

## Dissolution kinetics of steels exposed in lead–lithium and lithium environments

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An analysis of weight loss kinetics was made for type 316 stainless steel and Fe–12Cr–1MoVW steel in thermally convective Pb–17 at.% Li (500°C) and lithium (600°C). For both steels, the kinetics are similar in lithium and Pb–17Li if the comparison is made at a temperature where solubility-driven mass transport dominates. At the temperatures of this study, a model based on parabolic reaction kinetics accurately described the weight loss curves for type 316 stainless steel in both liquid metals, while the ferritic steel rapidly achieved weight losses that were linear with time. The differences between the kinetic behavior of the two steels can thus be interpreted in terms of the preferential dissolution reactions and localized attack observed for the austenitic alloy.

### 1. Introduction

Molten lithium and Pb–17 at.% Li (hereafter referred to as Pb–17Li) are potential coolants and/or tritium-breeding fluids for fusion reactors. Because such applications are normally nonisothermal, corrosion and mass transfer in response to temperature gradients are of particular concern. Measurements of the time dependence of weight loss under such conditions are therefore important for direct estimations of wall thinning, deposition burdens, and radionuclide transport in liquid metal systems. Moreover, these data and analyses provide valuable insights into the important corrosion mechanisms and facilitate the development of predictive capability. In this paper, selected aspects of the dissolution kinetics under temperature gradient conditions are examined and compared for lithium and Pb–17Li environments.

### 2. Experimental procedures

Weight loss data were obtained by use of thermal convection loops (TCLs) that have been described in detail previously [1,2]. These loops circulated purified lithium and Pb–17Li [1,2] at velocities of approximately 2 cm/s under a temperature differential of 150–200°C. A type 316 austenitic stainless steel (Fe–17Cr–12Ni–2Mo–2Mn–2Si–0.08C (wt.%)) and a Fe–12Cr–1MoVW ferritic/martensitic steel were used as specimen materials and were separately exposed in TCLs constructed from similar steels. In this paper, only data for specimens exposed at the maximum loop temperature are reported. Weight changes were measured as a function

of exposure time. For the lithium experiments, the specimen weights were measured after rinsing in warm water and the same coupons were then returned to the TCLs. In the case of Pb–17Li, the corroded specimens were cleaned by using low temperature (250°C) molten lithium [2] and were not reexposed.

### 3. Results

Distinct differences were found between the kinetic behavior of the two types of steel in both lithium

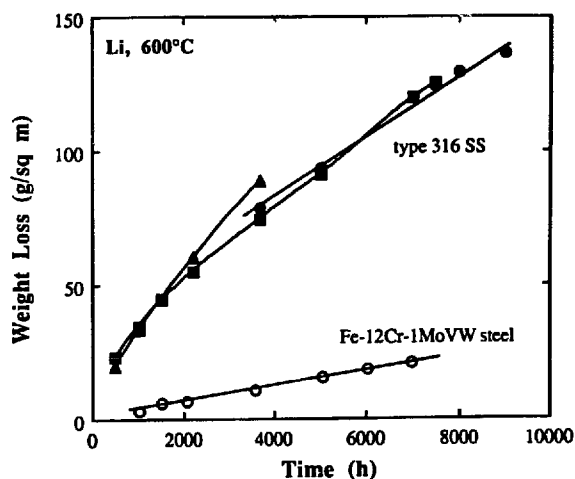


Fig. 1 Weight loss vs time for steels in thermally convected lithium at 600°C. Separate experiments are indicated by different symbols.

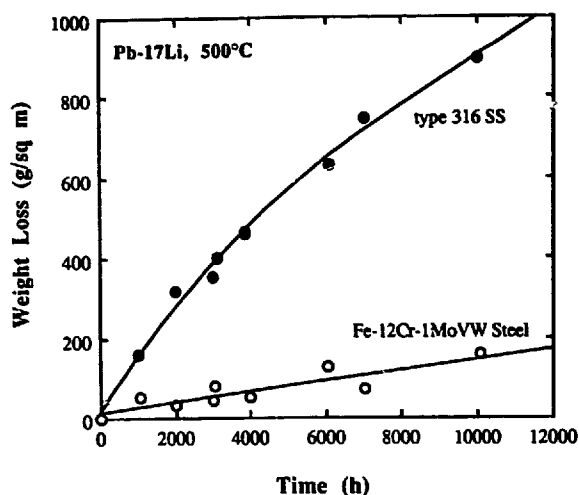


Fig. 2 Weight loss vs time for steels in thermally convected Pb-17 at % Li at 500°C

(600°C) and Pb-17Li (500°C). The austenitic stainless steel exhibited rapid, nonlinear weight losses during the first few thousand hours of exposure and nearly linear behavior at extended times (see figs. 1 and 2). In contrast, as also shown in figs. 1 and 2, the Fe-Cr steel exhibited linear weight loss kinetics over almost all of the respective exposure periods.

The same qualitative differences in surface morphologies between the austenitic and Fe-Cr steels were observed in lithium and Pb-17Li. Corrosion of the type 316 stainless steel led to highly irregular, penetrated surface layers, which have been previously described [1,2]. On the other hand, the Fe-Cr steel tended to corrode by uniform surface removal in both liquid metals. Exposures to the lithium and Pb-17Li resulted in preferential dissolution of nickel and chromium from the type 316 stainless steel and the transformation of austenite to ferrite in the surface layers. No selective depletion of any elements was noted for Fe-12Cr-1MoVW steel exposed to Pb-17Li, while some relative chromium loss was found when this steel was held in Li.

#### 4. Discussion

Before analyzing the present kinetic data, the possible influences of specimen handling on the weight change results need to be addressed. For Pb-17Li, it has been demonstrated [2] that significant errors in weight change kinetics can result from multiple exposures of a single specimen. This is primarily due to possible loss of parts (or all) of the penetrated layer that forms on the exposed austenitic stainless steel in the process of removing the residual lead-lithium.

Reexposure of specimens that have undergone such cleaning leads to greater weight changes than for those measured for coupons that are held for the same total time but are not reinserted into the loop [2]. It can also be misleading to reexpose specimens in lithium loops to generate kinetic data [3]. It is now well known that, in many cases,  $\text{Li}_9\text{CrN}_5$  can form as a corrosion product on steels exposed to lithium and that it readily dissolves in water [4]. Therefore, if residual lithium is removed by water rinsing prior to weighing of the specimens (which is the normal procedure), the corrosion product is lost and reexposure of the same coupon introduces surfaces not representative of the actual condition after the specified amount of time in the lithium. This is of particular concern because  $\text{Li}_9\text{CrN}_5$  can act as a barrier to further reaction [4] and its continual artificial removal can thus affect the evaluation of corrosion kinetics for chromium-containing steels in lithium [3]. However, the present kinetic data for lithium are for specimens exposed at 600°C, which is above the temperature range where  $\text{Li}_9\text{CrN}_5$  should be stable for the measured nitrogen levels in the lithium (80–150 wt.ppm) [5]. As discussed previously [6], solubility-driven dissolution of the alloying elements is expected to dominate at this temperature and generally overrides the influence of solid reaction products and impurities on the net weight change. Furthermore, as shown in fig. 1, which contains three overlapping experimental weight loss curves for the type 316 stainless steel, weight losses at a particular time showed no dependence on the frequency with which the specimen had been weighed and reexposed. It can therefore be assumed that the reinsertion of specimens does not substantially alter the overall dissolution kinetics of type 316 stainless steel at 600°C in lithium.

For solubility-driven dissolution, the flux of a particular element,  $J_i$ , into lithium or lead-lithium can be expressed (assuming activity coefficients of unity) as

$$J_i = r_i(C_i^0 - C_i), \quad (1)$$

where  $C_i^0$  is the solubility of element  $i$  in the liquid metal,  $C_i$  is its actual concentration, and  $r_i$  is the mass transfer coefficient. While the weight change results for type 316 stainless steel showed a similar functional form in lithium and Pb-17Li, the actual weight losses were substantially higher in the latter environment (compare figs. 1 and 2). This difference can be attributed to the higher equilibrium solubilities of Fe, Cr, and Ni in Pb-17Li [7,8] and is consistent with solubility-controlled dissolution of the major alloying elements being the dominant mechanism of weight loss for type 316 stainless steel in these environments.

As shown in the present case and by others [9–13], there is preferential depletion of Cr, as well as Ni, from austenitic steels exposed to both liquid metals, but, for Fe-Cr steels, such leaching is only observed in lithium. As shown by eq. (1), the relative flux of a

particular element depends not only on solubility, but also on the release rate (kinetics) and/or its concentration in the liquid metal ( $C_l$ ) as set elsewhere in the loop by the efficiency of the elemental deposition processes or specific interactions with impurities. (Several such factors have been recently discussed for type 316 stainless steel in Pb-17Li [11].) The observation that chromium is preferentially depleted from the Fe-Cr steel only in lithium could be explained by reactions with nitrogen or carbon in the colder parts of the lithium TCL. Such processes, which are favored at the lower temperatures [3-5] could reduce  $C_{Cr}$  and lead to a greater relative flux of chromium into the lithium near the maximum temperature part of the loop despite a solubility that is expected to be the same as that of iron. Additionally, a contribution from the loss of a chromium-containing product, possibly a reaction product or second phase [3,4,11,14] cannot be totally dismissed despite the evidence that solubility-driven dissolution of the principal elements dominates the weight loss process.

The experimental weight change data for austenitic stainless steel in lithium and Pb-17Li indicate an early transient corrosion process which gives way to a steady-state dissolution regime [1,10,15]. Steady-state behavior is normally associated with linear weight change kinetics, while the exact functional form of the time dependence during the initial exposure period is not known. A  $t^{1/2}$  relation has been suggested for lithium based on curve fitting [1]. If the nonuniform surface recession can be explained by an interface destabilization model, as has been suggested for Pb-17Li [2], or by a phase transformation mechanism [14], a parabolic rate law (indicative of diffusion control) would apply during the time when the corrosion layer was growing. Therefore, assuming that the irregular ferrite layer forms at a rate proportional to  $t^{1/2}$  and that this layer (of constant composition) then corrodes linearly with time, kinetic relationships based on parabolic behavior can be developed by adapting the treatment of Haycock [16] to the present case. Referring to fig. 3,  $x_1$  is the average distance between the original

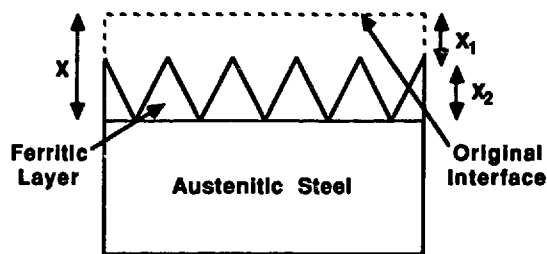


Fig. 3 Simplified schematic depiction of irregular ferrite layer formed upon exposure of type 316 stainless steel to lithium and Pb-17 at % Li.

specimen surface and the liquid-solid interface of the irregular corrosion layer (of thickness  $x_2$ ) such that

$$x = x_1 + x_2. \quad (2)$$

The total measured weight loss per unit area can be expressed as

$$w = ax_1 + bx_2, \quad (3)$$

where  $a$  is the density of the starting steel and  $b$  is a density conversion factor for the irregular corrosion layer. The rate of consumption of sound metal is determined by the growth of the corrosion layer into the unaffected solid, which is given by

$$dx/dt = k_p/2x_2, \quad (4)$$

where  $k_p$  is the parabolic rate constant based on the above assumptions. It also follows that

$$x_1 = k_1 t, \quad (5)$$

for the dissolution of the ferrite layer as characterized by the linear rate constant  $k_1$ . The use of eqs. (2), (4) and (5) yields expressions for the total loss of the sound metal surface as a function of time [16]:

$$x = \left( \frac{k_p}{k_1} \right) \ln \left\{ \frac{k_p}{[k_p - k_1(x - k_1 t)]} \right\}, \quad (6)$$

and the thickening of the corrosion layer:

$$\frac{dx_2}{dt} = \left( \frac{k_p}{x_2} \right) - k_1 = k_p \left( \frac{1}{x_2} - \frac{k_1}{k_p} \right). \quad (7)$$

This layer approaches a limiting thickness (when  $dx_2/dt = 0$ ) given by  $x_2 = k_p/k_1$ , after which the overall corrosion process becomes essentially linear, as experimentally observed for lithium and Pb-17Li [1,10,15]. The thickness of the irregular corrosion layer should then remain constant as the rate of sound metal recession equals the disappearance of the ferrite layer. If  $k_1/k_p \gg 1/x_2$ , an apparently linear time dependence would be observed over the entire exposure time, while, conversely, if  $k_1/k_p \ll 1/x_2$ , the kinetics would resemble pure parabolic behavior. The data for austenitic steels falls between these two limiting cases and a plot of  $x$  vs  $t$  based on eq. (6) yields a curve very much like any one of those measured for the weight losses in the subject liquid metals (such as those shown in figs. 1 and 2) using the appropriate (fitted) values of  $k_p/k_1$  and  $b$ . Therefore, treating the weight loss data of austenitic stainless steels in terms of parabolic kinetics yields an analytically tractable solution and tends to confirm the importance of a  $t^{1/2}$  process during the transient period.

As illustrated by the data in figs. 1 and 2 and the work of others [13,15], ferritic/martensitic steels normally exhibit linear behavior over virtually the entire exposure period. This linear trend is manifested when the weight losses are controlled by dissolution processes involving the main constituents of the steel

rather than by impurities or solid reaction products. Below 500°C, a relatively brief rapid transient period (compared to that for austenitic steel) has been reported for ferritic steel in lithium [17]. It was shown that during this initial time, characterized by more rapid weight loss, corrosion could be related to chemical reactions with nitrogen [17], which, as discussed above, can dominate at lower temperatures. The lack of any such transient period for these steels in Pb-17Li and in higher temperature lithium is due to the absence of any substantial depletion of a particular element and the associated irregular corrosion layer.

Another type of initial weight loss period has been observed for Fe-Cr steels in Pb-17Li [13,15]: a low linear rate is followed by a second higher one more consistent with the rate measured here. Such behavior is attributed to the long incubation time needed to dissolve oxide layers on the original steel surfaces. After this period, corrosion proceeds by dissolution of iron and chromium [13]. Such delays are not observed in lithium because of its strong affinity for oxygen, which causes rapid removal of surface oxides.

When an appreciable ferrite layer has formed on the type 316 stainless steel and dissolution of iron and chromium predominates (at extended exposure times), the weight loss of austenitic and Fe-Cr steels in lithium and Pb-17Li can be characterized in terms of a linear rate law. However, the linear rate constants for the two types of steels differed (see figs. 1 and 2 and ref. [15]). The linear dissolution rate of the austenitic steel was significantly greater than that for the Fe-Cr steels. This may indicate that there is still a transient (preferential dissolution) contribution to the weight losses of austenitic stainless steel at extended times (that is,  $k_p/k_1$  is such that  $x_2$  has not reached its limiting thickness, see above). However, even at steady state, there should still exist a flux of nickel into the liquid metal in proportion to its starting concentration [18]. Otherwise, the steady-state thickness of the corrosion layer could not be maintained in contradiction to existing evidence (see, for example, refs. [1,11,15]). In addition, the much larger Fe-Cr surface area in contact with the liquid metal due to the formation of the highly irregular corrosion layer is not taken into account in the measurements. If corrected for this (by determination of  $b$ , see eq (3)), the differences in dissolution rates would diminish.

## 5. Summary and conclusions

For both austenitic and ferritic/martensitic steels, weight loss kinetics are similar in lithium and Pb-17Li if the comparison is made at a temperature where dissolution of principal alloying elements dominates. Nitrogen reactions in lower temperature lithium and

possible surface oxide effects in Pb-17Li can lead to substantially different corrosion kinetics.

At sufficiently high temperatures, austenitic steels show mixed reaction kinetics in both lithium and Pb-17Li, while ferritic steels rapidly achieve weight losses that are linear with time. A parabolic rate law accurately describes the functional dependence of the weight losses of type 316 stainless steel vs time for both liquid metals. The dominance of a  $t^{1/2}$  behavior of the austenitic steels during the first few thousand hours of exposure indicates a diffusion control associated with preferential leaching, which leads to the establishment of an irregular, ferritic surface layer. The linear kinetic behavior of both types of steel are related to the dissolution of Fe-Cr surfaces. However, the rate constant for the austenitic steel is greater than that for ferritic steels, thereby indicating a continued contribution from nickel dissolution as well as the much larger surface area from which dissolution can take place.

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