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CORROSION OF TYPE 316 STAINLESS STEEL IN MOLTEN LiF-LiCl-LiBr

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The properties of LiF-LiCl-LiBr salt make it attractive as a solvent for extracting tritium from a fusion reactor lithium blanket. Consequently, the corrosion of type 316 stainless steel by flowing (about 15 mm/s) LiF-LiCl-LiBr at a maximum temperature of 535°C was studied to determine whether compatibility with the structural material would be limiting in such a system. The corrosion rate was found to be low ($< 2 \mu\text{m/year}$) except immediately after the addition of a small amount of lithium metal to the salt. The lithium addition increased the corrosion rate to $\sim 13.5 \mu\text{m/year}$ at 535°C (approximately that of type 316 stainless steel exposed to lithium flowing at a similar velocity). At the proposed operating temperature ($\leq 535^\circ\text{C}$), however, it appears that type 316 stainless steel has acceptable compatibility with the tritium-processing salt LiF-LiCl-LiBr for use with a lithium blanket.

1. INTRODUCTION

The removal of tritium from lithium is an important consideration in the use of liquid lithium as a tritium-breeding fluid (blanket) in fusion reactors operating on the D-T fuel cycle. A LiF-LiCl-LiBr salt mixture has been proposed and used as a solvent for extracting tritium from a lithium blanket [1]. In this technique, the salt is directly contacted with a side stream of lithium from the blanket region, separated, and processed to remove the extracted tritium (by electrolysis using an argon-sparged electrode). Tests of the salt have shown it to be very effective in removing tritium from the lithium and in recovering it for subsequent use [1]. Consequently, we have studied the corrosion of type 316 stainless steel by flowing LiF-LiCl-LiBr to determine whether compatibility with a prime structural material will be an important concern in such a tritium/extraction system. The only previous work with this salt [1] indicated possible surface attack and intergranular penetration of type 304 stainless steel exposed to salt under actual processing conditions. The purpose of the present work was to study the corrosion by LiF-LiCl-LiBr under controlled conditions of salt velocity and temperature.

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228

2. EXPERIMENTAL PROCEDURES

A schematic drawing of the type 316 stainless steel thermal-convection loop (TCL) used in this study is shown in Fig. 1. The TCL is heated on the bottom and one vertical side. Cooling the other two sides causes the molten salt in the tubing to flow because of a density difference. The average velocity of the salt is about 15 cm/s. Other important features of the loop are the removable corrosion specimens in the two vertical legs and the accesses for insertion of electrodes for voltammetry. Standpipes are mounted above the vertical legs to give access to the corrosion specimens as well as the salt. Coupon weight changes, optical metallography, and electron microprobe analysis of selected specimens were used to characterize the corrosion of type 316 stainless steel by flowing LiF-LiCl-LiBr (9.6-22.0-68.4 wt %).

One of the most significant advances for studying corrosion processes in thermal-convection loops has been the application of voltammetry to follow electrode reactions in the salt. Controlled-potential voltammetry is increasingly used as a technique to examine the nature of an electrochemical reaction in different media, such as aqueous and nonaqueous

x

Figure 1 : Type 316 stainless steel thermal-convection loop. The designations on each indicate the sample numbers.

solutions and high-temperature salt systems [2,3]. For the present measurements, the electrodes consisted of the loop itself, which served as the counter electrode, and two iridium electrodes, which were the quasi-reference and working electrodes. These electrodes were typically 25-mm lengths of 1-mm-diam iridium wires welded to 3-mm-OD (1/8-in.) nickel risers. The electrode area exposed to the melt was 10 to 20 mm². The voltammograms were recorded versus the iridium quasi-reference electrode (Ir QRE), which was poised at the equilibrium potential (E_{eq}) of the melt. In this manner, relative changes in the oxidation potential of the salt and in the concentration of certain impurities and corrosion products can be qualitatively monitored. The equilibrium potential of the salt is a measure of the tendency of the melt to react with oxidizable or reducible materials that it contacts. For melts that are not poised by a redox buffer, relative changes in the equilibrium potential are conveniently observed by determining voltammetrically the potential difference (ΔE) between the melt equilibrium potential and the cathodic limit of the melt, which for

LiF-LiCl-LiBr is the reduction of Li^+ . We define the cathodic limit for these measurements as the potential at 16-mA cell current (see Fig. 2). Other reference markers may also be used as long as the same conditions are maintained. A decrease in the absolute value of ΔE , resulting in a cathodic shift in E_{eq} , for example, indicates that the melt has become less oxidizing; an increase in the magnitude of ΔE indicates the opposite.

x

Figure 2 : Typical voltammetry scan for pure LiF-LiCl-LiBr salt.

3. RESULTS

Coupons of type 316 stainless steel were exposed to flowing LiF-LiCl-LiBr for a total of 7855 h. After 2675 h of exposure, 0.8 g of lithium was added to the loop salt (7.3 kg). The resulting weight change behavior as a function of time for the specimen at the maximum temperature (535°C) position is shown in Fig. 3. Note that after 2175 h of coupon exposure (~3785 h of salt circulation) with a constant corrosion rate, the specimen weight loss increased dramatically when lithium was added to the salt. The corrosion rate then quickly decreased to a value smaller than that measured before to the lithium addition. This type of behavior was not limited to the 535°C specimen. As shown in Table 1, all the loop coupons exhibited similar trends in weight loss rate with exposure time. The corrosion rates in Table 1 are those measured during the 2175-h period before the lithium addition (period 1), during the 430 h immediately following the addition (period 2), and during the remainder of the loop test (period 3). They are taken from the slopes of the least-squares fitted lines in the given time intervals. The data show that the lithium addition caused an increased specimen weight loss at all loop positions for a short period of time. The data in Table 1 also indicate that the lower corrosion rates during periods 1 and 3 were not very

sensitive to specimen position or to temperature within the loop. Indeed, every loop coupon suffered weight losses ranging between 2.0 and 0.6 $\mu\text{m}/\text{year}$. During period 2, the rate of weight loss appeared to depend weakly on temperature in that the average hot leg corrosion rate was 37% greater than that of the cold leg. (see Table 1).

x

Figure 3 : Weight loss versus exposure time for type 316 stainless steel in flowing LiF-LiCl-LiB at 535°C .

x

Examination of metallographic cross sections after 7855 h revealed evidence of both attack and reaction layers on the hot leg coupons (see Fig. 4). The reaction layer was discontinuous in most cases, but the underlying attack zone

was continuous though somewhat uneven in depth (particularly on the surface of the 535°C specimen.) The attack morphology is shown at higher magnification in Fig. 5. Reaction layers like those shown in Fig. 4 were not observed on the cold leg specimens, which did, however, exhibit evidence of attack (see Fig. 6). The extent of attack was less for the coupon exposed at the lowest temperature [Fig. 6 (b)]. It should be emphasized, however, that in the worst case the combined depth of the reaction layer and attack zone on a loop coupon was only 5 μm .

x

Figure 4 : Discontinuous reaction layer on type 316 stainless steel exposed to LiF-LiCl-LiBr for 7855 h (with lithium added during exposure). Attack zone on specimens is not easily seen at this magnification. (a) Exposed at 535°C. (b) 510°C. (c) 490°C.

x

Figure 5 : Attack zone in type 316 stainless steel exposed to LiF-LiCl-LiBr for 7855 h (with lithium added during exposure). Taken at gaps in reaction layer. (a) Exposed at 535°C. (b) 510°C. (c) 490°C.

x

Figure 6 : Type 316 stainless steel exposed to LiF-LiCl-LiBr for 7855 h (with lithium added during exposure) in cold leg. (a) Exposed at 500°C . (b) 465°C .

Electron microprobe analysis was used to define the concentration profiles of Fe, Ni, Cr, and Mo in the near-surface area of selected specimens. These results, shown in Fig. 7, indicated that nickel was somewhat depleted from the surfaces of the coupons exposed at 535 and 510°C since the nickel lines drop off below the respective coupons surfaces. Chromium may be slightly depleted also. The specimen exposed at 465°C did not appear to have been depleted of these elements [see Fig. 7(c)]. Analysis of the salt after 675 h of loop operation revealed no significant increase in the concentration of chromium, nickel, or iron. This would therefore indicate that the nickel was depleted from the steel after the lithium was added.

Periodic voltammetry scans of the salt were taken throughout the time the loop was operating. The behavior of ΔE during this time is shown in Fig. 8. In general, ΔE was approximately constant until the lithium was added to the salt. Then it shifted very close to zero potential and then gradually increased as loop operation continued. The data points in Fig. 8 that represent measurements taken with the specimens out of the loop are denoted by open circles. Comparing with the data points immediately following the open circles shows that in all cases (except just after the lithium was added) ΔE became more greater when the specimens were reinserted and then rapidly returned to approximately its former value. These relatively small changes indicate the transient effect of impurities introduced during specimen insertion on the oxidation potential of the salt.

x

Figure 7 : Microprobe traces of near-surface areas of type 316 stainless steel coupon cross sections after 7855 h exposure to LiF-LiCl-LiBr (with lithium added during exposure).
(a) Exposed at 535°C. (b) 510°C. (c) 465°C.

x

Figure 8 : Limit potential versus salt circulation time for the type 316 stainless steel thermal-convection loop operated between 535 and 465°C.

3.1 Discussion

Two general aspects of halide salts become important in defining their corrosivity. Halides of the type used in this investigation are relatively stable in the presence of the metallic elements composing austenitic stainless steels; that is, reactions between these salts and containment materials are limited thermodynamically. On the other hand, materials exposed to molten halides generally do not form passivating films because the corrosion products tend to have relatively high solubilities. Molten fluoride salts, which have been extensively studied in previous TCL investigations, afford relevant examples of the aforementioned behavior [2,4,5]. Typically, flowing nonisothermal fluoride salt will oxidize and remove the least noble element from the metal container and then may subsequently deposit it in another portion of the system. Results from a nickel-base molybdenum-chromium-iron alloy (Hastelloy N) in a circulating, nonisothermal salt composed of $\text{LiF}-\text{BeF}_2-\text{ThF}_4-\text{UF}_4$ have shown that fluoride salts will oxidize chromium by reaction first with impurities in the salt such as HF , NiF_2 , and FeF_2 and later by possible reaction with constituents of the salt [4]. Impurity reactions expected are

These reactions of impurities with the container will occur at a high rate initially but will slow down as the impurities are consumed. If no additional impurities are added to the system, these initial reactions are not expected to significantly contribute to corrosion after a relatively short time.

Consideration of the weight change data (Fig. 3) reveals that in the absence of free lithium the corrosion rate of type 316 stainless steel by slowly flowing $\text{LiF}-\text{LiCl}-\text{LiBr}$ under a small impressed temperature difference is low. The effects of impurities, which were introduced during each specimen insertion (see Fig. 8), on the corrosion rate was obviously small. Also, the observation of weight losses at every coupon position indicates that solubility limits of impurities in salt had not been exceeded. Longer operating times or larger amounts of impurities would likely result in deposition at lower temperature. The slightly higher corrosion rate measured initially, relative to the rate measured during the last few thousand hours, suggests a greater concentration of impurities and greater oxidizing potential during the first 3875 h of salt circulation in the TCL. The overall low corrosion rate of the steel in the salt, however, is indicative of the relative stability of the lithium halides.

The presence of free lithium in the LiF-LiCl-LiBr is typical of the actual conditions in the salt when it is being used to extract tritium from lithium. The large increase in the corrosivity that occurred when lithium was added to the salt (see Fig. 3) is therefore of concern. The free lithium may affect the corrosion rate of the stainless steel exposed to the salt by its effect on the potential of the salt and by directly reacting with (dissolving) the steel. With respect to the first possibility, the lithium may be expected to serve as a buffer and lower the oxidation potential and, consequently, the corrosion rate, of the salt in the same manner as has been reported [2] for beryllium additions to LiF-BeF_2 . This should be consistent with what we observed electrochemically, but the shift in ΔE to approximately zero could also be due to the oxidation of lithium at the counter electrode just balancing the lithium reduction half reaction. Regardless of this, as shown in Fig. 3, the corrosion rate dramatically increased rather than decreased. We must therefore ascribe the change in corrosion rate to the lithium acting independently to dissolve the containment material despite its relatively small concentration in the salt. The observed depletion of nickel from the exposed coupons (Fig. 7) is consistent with this behavior since preferential leaching of nickel from type 316 stainless steel is characteristic of corrosion by flowing lithium [6]. The extent of depletion of chromium from this steel when exposed to slowly flowing lithium at 500°C is not great [6], and the small amount we observed could be due to the free lithium or to removal of chromium by the salt.

As described above, metallographic examination revealed a continuous, though shallow, zone of attack on all the loop coupons with a thin, distinct, discontinuous, overlying reaction layer on the hot leg specimens. The type of attack shown in the micrographs of Figs. 4, 5, and 6 has some similarities to that induced by lithium dissolution, which leads to the formation of porous surface layers on type 316 stainless steel [6]. However, the observation of the discontinuous reaction layer on the loop's hot leg specimens is not consistent with lithium-induced corrosion, and we are unsure of its origins. Since the reaction layer is above the attack zone we may assume that it formed after the rapid dissolution due to the lithium addition. However, our microprobe examination failed to detect the presence of any halide ions in the reaction zone, although this may have been due to the thin and discontinuous nature of the film.

Our results show that, although type 316 stainless steel is compatible with slowly flowing LiF-LiCl-LiBr at temperatures up to 535°C , significant corrosion may occur if lithium is entrained in the salt. In addition, the extraction of tritium could affect impurity-induced reactions in the salt of the type shown

as Eq. (1). However, we expect that the corrosion will not be sufficiently severe at such temperatures to limit the use of the salt, because the corrosion in the lithium system itself will most probably be the limiting factor.

4. SUMMARY

The results from this study indicate that type 316 stainless steel has a low corrosion rate ($<2 \mu\text{m}/\text{year}$) in slowly flowing LiF-LiCl-LiBr . The effect of free lithium in the salt is to increase the dissolution rate so that it is nearer that of type 316 stainless steel exposed to flowing lithium. At the proposed operating temperature ($\sim 500^\circ\text{C}$), however, it appears that type 316 stainless steel has acceptable compatibility with the tritium-processing salt LiF-LiCl-LiBr .

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FOOTNOTES:

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