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THERMAL-GRADIENT MASS TRANSFER IN LITHIUM-STAINLESS STEEL SYSTEMS*

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The corrosion of type 316 stainless steel by flowing Li was studied as a function of time in thermal-convection loops. After a transient period, the corrosion rates were observed to be constant with time with values ranging from 10 to 20 mg/m² h. Preliminary analysis indicated that the corrosion rate is controlled by the diffusion of Fe through the liquid Li boundary layer. The deposition processes involved the formation of crystals of nearly pure Cr in the cold legs of the loops.

1. INTRODUCTION

The possible uses of Li as a coolant and/or breeding material in fusion reactors have renewed interest in the compatibility of molten Li with engineering materials. Both loss of structural material due to corrosion and the development of flow restrictions by mass transfer of the dissolved elements to the cooler parts of the system are areas of concern. In this paper, results of the corrosion of type 316 stainless steel by circulating Li in thermal-convection loops are reported and a preliminary analysis of the data is presented.

2. EXPERIMENTAL PROCEDURES

The Li used in this study was purified by cold-trapping and subsequent heating at 815°C for 100 h in a titanium-lined pot containing zirconium. Typical impurity concentrations of the purified Li were 30 to 80 wt ppm N and 30 to 130 wt ppm O. This Li was then used to fill three type 316 stainless steel loops (see Fig. 1) that contained corrosion coupons (19.1 by 7.9 by 0.9 mm) of the same composition. The coupons can be retrieved and placed back in the heated (hot) and cooled (cold) legs of the loop without stopping the lithium flow. This type of loop differed from some previously reported ORNL thermal-convection loops [1], which were smaller, had a different temperature profile, and were destructively examined after a fixed period of time. As shown in Fig. 1, the coupons are labeled according to their positions in the hot (H) or cold (C) legs. They are weighed before the start of a loop test and at programmed intervals during the experiment to establish weight change profiles as a function of time. Additionally, small quantities of a loop's circulating Li can be removed

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Fig. 1. A thermal-convection loop with accessible corrosion coupons.

periodically to check the impurity concentrations. During test, the concentrations of nitrogen and oxygen never were above 140 wt ppm. The circulation of Li was maintained by establishing a fixed thermal gradient along the loop. The maximum temperature was held at 600°C at the top of the hot leg, while the flow rate was adjusted by means of a tapered valve at the bottom of the hot leg surge tank, so that the lowest temperature was about 450°C (at the

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bottom of the cold leg). The Li flow velocity in these loops for this ΔT of 150°C was approximately 30 mm/s.

3. RESULTS

The three thermal-convection loops operated under nominally the same design and temperature conditions. Corrosion coupons were removed and weighed at 500 to 3700-h intervals during the operation of each loop. Loop 3 developed an unexplained flow restriction after 500 h, necessitating draining the loop and refilling it with fresh Li. It then operated an additional 2030 h without further flow perturbations. Loops 1 and 2 exhibited signs of a flow restriction after 8000 and 3500 h, respectively.

The corrosion in a nonisothermal loop of flowing Li is a function of position (temperature) in the circuit. Material is transferred from the hotter part of a loop to the colder region, and this is reflected by a temperature-dependent pattern of weight gains and losses among the corrosion coupons. This mass transfer is clearly illustrated in Fig. 2, which is a plot of weight change versus coupon position for loop 1 after 9000 h. Approximate temperatures ($\pm 5^\circ\text{C}$) are also noted on the abscissa of the plot. Note that the specimens in positions H2, H3, and H4 exhibited the greatest weight losses. The same was true for the other two loops.

Fig. 2. Weight changes versus coupon position in a loop operated for 9000 h.

A major objective of these loop tests was to monitor corrosion as a function of time. This type of data is shown in Fig. 3, in which the H3 weight losses (see Fig. 1) are plotted against exposure time for loops 1, 2, and 3. After an initial transient period, which seemed to last about 1000 h, the weight losses became linearly dependent on time. Constant, or steady-state, corrosion rates for the coupons were then determined from the slope of the best fit line to the linear portion of such plots (see Fig. 3). The maximum corrosion rates (which are for the coupons in the H3 positions) are given in Table 1.

Fig. 3. Weight change versus exposure time for loops 1, 2, and 3 for coupons in position H3.

Table 1
Maximum steady-state corrosion rates for coupon H3 (600°C)

Loop	Steady-State Corrosion Rate (R_s)	
	(mg/m ² h)	($\mu\text{m}/\text{year}$)
1	-12	-11
2	-20	-19
3	-13	-12

In a similar manner to the method for the determination of the corrosion rates, the rates of weight gain for coupons C4 through C8 were measured from the slopes of the weight change versus exposure time plots for times greater than or equal to 1000 h. These values are presented in Table 2. The position of the maximum rate of weight gain differed among the three loops.

Table 2
Rate of weight gains for coupons C4 to C8

Coupon	T (°C)	Weight Gain Rate, mg/m ² h		
		Loop 1	Loop 2	Loop 3
C4	523	1.4	2.9	8.0
C5	509	2.8	4.3	9.2
C6	492	3.2	4.3	7.8
C7	477	4.3	3.9	8.3
C8	462	3.5	5.1	7.7

Metallographic examinations were made of several of the 9000-h coupons from loop 1. Coupons H2 through H5 had a very porous near-surface layer with little evidence of grain boundary attack. Figure 4 is an optical micrograph of coupon H3, which suffered the greatest weight loss. Energy dispersive x-ray analysis of its surface showed a preferential loss of

Fig. 4. Coupon H3 from loop 1 after 9000 h (~596°C).

Ni and Cr. The material released by coupons in the hotter region was transported to the colder part of the loops. Figure 5 is a scanning electron micrograph of the surface of a cold-leg coupon after approximately 1700 h. Energy dispersive x-ray analysis showed that these crystalline deposits were about 95% Cr, with <5% Fe and <1% Ni. At longer times, the composition of the upper layer deposits tended to approach that of stainless steel.

Fig. 5. Surface of a cold-leg coupon.

4. DISCUSSION

When stainless steel is exposed to circulating Li, Ni and Cr are preferentially dissolved from the hottest samples, thereby

leading to an enrichment in Fe on the surface suffering weight losses [1]. The depletion of Ni from the near-surface regions destabilizes the austenitic phase, which then transforms to a ferritic structure. This transformation was observed in the present experiments by optical metallography (Fig. 4) and magnetic measurements of the amount of surface ferrite. Since the extent of ferritization is directly related to the dissolution process, this latter type of data revealed that the relative amount of ferrite followed the same dependence on loop position as the weight losses of Fig. 2.

The observed corrosion is analogous to that observed in Na-stainless steel systems (for example, see refs. [2] and [3]), so it is of value to review the relatively extensive evaluations of corrosion kinetics in these systems as a model for interpreting the present results. Brush [2] showed that the onset of steady-state corrosion in the Na-stainless steel system corresponds to the point at which each element of the stainless steel dissolves in proportion to its bulk concentration; the preferential corrosion of Ni and Cr is exactly balanced by their reduced surface concentrations so that Fe predominates as the species being transferred.

As seen in Fig. 2, the weight loss data from a thermal-convection loop can be used to analyze mass transfer rates as a function of temperature. As a preliminary approach to this analysis, we have used Holman's [4] expression for the corrosion rate (R_g), (which he applied to the Na-stainless steel system):

$$R_g = k \frac{dC_{\text{sat}}}{dT} \Delta T. \quad (1)$$

Here, C_{sat} is the solubility of the rate-controlling element in Li at temperature T and ΔT is the difference between T and the temperature of the point in the hot leg where $R_g = 0$, which is about 509°C for these loops. Equation (1) is derived from the rate equation

$$R_g = k(C_{\text{sat}} - C), \quad (2)$$

where C is the concentration of the particular element in the Li. The latter equation is independent of time for a dissolution process controlled either by diffusion through a liquid boundary layer or by a first order reaction at the alloy surface [5]. We will assume that

$$k = k_0 \exp(-Q/RT), \quad (3)$$

and

$$C_{\text{sat}} = A \exp(-\Delta H/RT). \quad (4)$$

Here, Q is an "activation" energy, which depends on the rate-controlling mechanism, and ΔH is the heat of solution of the corroding element in Li. From Eq. (4),

$$\frac{dC_{\text{sat}}}{dT} = (A \Delta H/R)(1/T^2) \exp(-\Delta H/RT), \quad (5)$$

if ΔH does not vary greatly with temperature in the range of interest [6]. Combining Eqs. (1), (3), and (5) results in

$$R_p = R_0 \exp(-Q/RT) \exp[-(\Delta H)/RT], \quad (6)$$

or

$$\ln(R_p T^2 / \Delta T) = \ln(R_0 \Delta H / R) - (Q + \Delta H) / RT. \quad (7)$$

According to Eq. (7), a plot of the $\ln(R_p T^2 / \Delta T)$ versus $1/T$ should be a straight line. This analysis was applied to the steady-state corrosion rates of H3 (596°C), H4 (577°C), H5 (557°C), and H6 (538°C) in each of the three loops. (Coupon H2 was in the surge tank under different flow conditions and therefore was excluded from the analysis.) The correlation with Eq. (7) was satisfactory for loop 2 (see Fig. 6), but the agreement was poorer for loops 1 and 3. Reasons for the disagreement may be uncertainty in the measurements of the temperature profile and statistical inaccuracy due to the relatively small number of data points.

Fig. 6. Temperature analysis of the corrosion rates from loop 2.

Referring to Fig. 6, the slope of the best-fit line was equated to $(Q + \Delta H)/R$ and led to a value of 81.2 kJ/mol (19.4 kcal/mol) for $Q + \Delta H$. From the solubility data of Leavenworth and Cleary [6], the ΔH for Fe in Li can be estimated as 59 kJ/mol (14 kcal/mol). (The ΔH is approximately the same for Fe, Cr, and Ni in Li.) This leads to a Q of 25 kJ/mol (about 6 kcal/mol), a value that is much smaller than the activation energies for solid-state diffusion of Fe, Cr, or Ni in stainless steel. However, this value is of the same order of magnitude as the activation energy for the diffusion of Fe in liquid Na [7] and, presumably, for the diffusion of Fe in Li. On the basis of this low activation energy, we believe that the rate-controlling mechanism in the present case is the diffusion of Fe from

the solid surface through the liquid Li boundary layer to the region of turbulent flow. This is also consistent with the fact that linear corrosion rates are indicative of the prime variable of the rate-controlling process being outside the alloy phase [2]. If this conclusion is correct a significant flow velocity effect on the corrosion rate is to be expected for this Li-type 316 stainless steel system. However, in Na liquid phase diffusion ceases to be rate controlling above a velocity threshold (see, for example, ref. [3]), and the corrosion is controlled by the rates of the solution reactions occurring at the alloy-liquid metal interface or by solid-state diffusion.

Flow was restricted in several of our loops (see Sect. 3) by metal crystals formed by the transfer of material to the colder regions (see Fig. 5). Although this deposition appears to be a potentially serious problem for Li-stainless-steel systems, few investigators have treated the deposition phenomena in circulating liquid metals. Polley [8] has shown that, while the corrosion rate is predicted to be proportional to composition (see above), the deposition rate in general is not. We used Eq. (7) also to obtain $Q + \Delta H$ from the data of Table 2 by plotting the rate of weight gain versus $1/T$ and measuring the slope. This procedure resulted in a satisfactory straight-line fit and a value of $Q + \Delta H$ for a given loop, but the slopes varied by more than a factor of 2 among the loops. The corresponding variation in Q (4–80 kJ/mol) precludes speculation on the rate-controlling processes for the deposition step. However, the observed formation of almost pure Cr crystals on the surface is indeed indicative that a stoichiometrical relationship does not hold for deposition (at a given location) in accordance with arguments by Polley [8].

Table 1 shows that the steady-state corrosion rate of loop 1 is less than that of loops 2 and 3. This can possibly be because the rates in these latter two loops would decrease if longer term data were added. This would decrease the weighting of the 1000 h data since these shorter exposure times may still reflect some of the initial transient behavior (see Fig. 3). Additionally, the frequency of sampling (which was greater for loops 2 and 3) may affect the corrosion rate. We have not yet assessed this effect.

The conversion of the steady-state mass corrosion rates in Table 1 into terms of surface recession ($\mu\text{m/year}$) requires at least one caveat. As seen in Fig. 4, the near-surface layer of type 316 stainless steel in the hotter region was very porous after exposure to circulating Li. Therefore, even in the absence of grain boundary penetration, such a surface recession rate does not completely reflect the effect of the corrosion on the stainless steel. Such porosity, coupled with below-surface depletion of Ni and Cr, causes errors in the

calculation of surface recession from weight loss data and may affect the mechanical behavior of the material.

5. SUMMARY

In a Li-type 316 stainless steel thermal-convection loop system, a steady-state corrosion behavior, in which the rate is constant with time, is attained after several thousand hours of operation. This rate is approximately $10 \text{ mg/m}^2 \text{ h}$ for flow velocities of about 30 mm/s .

Preliminary analysis of the weight loss data indicated that the corrosion rate is controlled by the diffusion of iron through the liquid Li boundary layer.

Material was transferred to the cooler regions of the loops, where, initially, Cr was found to preferentially deposit as needle-like crystals.

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