

MASTER

EFFECT OF FISSION PRODUCT INTERACTIONS ON THE CORROSION AND MECHANICAL PROPERTIES OF HTGR ALLOYS*

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ABSTRACT

Preliminary experiments have been carried out to determine how fission product interactions may influence the mechanical integrity of reference HTGR structural metals. In this work Type 304 stainless steel, Incoloy 800 and Hastelloy X were heated to 550-650°C in the presence of CsI. It was found that no corrosion of the alloys occurred unless air or oxygen was also present. A mechanism for the observed behavior is proposed. A description is also given of some long term exposures of HTGR materials to more prototypic, low concentrations of I₂, Te₂ and CsI in the presence of low partial pressures of O₂. These samples are scheduled for mechanical bend tests after exposure to determine the degree of embrittlement.

1. INTRODUCTION

Fission products, such as cesium, tellurium and iodine, if deposited and concentrated on the surface of metals at elevated temperatures, could alter the nature of the protective oxide scale and affect the mechanical properties. A program has been initiated to quantitatively evaluate this effect for some of the more common fission product species and structural alloys found in an HTGR. In particular, cesium, tellurium and iodine are being investigated since significant quantities of these elements are generated during reactor operation.

Partial pressures of fission products in the helium gas environment can be estimated from calculated values of the gas borne inventory in a reactor. The estimated partial pressures of Cs, Te₂ and I₂, based on the gas borne inventory in a 3150 MW HTGR after four years of operation¹ are in the range of 10⁻¹¹ to 10⁻¹² atmosphere, with a design limit higher by three orders of magnitude, 10⁻⁸ to 10⁻⁹. These partial pressures are very low, in the range of very high vacuum. The chemical reactivity of the fission products will also be low leading to minimal interaction with HTGR alloys. Nevertheless, over a period of years significant corrosion of the HTGR alloys could occur especially in localized areas, e.g., grain boundaries and highly stressed regions.

The fission products may be in elemental form, i.e., Cs, Te₂, I₂, when interacting with the metals or they may combine to form compounds. A particularly stable and, therefore, likely compound is CsI. Recent electron microprobe work² has indicated the presence of CsI in the pyrocarbon coatings of uranium carbide fuel particles. CsI has also been identified³ as a product formed from a synthetic mixture of (U,Pu)O_{2+x}, Cs₂O and PdI₂ heated to 1150°C in the hot end of a sealed stainless steel temperature gradient capsule.

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This paper will first describe work which has been performed on the chemical interaction of CsI with HTGR alloys in the presence of either oxygen or water vapor. The preliminary phase of a study of the mechanical properties of HTGR metals exposed for extended periods to tellurium, iodine, cesium and cesium iodide will then be outlined.

2. THE INTERACTION OF CsI WITH HTGR ALLOYS IN AN OXIDIZING ENVIRONMENT

An experimental program was undertaken to obtain information on the interaction of CsI with the reference HTGR alloys, Type 304 stainless steel, Incoloy 800 and Hastelloy X. Nominal compositions are given in Table 1. Also given are the compositions of Inconel X-750 and Inconel 718 which were used in other experiments described below.

Table 1

Nominal Compositions of Test Materials

	Composition (Weight %)							
	C	Ni	Mn	Cr	Si	Mo	Others	Fe
T304 SS	0.06	9.0	1.0	18.5	0.5			Bal.
I-800	0.06	32.0	1.0	20.0	0.5		0.4 Ti, 0.4 Al	Bal.
Hastelloy X	0.10	Bal.	0.5	20.0		9.0	2.0 Co, 0.6 W	18.0
Inconel X-750	0.04	Bal.	0.7	15.0	0.3		1.0 Nb, 2.5 Ti, 0.9 Al	7.0
Inconel 718	0.04	52.0	0.3	19.0	0.3	3.0	5.0 Nb, 0.5 Ti, 0.5 Al	Bal.

Mixtures of CsI with Type 304 stainless steel, Incoloy 800 and Hastelloy X turnings as well as with Fe, Ni and Cr powders were heated either in air, oxygen or in helium for periods of several hours at temperatures of 550^o to 650^oC. In helium, no corrosion of the metals occurred either in the presence or absence of CsI. The data obtained in air and oxygen, to be discussed below, were similar indicating that only oxygen played a significant role in the interaction of metals with CsI. The most extensive data were obtained on samples exposed to air at 620^oC for four hours. The results are shown in Table 2.

We observe in Table 2 that exposure of Type 304 stainless steel, Hastelloy X and Incoloy 800 to air at 620^oC resulted in the formation of a blue surface film. The metal surface remained shiny. The presence of CsI resulted in a dull grayish-brown tarnish film on all three alloys. Rinsing the turnings in distilled water imparted a yellow color to the water. A positive qualitative test for Cr⁺⁶ was obtained (nitric acid, ethyl ether, hydrogen peroxide, blue color in ether layer) on the rinsings from the Incoloy 800, Hastelloy X and Type 304 stainless steel turnings. Negative results were obtained on tests to identify nickel and iron ions.

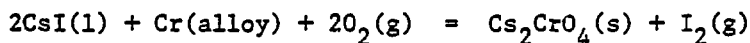
The data on the alloys indicate that CsI interacts with the chromium in the presence of an oxidizing atmosphere. This observation was confirmed by exposing mixtures of CsI and either iron, nickel or chromium powders to air at 620^oC for four hours. Only chromium interacted with CsI with the formation of some Cr⁺⁶ ions.

Table 2

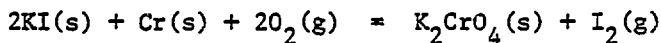
Data Obtained on Metal CsI Samples Exposed to Air at 620°C

<u>Material</u>	<u>CsI</u>	<u>Appearance</u>	<u>Aqueous Solution</u>	<u>Positive Test For</u>
Type 304 SS	absent	blue film	colorless	--
Type 304 SS	present	tarnish	yellow	Cr ⁶⁺
Incoloy 800	absent	blue film	colorless	--
Incoloy 800	present	tarnish	yellow	Cr ⁶⁺
Hastelloy X	absent	blue film	colorless	--
Hastelloy X	present	tarnish	yellow	Cr ⁶⁺
Iron Powder	absent	-----	colorless	--
Iron Powder	present	-----	colorless	--
Nickel Powder	absent	-----	colorless	--
Nickel Powder	present	-----	colorless	--
Chromium Powder	absent	green powder (Cr 0)	colorless	--
Chromium Powder	present	green powder (Cr 0)	yellow	Cr ⁶⁺
		yellow powder (Cr ⁶⁺)		

Additional information was obtained by measuring the visible spectra of the yellow aqueous solutions. The spectra of aqueous solutions of Na₂CrO₄, K₂Cr₂O₇ and CrO₃ were also obtained. It was found that the absorbance maxima for the three alloys occur at the same wavelength, 372 nm, as the absorbance maximum for Na₂CrO₄. CrO₃ and K₂Cr₂O₇ have absorbance maxima at 347 nm. Thus, it is likely that CsI reacts with chromium bearing alloys in the presence of oxygen to form Cs₂CrO₄. A reaction of the type given below probably occurs:



Thermodynamic data on Cs₂CrO₄ are not available. However, potassium and cesium compounds have similar thermodynamic properties. It is, therefore, instructive to look at the corresponding reaction of KI to form K₂CrO₄.



The reaction is highly exothermic. The standard enthalpy change at 25°C is -159 kcal⁵. Therefore, the postulated reaction of CsI with the alloys seems quite reasonable even taking into account the substitution of cesium for potassium, the lower activities of chromium (in the alloy), the difference in temperature (600°C vs. 25°C) and the use of enthalpy instead of free energy.

Additional experiments were performed to verify the formation of elemental iodine. Samples of Hastelloy X, Incoloy 800 and Type 304 stainless steel turnings were heated with CsI at 600°C in the presence of oxygen. After the oxygen was passed over the sample, it was bubbled through absolute ethanol. Elemental iodine dissolved in ethanol gives a brownish-red solution with an absorption maximum at 360 nm. Elemental iodine was identified as a reaction product. The rate of production of iodine was measured by inserting the exit tube into a spectrophotometer sample cell containing ethanol. The increase in absorbance

with time was followed. It is observed in Figure 1 that the rate of production of iodine was high for the first few minutes and then tapered off rapidly. This type of behavior is typical for a chemical reaction occurring at a solid surface.

An additional set of experiments was performed in which samples of Hastelloy X and Incoloy 800 turnings were heated with CsI in a gaseous environment of 2.5 volume percent water vapor in helium. Cs_2CrO_4 did not form under these conditions and elemental iodine was produced only at temperatures of 900°C and above. A dark oxidation layer formed on the turnings at 900°C both in the presence and absence of CsI. An interesting difference in the nature of the oxidation layer was observed. The layer formed in the absence of CsI was strongly adherent to the metal and was not affected by exposure to water at room temperature. The layer formed in the presence of CsI, when exposed to water, slowly crumbled and flaked off exposing the unoxidized metal underneath. Thus, the mechanism of oxidation by water vapor seems to be strongly influenced by CsI.

The experimental results indicate that CsI strongly affects the oxidation of HTGR metals in air, oxygen and water vapor. A preliminary set of experiments was performed to investigate the effect of CsI on the mechanical properties of HTGR metals. Bend test samples (3.2 cm long, 9.64 cm wide and 0.32 cm thick) of Type 304 stainless steel, Hastelloy X, Inconel X-750 and Inconel 718 were exposed to the following test conditions:

- i. Four hour heating in air at 750°C (designated "preoxidized").
- ii. Eight day heating at 750°C in a sealed, evacuated (~ 1 torr) quartz capsule.
- iii. Eight day heating at 750°C with CsI in a sealed, evacuated (~ 1 torr) quartz capsule.
- iv. Eight day heating at 750°C with CsI in a sealed, quartz capsule containing 0.5 atmosphere of oxygen.
- v. Eight day heating of "preoxidized" samples at 750°C with CsI in a sealed quartz capsule containing 0.5 atmosphere of oxygen.

After exposure, samples were ground and polished and examined metallographically. Their bending behavior was also examined. No marked differences in appearance or mechanical properties were observed that could be attributed to the presence of CsI. Metallographic samples of Type 304 stainless steel exposed to experimental condition iv is shown in Figure 2. The presence of CsI and oxygen under experimental condition iv had no apparent effect on the samples. The most significant general observation on this group of samples was that Inconel 718 was much more susceptible to oxidation at 750°C than the other metals. A fairly thick surface layer was observed on the Inconel 718 whereas, in the cases of Hastelloy X, Type 304 stainless steel and Inconel X-750, a thin surface layer present initially protected the samples from further oxidation.

3. LONG TERM EXPOSURE OF HTGR ALLOYS TO FISSION PRODUCTS

A program was initiated to determine the effects of long term (>1000 hours) exposure of HTGR alloys to I_2 , Te_2 , CsI and Cs in gaseous environments and at temperatures which reflect normal HTGR operating conditions.

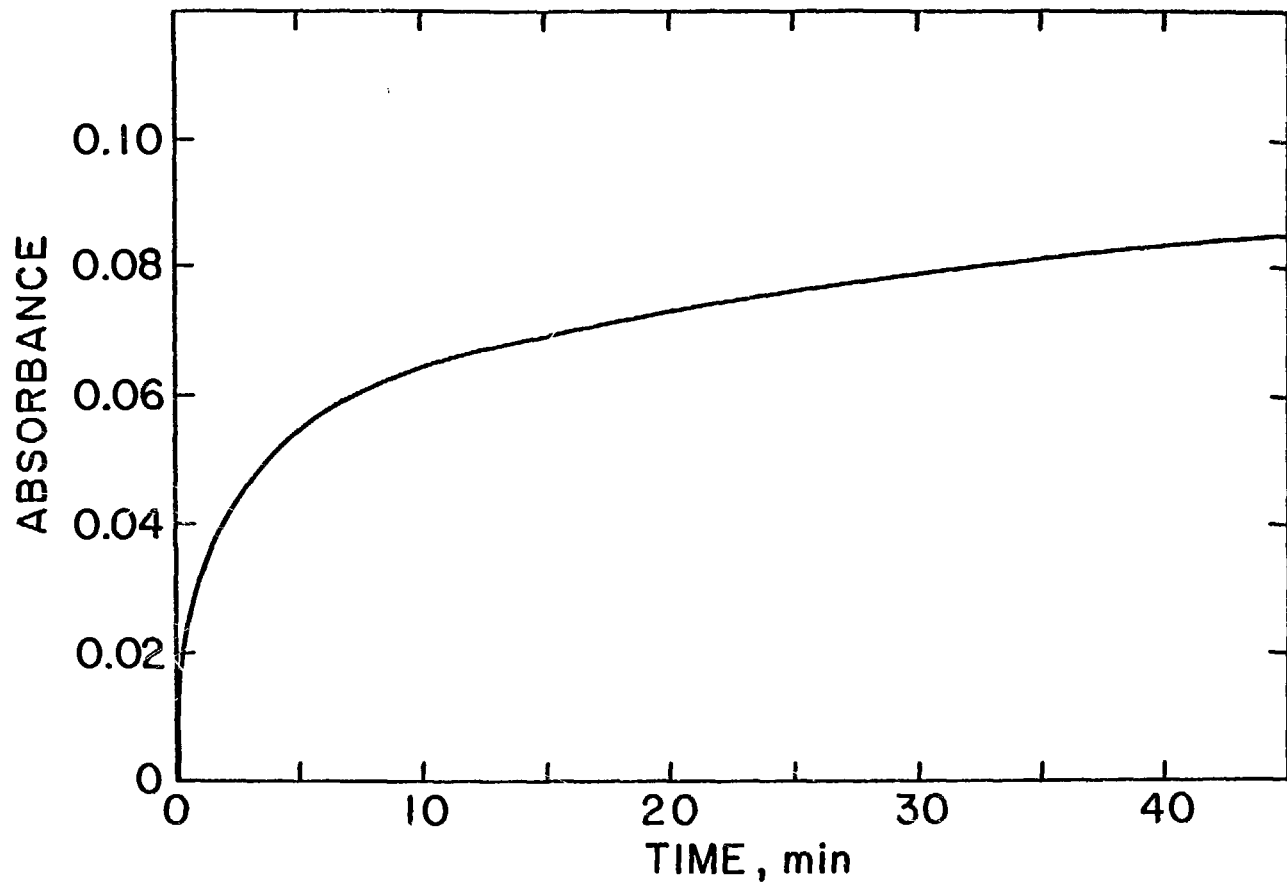


Fig. 1. Increase in absorbance with time of an alcohol solution of iodine. The absorbance is proportional to the concentration of iodine.

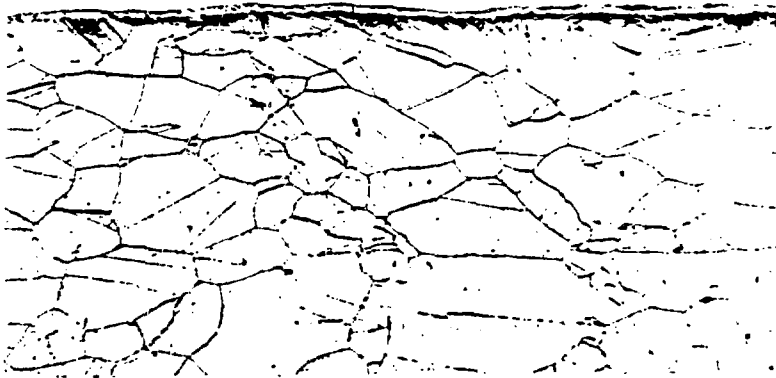


Figure 2. Photomicrograph of a Type 304 stainless steel sample heated for 8 days at 750°C with CsI in a sealed quartz capsule containing 0.5 atmosphere of oxygen. Oxalic acid etch, magnification 250X.

Testing of a first group of capsules is under way. A typical test set-up is shown in Figure 3. In this test metallographically polished rectangular samples (2.5 x 0.65 x 0.32 cm) of Type 304 stainless steel, Incoloy 800, Hastelloy X and Inconel 718 in a quartz sample holder (not shown) are heated at 800°C in an evacuated ($\sim 10^{-7}$ atm.) quartz tube. The simulated fission product, in powder form, is held in a quartz crucible at the other end of the quartz tube. The natural temperature gradient of the tube furnace is used to keep the temperature of the tellurium powder at 400°C. The vapor pressure of tellurium at 400°C is 10^{-5} atm. The encapsulated magnet was used to push the tellurium from near the left end of the quartz tube to the right end after the quartz tube was sealed in vacuum. The Ni-NiO powder at 800°C maintains the partial pressure of oxygen at 10^{-14} atm. This oxygen pressure is below the level at which TeO will form.

Five tests are currently under way using Te₂, CsI, and I₂ as simulated fission products. The metal samples in all the tests are at 800°C. The temperatures and partial pressures of the simulated fission products are shown in Table 3. After completion of the tests, the metal samples will be examined microscopically and metallographically and will be bent to determine whether the fission product reactions on the surface have caused embrittlement.

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2. KLEYKARMP, H., Report KFK-2213, Karlsruhe, Germany, 1975.

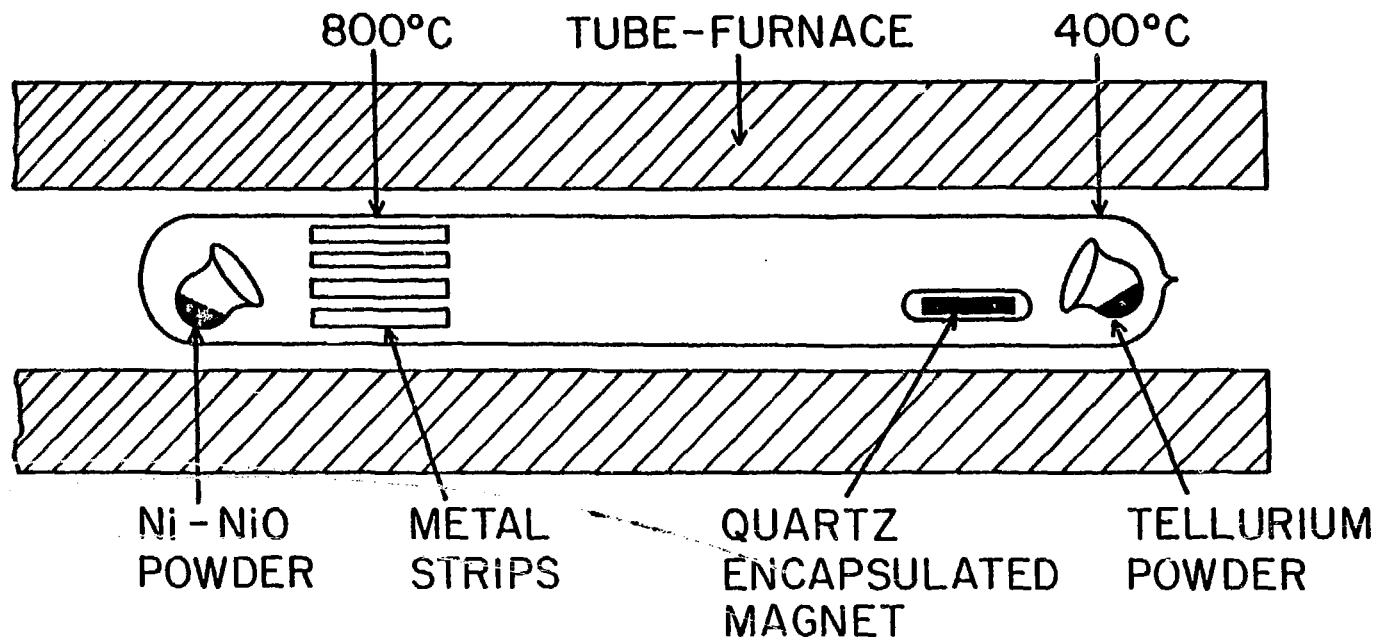


Figure 3. Test setup to study the interaction of HTCR metals with gaseous tellurium, Te_2 , at a controlled oxygen partial pressure.

3. AITKEN, E. A., EVANS, S. K. and RUBIN, B. F. in Behavior and Chemical State of Irradiated Ceramic Fuels, IAEA, Vienna, 1974, pp. 269-85.
4. ROBERTS, D. I., Materials Selection for High-Temperature Gas-Cooled Reactor Systems, GA-Al3039, 1974.
5. The Handbook of Chemistry and Physics, 51st Edition, Chemical Rubber Co., Cleveland, Ohio, 1971, p. D-168.

Table 3

Fission Product Vapor Pressures for HTGR Metal Samples

	<u>Simulated Fission Product</u>	<u>Fission Product Source Temperature</u>	<u>Vapor Pressure at Source (atm.)</u>
1.	Te ₂	400 ^o C	10 ⁻⁵
2.	Te ₂	400 ^o C	10 ⁻⁵ (1)
3.	CsI	500 ^o C	10 ⁻⁵
4.	CsI	500 ^o C	10 ⁻⁵ (1)
5.	I ₂	25 ^o C	10 ⁻⁴

Note: (1) A Ni-NiO mixture maintained at 800^oC to give an oxygen partial pressure of 10⁻¹⁴ atm.