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MASS TRANSFER BEHAVIOR OF A MODIFIED AUSTENITIC STAINLESS STEEL IN LITHIUM*

P. F. TORTORELLI and J. H. DeVAN

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

An austenitic stainless steel that was developed to resist neutron damage was exposed to lithium in the high-temperature part of a thermal convection loop for 6700 h. Specimens of this Prime Candidate Alloy (PCA) composed of 65.0 Fe-15.9 Ni-13.0 Cr-1.9 Mo-1.9 Mn-1.7 Si-0.5 Ti-0.05 C (wt %) were exposed at 600 and 570°C in both solution annealed and cold worked forms. The dissolution process was found to be similar to other austenitic alloys in flowing lithium; weight losses of PCA eventually became linearly proportional to exposure time with the specimen surfaces exhibiting porous layers depleted in nickel and chromium. However, the measured weight losses and dissolution rates of these PCA specimens were higher than those of type 316 stainless steel exposed under similar conditions and can be attributed to the higher nickel concentration of the former alloy. The effect of cold work on dissolution rates was less definitive, particularly at 570°C. At longer exposure times, the annealed PCA specimen exposed at 600°C suffered greater dissolution than the cold worked material, while no effect of prior deformation was observed by analysis of the respective surfaces.

1. INTRODUCTION

For fusion technology, the compatibility of possible structural alloys with the reactor coolant and the tritium-breeding material must be considered in the alloy development and reactor design efforts. In order to do this, corrosion studies of appropriate materials in possible fusion reactor environments are required. Since molten lithium can serve as an efficient coolant and/or tritium-breeding fluid for fusion reactors, it is important to determine if corrosion effects would limit the use of a particular alloy in nonisothermal lithium. This paper contains corrosion results from a thermal-convection loop experiment with a modified austenitic stainless steel (denoted Prime Candidate Alloy or PCA) that was primarily developed for improved resistance to neutron damage.¹ The purposes of this experiment were to investigate the corrosion of both solution-annealed and cold-worked PCA by flowing lithium and to compare the PCA results

with data for standard annealed type 316 stainless steel to determine the effect of the difference between these two austenitic alloys on their corrosion behavior in lithium. Prior work with lithium loops has yielded baseline data for type 316 stainless steel exposed to thermally convective lithium²⁻⁴ and has demonstrated the effect of nickel concentration on the corrosion of Fe-Ni-Cr alloys.^{5,6} The only other results for PCA in lithium have come from a recent experiment in a forced convection loop.⁷

2. EXPERIMENTAL PROCEDURES

The corrosion data were obtained using a lithium thermal convection loop (TCL) of the type previously described in detail.^{2,4} The lithium density gradient caused by the imposition of a temperature difference of 150°C (600-450°C) across the loop resulted in a lithium velocity of approximately 30 mm/s. Such a slow rate would be characteristic of

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lithium being used as a semistagnant tritium breeding fluid. The loop is designed to allow the coupons to be inserted and removed from the hot and cold legs without stopping the lithium flow. In this way, specimen weight and microstructural changes can be measured as a function of exposure time. In addition, the location of specimens in both the dissolution and deposition parts of the loop permits the measurement of any mass transfer tendencies. The TCL was constructed of type 316 stainless steel and had circulated lithium for many thousands of hours prior to the insertion of the specimen set used in this study. The interior surface of the upper hot leg tubing was therefore depleted in nickel due to preferential leaching of this element.³ The presence of the resultant ferritic surface may have an effect on the dissolution of the fresh austenitic loop coupons. However, this effect has been measured and has been taken into account when comparing the present dissolution data to prior results for type 316 stainless steel by using only data typical of such loop conditions.

The lithium used in the loop was purified by cold trapping and subsequent heating at 815°C for 100 h in a titanium-lined pot containing zirconium foil. Typical impurity concentrations of the purified lithium were 30 to 80 wt ppm nitrogen and 30 to 130 wt ppm oxygen.

The loop specimens were rectangular coupons measuring ~25 × 8 × 1 mm. All the specimens in the cold leg and in most of those in hot leg locations were type 316 stainless steel while PCA coupons were placed at the hot test (600 and 570°C) specimen positions. The compositions of these alloys are given in Table 1. Unlike the other specimen locations, the PCA positions contained two coupons each (attached on opposite sides of the specimen rod). These sets of two coupons were composed of a PCA specimen that was 20–25% cold worked (A3) and one

that was cold worked then solution annealed at 1100°C for 30 min (A1).

Table 1. Compositions of PCA and type 316 stainless steel

Element	PCA (Actual)	Concentration, wt %
		Type 316 stainless steel (nominal)
Fe	65.0	67
Cr	13.0	17
Ni	15.9	11
Mo	1.9	2
Mn	1.9	2
Si	1.7	1
Ti	0.5	
Al	0.05	
C	0.05	0.08

The specimen weights were measured eight times during the 6700 h of coupon exposure to lithium in the TCL. At the end of this period, the PCA specimens were metallographically examined and selected surfaces were analyzed by scanning electron microscopy and associated energy dispersive x-ray analysis.

3. RESULTS

Weight change measurements of PCA as a function of time at the 600 and 570°C positions revealed that, at 600°C, the cold-worked specimen (PCA-A3) initially had slightly higher weight losses than the annealed specimen (PCA-A1) but, at longer times (>3000 h), the latter material had significantly higher cumulative weight losses (Fig. 1). This figure also shows that both specimens suffered greater weight losses than annealed type 316 stainless steel exposed under similar conditions. The data for the PCA specimens at 570°C do not show similar tendencies; while the cold-worked specimen initially had slightly greater weight losses than the annealed material, the overall weight losses are similar for the two at longer times. Furthermore, the weight loss data for

PCA falls within the scatter band for type 316 stainless steel.

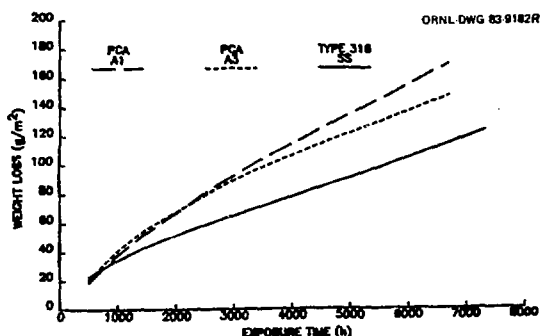


FIGURE 1
Weight loss versus exposure time for PCA and type 316 stainless steel exposed to thermally convective lithium at 600°C

The time dependence of the weight change of PCA was generally similar to that previously found for type 316 stainless steel (see Fig. 1); the rate of weight loss decreased with time until a steady state or linear dependence on time was reached. Once this steady state has been attained, the dissolution rate of a particular specimen is obtained from the slope of the weight loss versus time curve. When this was done for the data at 600 and 570°C, the dissolution rates noted in Table 2 were obtained. Note that, as with the long-term weight losses, the dissolution rate of PCA-A1 at 600°C is greater than that of PCA-A3 and both have higher dissolution rates than type 316 stainless steel (although the A3 dissolution rate is not much greater). At 570°C, the dissolution rates for A1 and A3 are the same and are about 40% greater than that for type 316 stainless steel. This result for the 570°C specimen is in contrast to the overall weight losses which, as reported above, are comparable for both compositions.

Table 2. Steady-state dissolution rates for PCA and type 316 stainless steel exposed to thermally convected lithium

T (°C)	Steady-state dissolution rate ^a (mg/m ² -h)		
	PCA-A1 ^b	PCA-A3 ^c	type 316 SS
600	20.8	15.7	13.6
570	12.3	12.1	8.5

^aSlope of weight loss versus time curves after linear dependence was established.

^bAnnealed

^cCold worked

Metallographic examination of polished cross sections of the PCA specimens revealed corrosive attack consistent with the dissolution rate measurements. As shown by the optical micrographs in Fig. 2 and the data in Table 3, the PCA-A1 specimen exposed at 600°C was attacked (as revealed by the depth of porosity) to a greater extent than the PCA-A3 material exposed at the same temperature. At 570°C, both A1 and A3 had similar depths of porosity. The depths of the porous layers on the PCA specimens were greater than those for similarly exposed type 316 stainless steel.

Table 3. Average depth of corrosive attack of PCA and type 316 stainless steel exposed to thermally convected lithium

T (°C)	Depth of Porosity ^a (μm)		
	PCA-A1 ^b	PCA-A3 ^b	type 316 SS ^c
600 ^d	91 ± 3	68 ± 6	52 ± 4
570	54 ± 4	51 ± 2	41 ± 4

^aAverage of twenty measurements across both sides of specimen coupons.

^b6700 h of lithium exposure

^c7500 h of lithium exposure

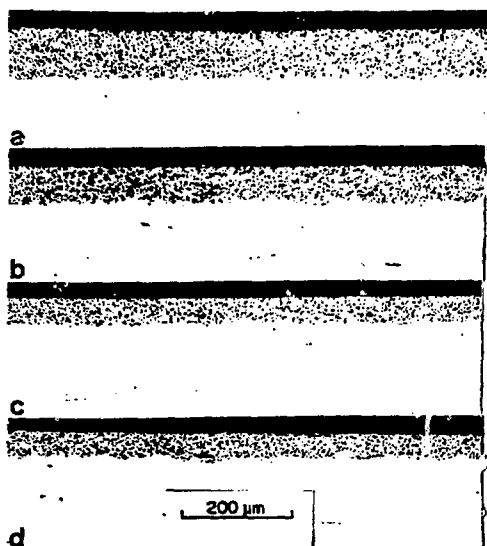


FIGURE 2

Polished cross sections of PCA exposed to thermally convective lithium for 6700 h. (a) A1, 600°C. (b) A3, 600°C. (c) A1, 570°C. (d) A3, 570°C

Scanning electron microscopy and associated energy dispersive x-ray analysis of the PCA specimens exposed at 600°C showed that A1 and A3 had similar porous surface morphologies layers (see Fig. 3). Energy dispersive x-ray spectra taken from these surfaces revealed significant depletion in nickel and chromium.

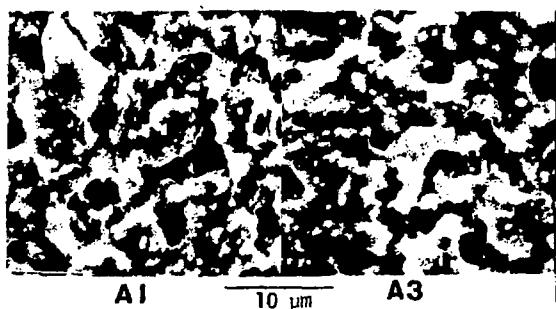


FIGURE 3

Scanning electron micrographs of PCA exposed to thermally convective lithium for 6700 h at 600°C

Analyses of a selected number of the nodules observed on these surfaces showed them to be enriched in molybdenum or titanium relative to the surrounding matrix.

4. DISCUSSION

In general, the characteristics of the corrosion of PCA in flowing lithium, in terms of the dissolution behavior with time and the effects of exposure on the surface morphology and composition, are very similar to what is observed when standard austenitic alloys are exposed under similar conditions. For example, as already mentioned in the Results section and as seen in Fig. 1, the weight losses of PCA follow a similar time dependence as that of type 316 stainless steel.^{2,3} This is to be expected for Fe-Ni-Cr alloys since it is thought that the higher, initial rates of weight losses correspond to the rapid preferential leaching of nickel and chromium while the final steady-state rate is characteristic of the dissolution of the corrosion-modified surface layer.² It is thus not surprising that an alloy with a composition like that of PCA exhibits this type of behavior. Furthermore, the porosity that developed when PCA was exposed to flowing lithium (Fig. 3) is very similar to that observed on type 316 stainless steel and higher nickel alloys.^{2,4,6,7} Finally, the reported depletion of nickel and chromium from PCA is also characteristic of the Fe-Ni-Cr class of alloys.^{4,6}

While it is apparent from the above discussion¹ that the corrosion reactions between flowing lithium and PCA are the same as those that occur in other lithium-nickel-bearing alloy systems, the extent of these reactions are not necessarily similar. For example, as measured by dissolution rates and depth of attack, the corrosion of PCA is greater than that of type 316 stainless steel.

Because of the role of nickel in the dissolution process, this greater susceptibility of PCA relative to type 316 stainless steel can be attributed to the higher nickel content of PCA. Indeed, prior work has shown that the mass transfer of Fe-Ni-Cr alloys in thermally convective lithium increased as the concentration of nickel was increased from 11 to 32 wt %.⁶ Furthermore, a recent study of PCA exposed in a lithium forced convection loop system yielded similar results on the accelerated corrosion of this alloy with respect to typical austenitic stainless steel.⁷ It is interesting to note that this compositional dependence is also observed in another liquid metal system: PCA suffered greater corrosion than type 316 stainless steel in Pb-17 at. % Li.⁸

The above data show that for long time exposures the corrosion of the annealed PCA specimen at 600°C was greater than that of the cold worked specimen exposed at this temperature, while, at 570°C, no difference was observed. The reason for the greater corrosion of the annealed material at 600°C is not apparent, particularly since other work has shown the opposite effect.⁷ However, these other experiments were not only conducted at lower temperatures but were also for shorter exposure times than the present study, which for short times showed slightly greater weight losses for the cold worked specimens. A possible explanation for the greater corrosion of the annealed material in this study may have to do with the respective starting grain sizes of A1 and A3. If the corrosion process is initiated by localized reactions at grain boundaries,⁶ the smaller grain size of A1 may lead to greater attack due to the higher density of grain boundaries exposed to the lithium. At lower temperatures (like those of the work reported in ref. 7), another reaction may control the overall corrosion process such that the cold

worked material is corroded more rapidly. In this regard, it is interesting to note that the present results show an effect at 600°C but not at 570°C.

The observation of molybdenum enriched nodules on lithium dissolved surfaces has also been reported previously for type 316 stainless steel.⁶ These features are thought to result from the resistance of molybdenum to dissolution in lithium such that the nodules are areas of molybdenum precipitates (or residual molybdenum since its carbide is unstable in lithium) that recede more slowly than the surrounding matrix. This same type of behavior probably explains the new observation of a titanium-enriched feature. Titanium is used in PCA as a carbide former and such titanium-containing nodules probably represent sites of this carbide (which is stable in lithium).

5. SUMMARY

The exposure of an austenitic alloy composed of 65.0 Fe-15.9 Ni-13.0 Cr-1.9 Mo-1.9 Mn-1.7 Si-0.5 Ti-0.05 C (wt %) to thermally convective lithium for 6700 h at 600 and 570°C resulted in corrosion reactions that were similar to what is observed for other austenitic alloys exposed under similar conditions: preferential depletion of nickel and chromium, porosity development, surface nodules, and constant dissolution rates at long times. However, when compared to baseline data of type 316 stainless steel, this PCA alloy was corroded more rapidly due to its higher concentration of nickel. The solution-annealed PCA corroded more than cold worked PCA at 600°C but both forms of this alloy showed similar corrosion rates at 570°C. Such an observation may indicate an influence of grain boundary density on the rate-controlling step for the corrosion process at higher temperatures.

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