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 STRESS CORROSION DUE TO REPROCESSING IMPURITIES

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Abstract

The potential degradation of LMFBR fuel cladding alloys by chlorides, when used in metallic fuel systems, was evaluated. The alloys tested were D-9 and HT-9 stainless steels, austenitic and ferritic alloys respectively. These two alloys were tested in parallel with and their performance compared to the austenitic stainless steel Type 316. All alloys were tested for 7400 hours in a stress rupture environment with chloride exposure at either 550°C or 650°C. None of the alloys tested were found to exhibit any degradation in time-to-rupture by the presence of chlorides under the conditions imposed during testing.

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1. Introduction

Argonne National Laboratory, operator of the DOE's Experimental Breeder Reactor-II (EBR-II), is currently developing a new liquid-metal cooled breeder reactor concept. The concept is known as the Integral Fast Reactor (IFR) and represents the state-of-the-art in metal-fueled reactor technology. The reader is directed to Reference 1 for background and detail.

Reprocessing is integral to the IFR concept as implied by its name. It is this reprocessing that has focused attention on the potential effects of those impurities which might result from this process. Initially, the impurity of most interest was chlorine, an element long known for its aggressive behavior when exposed to certain stainless steels. The effect on the performance of IFR candidate cladding alloys by chlorine present from the reprocessing stream as either contamination or as a process stream carry over was investigated. Three cladding alloys were tested in a stress rupture environment with chlorine exposures at prototypic temperatures.

Stress corrosion induced cracking cannot generally be attributed to a single aspect of a specific application. It is more generally associated with a combination of conditions, all of which contribute to the stress corrosion environment. Stress corrosion related failures in austenitic stainless steels, for example, can occur at various chloride concentrations. The range of concern might be a few thousand parts per

million (ppm) in a component with low fabrication stresses in a nonsusceptible condition at room temperature to less than 1 ppm in a structure involving components that have undergone cold work, large fabrication stresses, and are used in a susceptible condition at higher temperatures (2). Other concerns might involve mechanisms that would modify the environment during use, i.e., the potential concentration of chlorides. It is the nonobvious type of stress corrosion failure that generally proves to be the most surprising in nature and this is what we are attempting to prevent by performing the work described below.

2. Materials

The three alloys tested were Type 316, D-9, and HT-9 stainless steels (SS). Type 316 SS, the current EBR-II driver-fuel cladding alloy, for which there exists a large amount of information with respect to its irradiation performance and properties as a metal-fuel cladding alloy, was chosen to serve as the baseline material for comparison of experimental results because of this large data base. Another austenitic stainless steel, alloy D-9, very similar in composition to Type 316 SS, has been developed for improved irradiation swelling resistance and was included in this test.

The third alloy, HT-9, is a ferritic material over the operating temperature range. Specifically, HT-9 is heat treatable, forming martensite upon cooling, after which the mechanical properties can be adjusted by final heat treatment. The mechanical properties of the two austenitic alloys are controlled by solid solution strengthening, amount of cold work, and the precipitation of carbides. In comparison to the austenitics the HT-9 exhibits greater dimensional stability, lower

thermal expansion and is more resistant to irradiation induced deformation (3, 4). The compositions of the materials are listed in Table 1.

3. Experimental

Tests were conducted using pressurized capsules fabricated from actual fuel cladding. These capsules duplicate the geometry and configuration of EBR-II fuel elements and were assembled in a manner representative of standard fuel fabrication techniques. All tests capsules were all loaded with sodium, the proper amount of chlorine, pressurized and held at either 550°C or 650°C for 7400 hours. Samples were pressurized to produce a hoop stress at temperature which nominally should cause stress rupture failure at 7400 hours of exposure. Tag gasses were added to allow identification of failed capsules as intermittent failures occurred. Following testing, representative samples were submitted for detailed metallurgical examinations.

The pressurized capsules, shown in Figure 1, have proven useful and yielded consistent results in previous experiments where cladding performance is to be evaluated in a stress rupture environment. The particular capsule shown allows the use of hardware and fabrication techniques used presently for EBR-II fuel elements.

At the initiation of this test reprocessing details, e.g., specific impurities levels, were not available. Chlorine was seen to play an important role in reprocessing and was thought to have the potential of being an inadvertent additive to the reprocessed fuel. Since there was no existing information with respect to anticipated chlorine levels the test conditions were chosen to bracket the possible limits. The

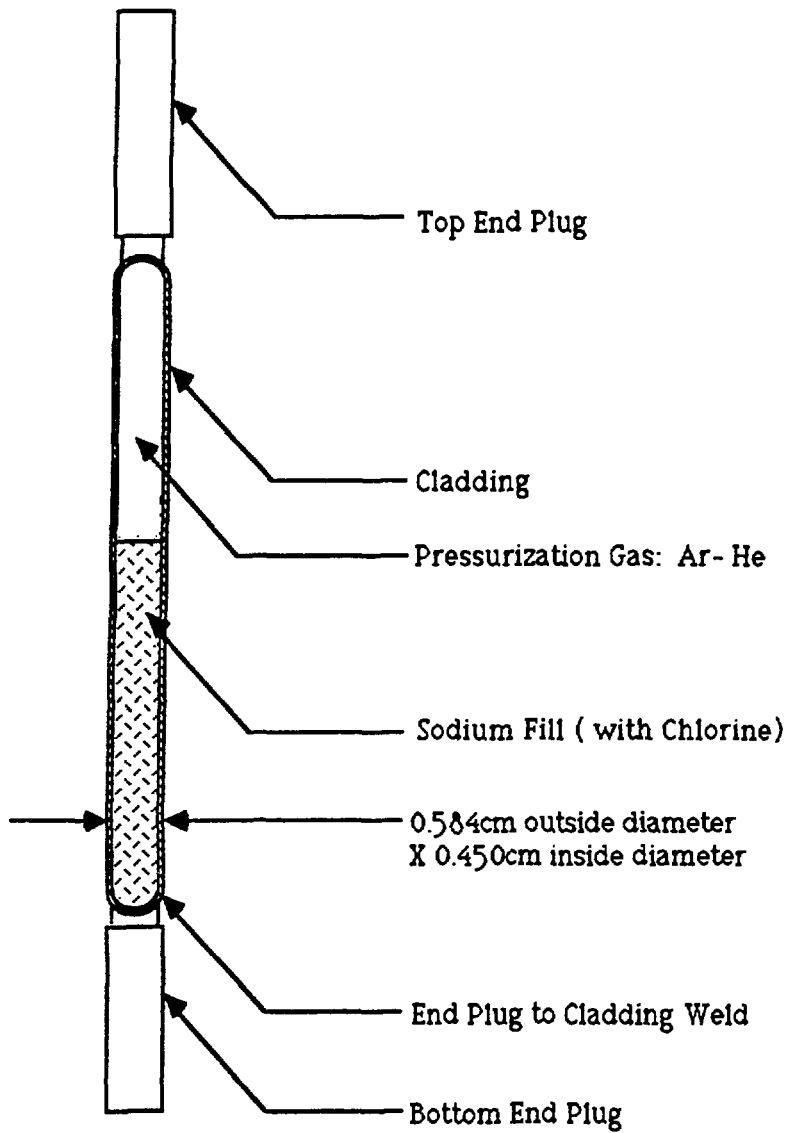


FIGURE 1. Schematic of the pressurized capsules tested.

TABLE 1

COMPOSITIONS OF THE FUEL CLADDING ALLOYS TESTED

ALLOY	CONSTITUENT (wt. %)									
	<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	<u>Ti</u>	<u>V</u>
316	0.08	2.0	0.045	.030	1.0	10-14	16-18	2-3	---	---
D-9	0.04	2.0	0.6	----	---	15.5	13.5	1.5	0.2	---
HT-9	0.2	0.5	0.02	0.01	0.4	0.5	12	1.0	---	0.3

maximum amount of chlorine for capsule tests was determined from the solubility of sodium chloride in sodium at testing temperatures. The mass of chlorine that was determined to represent saturation was multiplied by ten to arrive at the mass to be loaded into the chloride bearing capsules. A solution of liquid sodium saturated in sodium chloride was desired such that if the chlorine was removed from the solution, e.g. by some corrosion process, an adequate supply would thus remain in solution to continue the process. In this manner the excess sodium chloride allowed the experimental results to be conservative in nature.

The minimum chloride levels were calculated by a summation of the cladding surface chloride contamination specification with the residual chlorides contained in EBR-II secondary sodium, the sodium used in fabrication of fuel elements as well as the test capsules. The minimum chloride level therefore required no physical addition to the test capsules. The weight fraction of chlorine in the sodium loaded into the test capsules was approximately six parts per million and 85,000 parts per million for the minimum and maximum cases respectively.

The capsules were tested at 550°C and 650°C, bracketing anticipated reactor operating temperatures. Data, i.e., calculations of EBR-II peak cladding temperatures indicates the range of minimum temperatures to be 488-558°C with the corresponding maximum temperature range to be 522-600°C. These temperature ranges represent the outer and inner cladding wall temperatures respectively. Good agreement is seen between the testing temperatures and those calculated from actual reactor

operational parameters and likely bracket peak temperatures anticipated in innovative reactor designs.

Capsules were pressurized during assembly to produce the required stress levels during testing at temperature. Stress levels were calculated from available stress rupture life data for each alloy at temperature. Design life of approximately 8800 hr at 650°C resulted in different stress levels in each alloy. Table 2 lists the testing parameters stress levels.

4. Testing

Capsules were placed in high temperature vacuum chambers which in turn were placed in vertical tube furnaces. Vertical tube furnaces allowed test capsules to be in a prototypic orientation. Vacuum chambers were maintained at testing temperatures of 550°C and 650°C. Vacuum chamber atmosphere and temperatures were monitored at all times during testing. Any increase in the internal pressure of a vacuum chamber, indicating a capsule failure, prompted removal of a gas sample for analysis. Leaking or breached capsules were identified by analysis of the released tag gas.

5. Results

The total test duration was 7400 hours. During this time period only two failures were indicated by vacuum chamber pressure increases. Analysis of the tag gas showed that the suspect failures were not chloride bearing capsules. Since the suspect capsules did not contain chlorine, testing was allowed to continue without interruption. Following the completion of testing all suspect failures were confirmed as capsules not containing chlorides.

TABLE 2

PRESSURIZED CAPSULE TESTING PARAMETERS

<u>Cladding Alloy</u>	<u>Temperature °C</u>	<u>Hoop Stress MPa</u>
316	550*	76
316	650	76
D-9	550	76
D-9	650	76
HT-9	550	51
HT-9	650	51

* 6 capsules per condition; 3 with chloride addition and 3 per condition without.

5.1 Austenitics

The appearance of the Type 316 SS and D-9 were very much the same, being slightly discolored indicating the presence of residual oxygen in the vacuum chambers causing very minor oxidation. Other than the described oxidation these capsules were in excellent condition with no failures occurring in either of these alloys.

5.2 Ferritics

All HT-9 capsules were oxidized to the same approximate extent noted in the austenitic alloys. More significant than oxidation was the apparent response of the HT-9 to a stress rupture loading. The two failures were HT-9 capsules tested at 650°C. The failed capsules were not chloride bearing and were thus not considered to be stress corrosion induced. However, both of the failures exhibited typical marked localized failure strains, or ballooning at the failure sites. Two other HT-9 capsules tested at 650°C also showed a tendency to balloon but did not fail. It does appear however, from this experience with pressurized HT-9 capsules that the mechanism of ballooning is the predominant failure mode in stress rupture for the temperature range discussed.

5.3 Metallography

Prior to routine metallographic examination all capsules were laser punctured to measure their actual testing pressures, to relieve the internal pressure, and to facilitate the removal of sodium. Each capsule was sectioned both above and below the prior sodium level as well as through the lower weld. Two capsules fabricated from Type 316 SS were examined, one from each exposure temperature. One each of the D-9 and HT-9 alloy capsules were examined from those tested at

650°C. The rationale behind this sample was based upon two facts. It was anticipated that the austenitic stainless steel would be most susceptible to stress corrosion and Type 316 SS has been best studied, so one sample at each testing temperature was assumed to uncover any evidence of chloride effects which may not have caused failure. Secondly, the worst case would normally be the 650°C exposure so the examined D-9 and HT-9 capsules were taken from this exposure temperature.

Metallurgical results indicate that microstructurally very little took place within these samples over the test duration. Figure 2 shows the 316 SS microstructures from specimen exposed at both 650°C and 550°C. The 550°C specimen appears to exhibit a limited amount of both transgranular and intergranular attack. Either of these modes could be anticipated in such a sensitized condition (2). There also appears to have been a small amount of corrosion occurring in the 550°C specimen, seen as a loss of material at or near the grain boundaries. The 650°C micrograph, shown in Figure 2, indicates a limited amount of transgranular attack. Although this attack was greater than that observed in the 550°C exposure it was not by a significant quantity. In both cases, 550°C and 650°C, this attack is less than one grain in depth. Typical carbide precipitation at the grain boundaries is seen in the 316 SS but was not observed in the D-9 as shown in Figure 3. Although the D-9 did appear to lose some material, it was noticeably less than that lost by the 316 SS. The loss of material is likely a sodium corrosion effect,

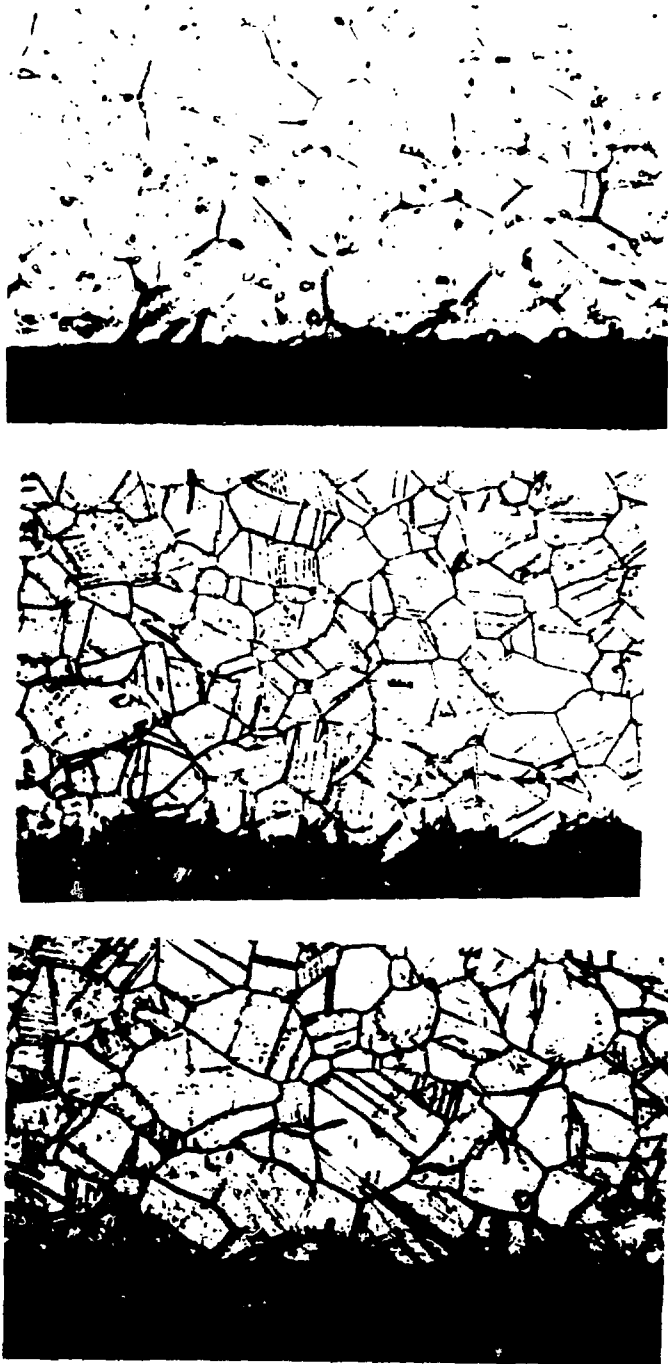


Figure 2. Microstructures from 316 SS capsules containing sodium and tested at temperatures of a) 550°C with chloride exposure, b) 650°C with chloride exposure, and c) 650°C without chloride



Figure 3. Microstructures from D-9 capsules containing sodium and tested at 650°C a) with chloride exposure and b) without chloride exposure.

evidenced by the fact that it was observed below the sodium level in both chloride spiked and unspiked specimens. The HT-9, shown in Figure 4, appears to have survived these exposures very well with no obvious indications of attack. It should be noted that all failures were located above the sodium level and were stress rupture in nature.

6. Discussion

The response of these alloys, in a stress rupture environment, to chloride exposure was essentially benign. The results shown here indicate that in the tests conducted the propensity to fail by stress corrosion was not exhibited. The more interesting point is why the austenitics, which are classically very sensitive to stress corrosion cracking when exposed to chlorides, did not fail. Researchers (5) have effectively shown the relationship of oxygen partial pressure on chloride induced stress corrosion failures. These researchers have in general shown that the tendency to stress corrosion crack is inversely proportional to the oxygen content of the stress corrosion media. Hisida and Nakada (6) investigated the effect of varying the concentration of chloride ions and oxygen, in high purity aqueous systems, on the tendency of austenitic stainless steels to stress corrosion crack. They found no influence on stress corrosion cracking from chloride ion additions at or below dissolved oxygen levels of 0.01 ppm. Making use of Henry's Law and some simplifying assumptions (7) this oxygen concentration is approximately equal to an oxygen partial pressure of $4 \times 10^1 \text{Pa}$ ($4 \times 10^{-4} \text{atm}$), the actual quantity being of less importance than its magnitude.

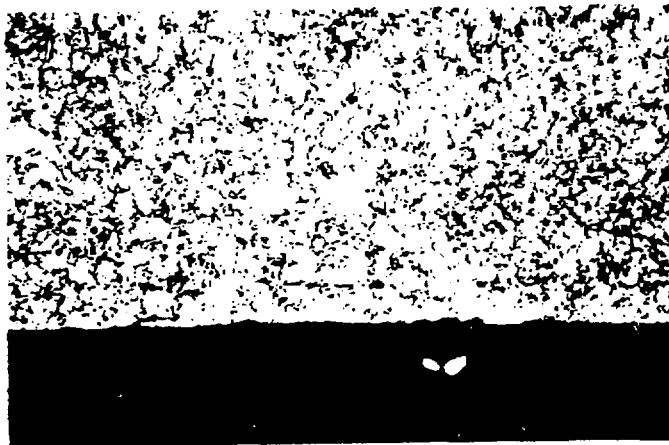
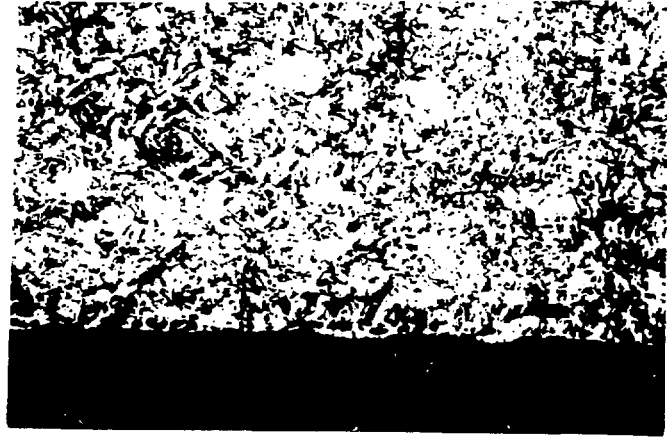


Figure 4. Microstructure from HT-9 capsules containing sodium and tested at 650°C a) with chloride exposure and b) without chloride exposure.

Perhaps the behavior of these alloys can be better understood by considering the test capsules to be a closed system. The system then consists of a given cladding alloy filled with sodium, some chlorine, and an inert cover gas. The oxygen partial pressure for this system is controlled by the chromium in the cladding, at temperatures of about 550°C and greater. Inspection of an Ellingham diagram (8) allows the partial pressure of oxygen to be assessed as a function of temperature. The partial pressure of oxygen within the capsules during testing was approximately 1.3×10^{-36} Pa (1.3×10^{-41} atm) and 1.3×10^{-31} Pa (1.3×10^{-36} atm) corresponding to 550°C and 650°C respectively. From these oxygen pressures it is seen that there is very little free oxygen in the system. Additionally, these quantities are many orders of magnitude below those values that have been shown to influence stress corrosion cracking in austenitic alloys.

In actual reactor operation the closed system that exists within a fuel element would include a metallic uranium alloy fuel pin. The oxygen partial pressure in this fuel bearing system would be a function of the fuel itself and not the chromium as described above. The oxygen partial pressure for the fuel bearing system would range from approximately 1.3×10^{-58} Pa (1.9×10^{-62} atm) to 1.3×10^{-52} Pa (1.9×10^{-56} atm) for 550°C and 650°C respectively. This oxygen partial pressure is 22 to 25 orders of magnitude less than that of the capsule system tested. For the purpose of comparison, the capsule experiment discussed herein contained an oxygen partial pressure in the range of 30 to 35 orders of magnitude lower than the above cited example, and the fuel bearing system in the range of 55 orders of magnitude lower.

When compared to the oxygen partial pressures that appear to be required to influence stress corrosion cracking, it is seen why the system, as tested, was benign. Indications are that the actual fuel bearing system would have such a small free oxygen activity, as compared to either the system tested or to those values listed in the literature, that the potential influence of chlorine on stress corrosion cracking should be of no concern.

7. Conclusions

The effect of oxygen partial pressure (inversely proportional) on the ability of chloride ions to influence stress corrosion of austenitic stainless steels in aqueous systems appears to apply in the nonaqueous system tested. Chloride ions, in the presence of very low partial pressures of oxygen, at a temperature range of 550°C to 650°C, appear to have little or no effect on the stress rupture life of HT-9, D-9, or Type 316 stainless steel. Chloride ions in the presence of very low partial pressures of oxygen at 550°C and 650°C appear to have little obvious effect on the microstructure of HT-9, D-9, or Type 316 stainless steels. The oxygen available to promote stress corrosion within a fuel element will be controlled by the fuel constituents and will be significantly lower than that present in this test by several orders of magnitude and should therefore, ensure that chloride stress corrosion cracking should not occur.

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