃ in alumina container resulted in PuO ₂ plus perovskite-type compound PuAlO ₃ .	7
	1500	2 hr	hydrogen	B	Reactants PuO ₂ and Al(OH) ₃ with 10% excess in thoria container resulted in perovskite-type compound PuAlO ₃ .	7
	arc-melted		argon	B	Reactants PuO ₂ and Al(OH) ₃ with 10% excess resulted in PuO ₂ +Pu ₂ O ₃ +perovskite-type compound PuAlO ₃ .	7

Element or Compound	Heat Treatment			Type of Analysis	Results	Reference
	Temperature (°C)	Time	Test Environment ^a			
Cr	1325	2 hr	argon	A, C}	Undetermined reaction occurred; extent increases with time and temperature. Electron microprobe found no interaction between Cr and Pu.	8
	1425	2&7 hr	argon	A, C}		
CrO ₃	1316	4 hr	hydrogen	A	No interaction.	4
	1500	2 hr	hydrogen	B	Mixed powders in thoria container resulted in perovskite-type compound PuCrO ₃ .	7
	1300	2 hr	hydrogen	B	Mixed powders of CrO ₃ , PuO ₂ , and Pu ₂ O ₃ resulted in PuO ₂ and perovskite-type compound PuCrO ₃ .	7
Fe	1325	2 hr	argon	A	No conclusive information.	8
	arc-melted with PuO ₂		argon	A	Interaction.	5
	1300	100 min.	vacuum	A, B	10% PuO ₂ reduced to β-Pu ₂ O ₃ .	6
	1350	2 hr	vacuum	A, B	10% PuO ₂ reduced to β-Pu ₂ O ₃ .	6
MnCO ₃	1500	2 hr	hydrogen	B	Reactants PuO ₂ and MnCO ₃ in alumina container resulted in perovskite-type compound PuMnO ₃ .	7
	1500	2 hr	hydrogen	B	Reactants PuO ₂ and MnCO ₃ in thoria container resulted in PuO ₂ .	7

Element or Compound	Heat Treatment		Test Environment ^a	Type of Analysis	Results	Reference
	Temperature (°C)	Time				
Mo	800		argon	A, C	Mass transport by MoO ₃ .	1
	1000		argon	A, C	Mass transport by MoO ₃ .	1
	1200		argon	A, C	Mass transport by MoO ₃ .	2
	1500		argon	A, C	Mass transport by MoO ₃ .	2
	1700		argon	A, C	Mass transport by MoO ₃ ; grain boundary diffusion by Pu.	2
	1900		argon	A, C		
	1593	4 hr	hydrogen		No reaction.	4
	1371	20 hr				
	1650	12 hr		A, B	No reaction.	9
	1750	3 hr		A	No reaction.	9
Nb	1500	96 hr	argon	A, C	Intergranular attack and unidentified surface reaction.	2
	1593	4 hr	argon	A	No observable reactions.	4
	arc melted with PuO ₂		argon		No observable reactions.	5
	1700	24 hr	argon	A, C	Solution of Nb by PuO ₂ .	2
Nb ₂ O ₅				B	Formation of PuO ₂ ·2Nb ₂ O ₅ , a tetragonal distortion of the perovskite structure.	10
Ni	1325	2 hr	argon	A	No interaction.	8
	1425	2 hr	argon	A	No interaction.	8
Si	1325	2 hr	argon	A	Reaction occurs, possible formation of PuSi & PuSi ₂ .	8

Element or Compound	Heat Treatment			Type of Analysis	Results	Reference
	Temperature (°C)	Time	Test Environment*			
Si	arc-melted with PuO ₂		argon	A	Interaction.	5
SiO ₂	made into microspheres in plasma torch		argon enriched in oxygen	A, B	10 wt % PuO ₂ and 90 wt % SiO ₂ were homogenized by melting. No visual undis- solved PuO ₂ but slight indication of PuO ₂ by x-ray.	11
Th	1000	100 min.	vacuum	A, B	Complete reduction of PuO ₂ to Pu ₂ O ₃ .	6
	1200	100 min.	vacuum	A, B	50% reduction of PuO ₂ to Pu metal. The above reduction of PuO ₂ to β-Pu ₂ O ₃ and then to δ-Pu begins at 800°C, δ-Pu going into solid solution with ThO ₂ .	6
ThO ₂	1000	16 hr	air	B	Complete solid solubility.	12
	1650	6 hr	helium	B	Complete solid solubility.	13
Ti	1593	4 hr	argon	A	Interaction.	4
V	1593	4 hr	argon	A	No reaction.	4
V ₂ O ₅	1500	2 hr	hydrogen	B	Formation of orthorombic perovskite-type compound PuVO ₃ .	7
W	1000	432 days	argon	A	No reaction detected.	2
	1200	365 days	argon	A, C	Formation of volatile oxides.	2
	1500	365 days	argon	A, C	Formation of volatile oxides.	2
W	1593	4 hr	hydrogen	A	Subsurface void formation in tungsten thought to be due to partial reduction of PuO ₂ and subsequent formation of gaseous WO ₃ .	4
	1371	20 hr				

A = metallographic examination
B = x-ray analysis
C = electron microprobe analysis

*Annealing in a hydrogen atmosphere could
cause partial reduction of PuO₂. The
degree of reduction is a function of the
water content.

APPENDIX B

CHEMICAL ANALYSIS OF FUEL USED IN SUPERALLOY COMPATIBILITY TESTS

<u>Element</u>	<u>Analysis of Fuel Batch (wt %)</u>	
	<u>PPX-18-1</u>	<u>69-S-37B</u>
Al	0.08	0.11
B	<0.06	0.05
Ca	0.09	0.11
Cr	0.10	<0.03
Cu	<0.03	<0.02
Fe	0.43	0.20
Mg	0.08	0.04
Mn	<0.03	-
Na	Trace	Trace
Ni	<0.05	<0.03
Pb	<0.27	-
Si	Trace	<0.02
Zn	0.32	0.03
Total	<1.54	<0.65

APPENDIX C

ANALYSIS OF SUPERALLOYS USED IN COMPATIBILITY TESTS

Test Material	Element (wt%)									
	Al	C	Co	Cr	Cu	Fe	H	La	Mg	Mn
Hastelloy N	0.06	0.04	0.1	7.3	0.01	3.3	0.0021	-	-	0.68
Hastelloy X	-	0.088	0.9	22.1	-	17.3	<0.001	-	-	0.4
Haynes 25	-	0.077	Bal (51.3)	20.1	-	1.9	<0.001	-	-	1.4
Haynes 188	0.2	0.080	Bal (40.9)	21.5	0.06	1.46	<0.0001	0.15	-	0.76
Inconel 625	0.1	0.048	0.05	20.8	0.05	2.7	<0.001	-	0.01	0.05
T.D. Nickel	0.05	0.005	0.1	-	0.001	0.02	<0.001	-	0.0001	0.001

Test Material	Element (wt%)									
	Mo	N	Nb	Ni	O	Si	Th	Ti	V	W
Hastelloy N	16.5	0.0058	-	Bal (71.0)	0.0127	0.7	-	-	0.25	-
Hastelloy X	8.9	0.034	-	Bal (49.5)	0.002	0.15	-	-	-	0.6
Haynes 25	-	0.033	-	10.1	0.001	0.04	-	-	-	15.1
Haynes 188	-	0.019	-	20.6	0.002	0.6	-	0.02	0.02	13.5
Inconel 625	9.2	0.051	1.1	Major (75.2)	0.002	0.3	-	0.2	0.01	-
T.D. Nickel	-	0.061	-	Major (97.8)	0.0239	0.001	1.9	-	-	-

APPENDIX D

TEST MATRIX FOR THE $^{238}\text{PuO}_2$ /NICKEL- AND COBALT-BASE COMPATIBILITY PROGRAM

<u>Temperature (°C)</u>	<u>Test Material</u>	<u>Time Period^a (days)</u>	<u>Fuel Batch Number^b</u>	<u>Capsule Design^c</u>
800	Hastelloy N	30, 60 ⁰ , 90, 181, 360	PPX-18-1	E-1
	Hastelloy X	30, 60 ⁰ , 90, 181, 360	PPX-18-1	E-1
	Haynes 25	30, 59, 91 ⁰ , 179	69-S-37B	E-2
	Haynes 188	30, 60 ⁰ , 90, 181, 360	PPX-18-1	E-1
	Inconel 625	30, 59, 91 ⁰ , 179	69-S-37B	E-2
	T.D. Nickel	30, 59, 91 ⁰ , 179	69-S-37B	E-2
1000	Hastelloy N	30, 60 ⁰ , 90	PPX-18-1	E-1
	Hastelloy X	30, 60 ⁰	PPX-18-1	E-1
	Haynes 25	30, 60, 90 ⁰ , 181	69-S-37B	E-2
	Haynes 188	30, 60 ⁰ , 90	PPX-18-1	E-1
	Inconel 625	30, 60, 90 ⁰ , 181	69-S-37B	E-2
	T.D. Nickel	30, 60, 90 ⁰ , 181	69-S-37B	E-2

^a D superscript indicates duplicate capsules.

^b See Appendix B for analysis.

^c See Appendix E.

APPENDIX E

Test Capsule E-1

Test Capsule E-2