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CORROSION OF FERRITIC STEELS BY MOLTEN LITHIUM: INFLUENCE OF COMPETING THERMAL GRADIENT MASS TRANSFER AND SURFACE PRODUCT REACTIONS*

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Abstract

An Fe-12Cr-1MoVW steel was exposed to thermally convective lithium for 6962 h. Results showed that the weight change profile of Fe-12Cr-1MoVW steel changed substantially as the maximum loop temperature was raised from 500 to 600°C. Furthermore, for a particular loop experiment, changes in the structure and composition of the exposed surfaces did not reflect typical thermal gradient mass transfer effects for all elements: the surface concentration of chromium was often a maximum at intermediate temperatures, while nickel (present at low concentrations in the starting material) tended to be transported to the coldest part of the loop. Such data were interpreted in terms of a qualitative model in which there are different dominant reactions for the various constituents of the ferritic steels (surface product formation involving nitrogen and/or carbon and solubility-driven elemental transport). This competition among different reactions is important in evaluating overall corrosion behavior and the effects of temperature. The overall corrosion rate of the 12Cr-1MoVW steel was relatively low when compared to that for austenitic stainless steel exposed under similar conditions.

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Introduction

Lithium is important in fusion technology because it can react with fusion-generated neutrons to produce tritium for use in reactors operating on a deuterium-tritium fuel cycle. Consequently, a molten lithium blanket surrounding the plasma chamber can be used to breed tritium for reactor operation and, because of lithium's excellent heat transfer properties, it can also serve as the reactor coolant. Such applications require an understanding of the corrosion of the containment material by the liquid lithium. Work to date has shown that the resistance of standard ferritic (Fe-Cr-Mo) steels to corrosion by lithium is normally superior to that of the austenitic steels [1], but that mass transfer, carburization/decarburization, and other possible reactions can be significant for the ferritic steels [2–7]. The purpose of the present study was to examine the corrosion of ferritic steels under thermally convective conditions at a temperature higher than previously studied to better understand the roles of preferential dissolution, thermal gradient mass transfer, and surface product reactions.

Experimental Procedures

The composition of the normalized (1050°C, 0.5 h) and tempered (780°C, 2.5 h) 12Cr-1MoVW steel exposed to thermally convective lithium in the present study was Fe-11.0Cr-0.8Mo-0.6Mn-0.5W-0.3V-0.3Si-0.5Ni-0.13C (wt %). Specimens (approximately 18 × 12 × 1 mm) were exposed to flowing lithium in a thermal convection loop that has been described in detail elsewhere [6]. The loop was constructed of 12Cr-1MoVW steel and allowed specimens to be inserted into and removed from both the hot and cold legs without having to interrupt the lithium flow. In this way, weight changes were measured as a function of time as well as loop position. The 12Cr-1MoVW steel specimens were located in both the hot and cold legs, as shown in Fig. 1, and the lithium circulated between 600 and 450°C.

The average flow velocity of the lithium in the loop experiment was approximately 25 mm/s. Such a velocity would be typical of lithium being used as a semistagnant tritium breeding fluid. Impurity concentrations of the cold trapped and hot gettered lithium were 30 to 100 wppm of nitrogen and 30 to 150 wppm of oxygen. The purification process and analytical procedures have been described previously [6].

Results

The 12Cr-1MoVW steel specimens were exposed to flowing lithium at 600 to 450°C for a total of 6962 h. The overall weight changes after this period of time are shown in Table 1. Note that net weight gains were recorded everywhere except at the highest loop temperature (T_{max}) and that the maximum weight gain was not at the coldest temperature. The weight changes of the loop specimens were measured several times during the course of the loop experiment; Fig. 2 shows the results for the specimens located at 600°C (T_{max}) and compares them with data from an earlier ferritic loop experiment conducted at a T_{max} of 500°C [6]. Assuming linear dissolution kinetics, the slope of the best fit line to the 600°C data in Fig. 2 yielded a dissolution rate of 3.0 mg/m^2·h, which is a relatively low rate for this temperature compared to austenitic stainless steel [1].

The surfaces of the exposed 12Cr-1MoVW steel specimens were examined by scanning electron microscopy and associated energy dispersive x-ray (EDX) analysis. The micrographs of Fig. 3 and the surface composition data in Table 1 summarize surface morphology and composition data as a function of loop position (see Fig. 1 for reference). The coupon exposed at T_{max} (600°C) showed little change in surface appearance during its 6962 h of exposure to lithium (apparently only some grain boundary grooving), but was depleted in chromium relative to its initial concentration. In contrast, there was enrichment in chromium at intermediate temperatures due to the presence of nodules containing significant concentrations of this element. More specifically, EDX analysis showed that small nodules on surfaces like those in Fig. 3(b) and (c) were slightly rich in iron and that the large nodules were highly enriched in chromium (see Fig. 4). The underlying matrix was found to have a similiar composition to that of the starting 12Cr-1MoVW steel. At the lower temperatures (positions H7, C6, C7, C8), the specimen surfaces tended to be uniformly covered with small nodules [see Fig. 3(d)] that were somewhat enriched in iron and nickel. Optical metallography of polished and etched cross sections of the loop specimens showed evidence of decarburization for the 600°C coupon and, possibly, slight carburization at intermediate temperatures (see Fig. 5).

Discussion

A "simple solution" reaction for a solid exposed to a liquid metal can be represented by

$$J = kA(C-c) \tag{1}$$

where J is the net rate at which an elemental species enters solution, k is the solution rate constant for the rate controlling step, A is a geometric constant (surface to volume ratio), C is the solubility of the particular element in the liquid metal, and c is the actual instantaneous concentration of this element in the melt. Under isothermal conditions, the dissolution rate (Eq. 1) would decrease with time as c increases, but in liquid metal circuits with thermal gradients, as in the present case, the movement of liquid tends to make c constant around the system. Dissolution of an element will occur at temperatures where $C > c$ and, at lower temperatures in the circuit where $C < c$, a particular element will tend to be deposited (if it does not remain in the liquid as a suspended particle). Therefore, in the absence of any other effects, thermal gradient mass transfer generally would result in the net movement of material from the hot zone of a liquid metal system to its cooler region; therefore, weight losses should occur in the hottest part of the circuit and weight gains should occur elsewhere. However, such weight change behavior was not observed in a previous loop experiment with 12Cr-1MoVW steel exposed to thermally convective lithium between 500 and 350°C for 10,088 h [6]. Some thermal gradient elemental transfer of iron and nickel was detected by surface analysis, but from a consideration of the weight change data (the greatest specimen weight loss was at the minimum loop temperature), surface compositions, and prior results for austenitic alloys, reactions with carbon and/or nitrogen were deduced to be the principal corrosion processes. However, it was postulated that, at higher temperature, solubility-driven mass transfer might become more important in nonisothermal 12Cr-1MoVW steel systems and the present data tend to show such a trend. The weight change data for this steel exposed between 600 and 450°C was somewhat more consistent with typical thermal gradient mass transfer behavior (see Table 1). The change in the weight change profile as T_{max} was raised from 500 to 600°C indicates a significantly greater contribution of dissolution and mass transport of dissolved species to the overall corrosion behavior of the system. However, at 600°C, metallographic examination showed that decarburization also contributed to the measured weight loss and probably was related to the concommitant depletion of chromium.

While this tendency for thermal gradient mass transport was more apparent in the case of the T_{max} = 600°C loop experiment, the surface composition data of Table 1 were not consistent with solubility-driven mass transfer of all the principal elements of the 12Cr-1MoVW steel. As shown, by the correlation of weight change and overall surface composition data in Table 1, net dissolution occurred at 600°C with a resulting decrease in chromium (and probably carbon) surface concentration of the H3 specimen. The substantial chromium enrichment observed at positions both upstream (H5, ≈560°C) and downstream (C4, ≈530°C) of the H3 coupon was due to chromium deposition and reaction. The formation of the large nodules led to significant weight gains for these specimens. At the C8 (450°C) position, a smaller weight gain was measured and an enrichment in nickel was detected. Therefore, it appears that the dissolution of chromium around T_{max} led to the transfer of this element to other, intermediate temperature parts of the loop, where it reacted to form the rather large modules shown in Figs. 3 and 4. The chromium products could also have formed in the liquid and then been preferentially deposited in this temperature range. Although the starting nickel concentration was only 0.5%, this element was apparently transported from the hot zone to the coldest part of the loop as predicted from solublity-driven mass transport considerations (Eq. 1). Such mass transfer of nickel is commonly observed in lithium thermal convection loops containing Fe-Ni-Cr alloys [1] and, as mentioned above, some evidence of such nickel transport was also found in the experiment with 12Cr-1MoVW steel at $T_{max} = 500°C$ [6].

Preferential depletion of chromium from 12Cr-1MoVW steel was also observed in lithium loops operated at lower temperatures [7] and was found to be associated with the formation of dimples that were somewhat similar in appearance to the small nodules observed on the H5 and C4 specimens. Apparently, in the intermediate temperature zone of the present experiment, both chromium depletion and deposition/reaction (see Fig. 4) are occurring on the surface of the same specimen such that the relative magnitudes of these processes help determine the extent of weight change (see below). It is possible that the surface product reaction/deposition of chromium might involve the formation of Li_9CrN_5 as reported by Barker et. al. [8] (albeit at relatively lower nitrogen and inital chromium activities in the present case). Although this product is not stable outside of the lithium environment and should dissolve when the residual lithium is removed during post-exposure specimen cleaning, the observed nodules may be only a remnant of such a product. Alternatively, the reaction may involve chromium carbide formation [2], but the size of the nodules and the microstructure of the underlying steel surface would indicate that such carbides could have served only as precursors. Chromium-rich nodules have also been observed in approximately the same temperature range for austenitic Fe-Cr-Mn alloys exposed to thermally convective lithium [11].

Consideration of the present results suggests a qualitative model in which there are different dominant reactions for the various constitutients of these steels. The overall corrosion behavior for the system would therefore represent a net effect resulting from competition among the various reactions. In this regard, it is instructive to simply express the measured weight change of a loop specimen, ΔW, as

$$\Delta W = W_J + W_S + W_R \qquad (2)$$

where W_J, W_S, and W_R are the changes in weight due to solubility-driven dissolution/deposition of a steel constituent, soluble reaction product formation, and insoluble surface reaction products, respectively. Such weight changes are obtained from intergration of their respective rates over time. For example, using Eq. (1),

$$W_J = -\int J dt \qquad (3)$$

W_J is therefore negative (a weight loss) when $C > c$. If it is assumed that W_S is relatively small, so that the bulk of the reaction product remains on the surface after cleaning (see above), then .

$$\Delta W = W_J + W_R \qquad (4)$$

In the absence of any surface product reaction, $W_R = 0$, and a "typical" solubility-driven weight change versus loop position profile (with greatest weight loss at T_{max}) would result. However, when W_R is significant over the relevant temperature range, then the resultant weight change profile would be modified accordingly. Such a competition between thermal gradient mass transport (which is the dominant reaction for the more soluble elements such as nickel, but also occurs for iron and chromium) and corrosion product reactions (apparently dominant over a certain temperature range for chromium and possibly for iron), can qualitiatively explain the unusual chromium distribution around the loop and overall corrosion behavior for the $T_{max} = 600°C$ loop experiment. The model of competing reactions can also account for the earlier results that indicatred an atypical mass change profile when 12Cr-1Mo steel was exposed in a loop experiment at a T_{max} of 500°C. At higher temperatures, thermal gradient elemental transfer (W_J) would tend to dominate such that a relatively large net weight loss might result at T_{max}. Such temperatures may be above the temperature range of stability of the surface product ($W_R = 0$) or preferential dissolution of chromium at this higher temperature may significantly reduce its activity at the surface to the point where W_R is relatively small. As the temperature range of a loop experiment is lowered, the relative importance of thermal gradient mass transfer decreases and corrosion product reactions can make a large contribution to the measured net weight changes and radically change the shape of the mass change profile. A more rigorous quantitative approach to the overall corrosion behavior as a function of temperature is being examined as part of a mass transfer modeling and experimental project with 12Cr-1MoVW steel in lithium [10].

There are several implications of this simple model for corrosion of ferritic steels in nonisothermal lithium systems. In view of the possibilty of competing reactions between thermal gradient mass transport and surface product reactions, it is not always possible to interpret data on the basis of a single thermally activated process over the temperature range at which such products may be stable. Indeed, there is now significant evidence that corrosiveness does not always scale with temperature in lithium-ferrous alloy systems [6,7,11,12]. Secondly, it appears that relatively small concentrations of certain elements can affect the overall corrosion behavior. Note that despite a starting concentration of just 0.5 wt % Ni in the 12Cr-1MoVW steel, transfer of this element from the hot to cold zone can clearly be detected by EDX analysis of hot and cold leg coupon surfaces (see Table 1). Other data has shown that similar transfer of manganese occurs for ferritic steels despite starting concentrations of only 0.7 and 2.4 wt % [13].

Summary

12Cr-1MoVW steel was exposed to thermally convective lithium between 600 and 450°C for 6962 h and the corrosion rate was relatively low compared to austenitic stainless steel. Chromium depletion was significant, particularly at 600°C, but chromium surface products formed at intermediate temperatures. Thermal gradient mass mass transfer was more important in this experiment than it was in one conducted between 500 and 350°C.

The competition between typical thermal gradient mass transfer (dissolution/deposition) processes and surface product reactions is important in determining and evaluating overall corrosion behavior, and the effects of temperature, in nonisothermal lithium environments.

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Figure Captions

Fig. 1. Schematic drawing of thermal convection loop showing positions of coupons during typical loop experiment.

Fig. 2. Weight loss versus exposure time for 12Cr-1MoVW steel in thermally convective lithium (25 mm/s, $\Delta T = 150°C$).

Fig. 3. Scanning electron micrographs of 12Cr-1MoVW steel specimens exposed for 6962 h to thermally convective lithium circulating between 600 and 450°C. (a) Loop position H3, 600°C. (b) H5, 560°C. (c) C4, 530°C. (d) C8, 450°C.

Fig. 4. Scanning electron micrograph of 12Cr-1MoVW steel exposed for 6962 h to thermally convective lithium at about 560°C; approximate compositions in wt % were obtained by energy dispersive x-ray analysis and represent average of data taken from several surface features of similar type.

Fig. 5. Optical micrographs of polished and etched cross sections of 12Cr-1MoVW steel exposed for 6962 h to thermally convective lithium. (a) Loop position H3, 600°C. (b) H5, 560°C.

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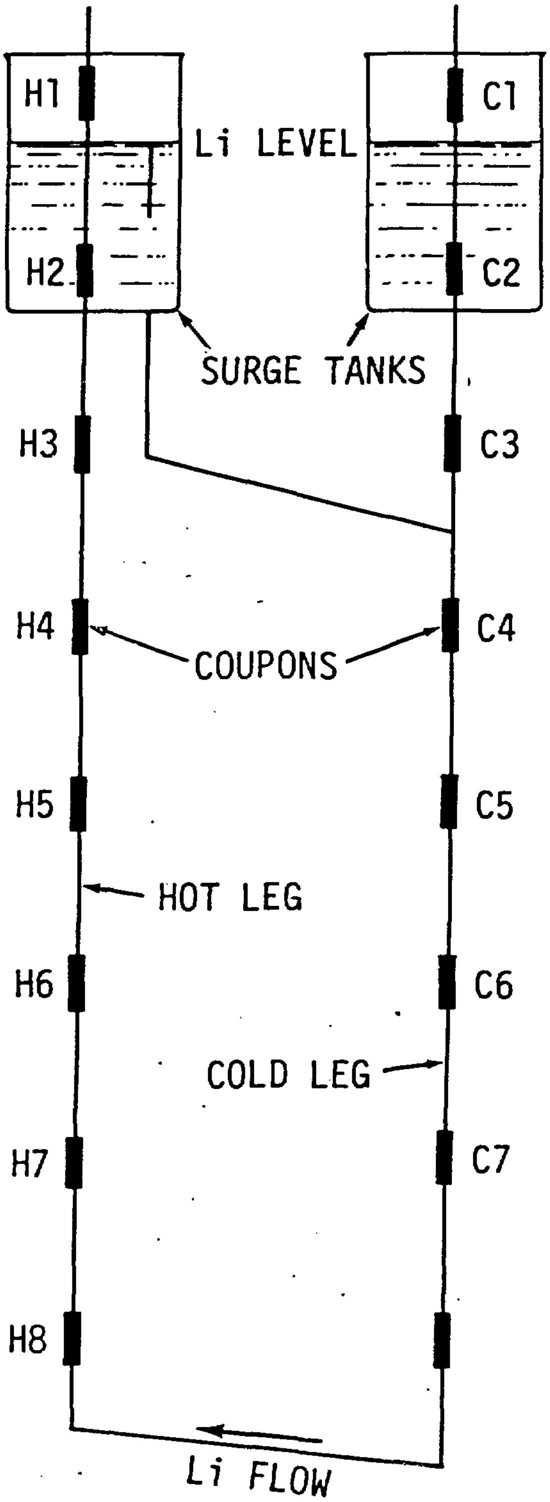
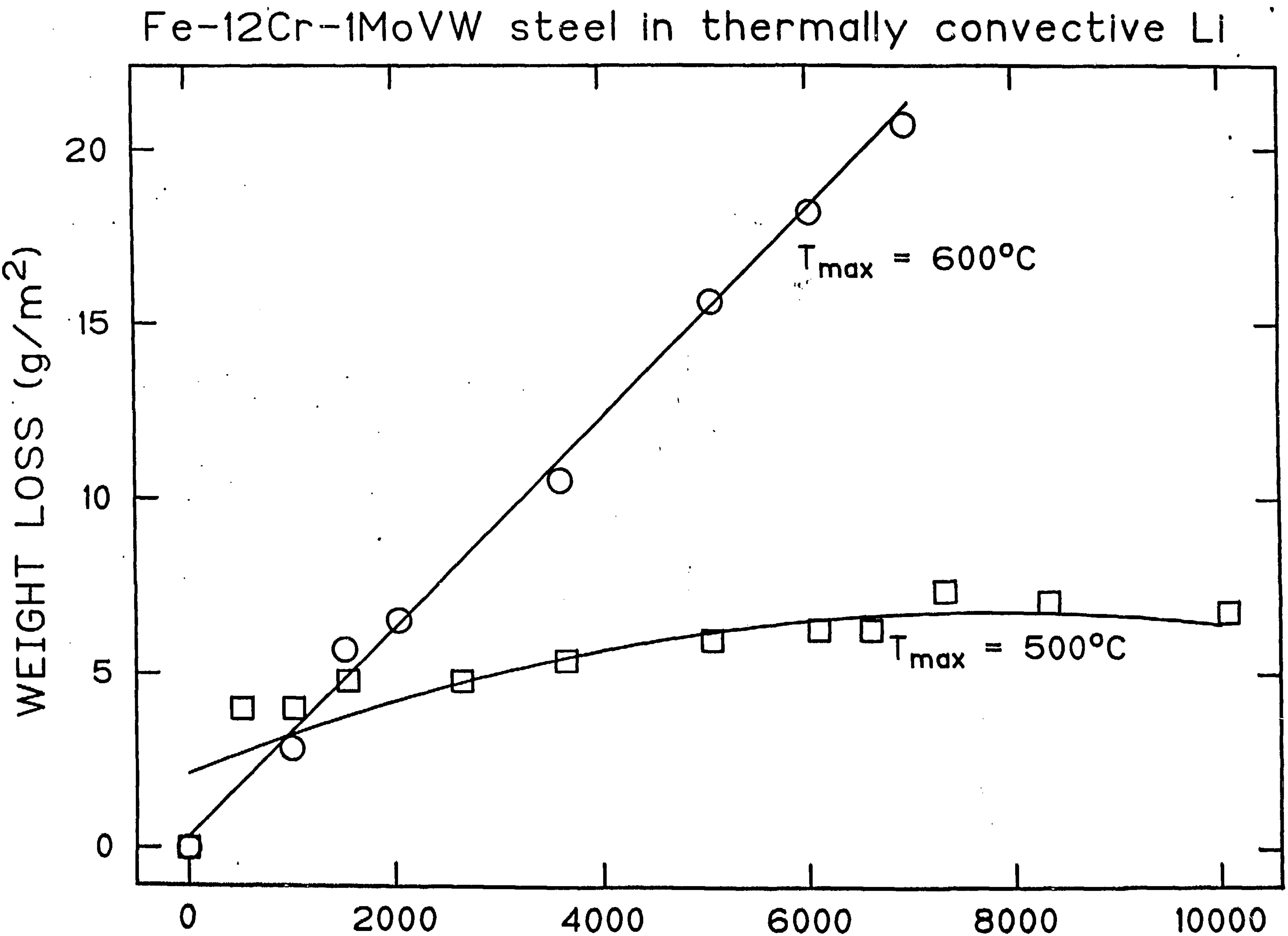
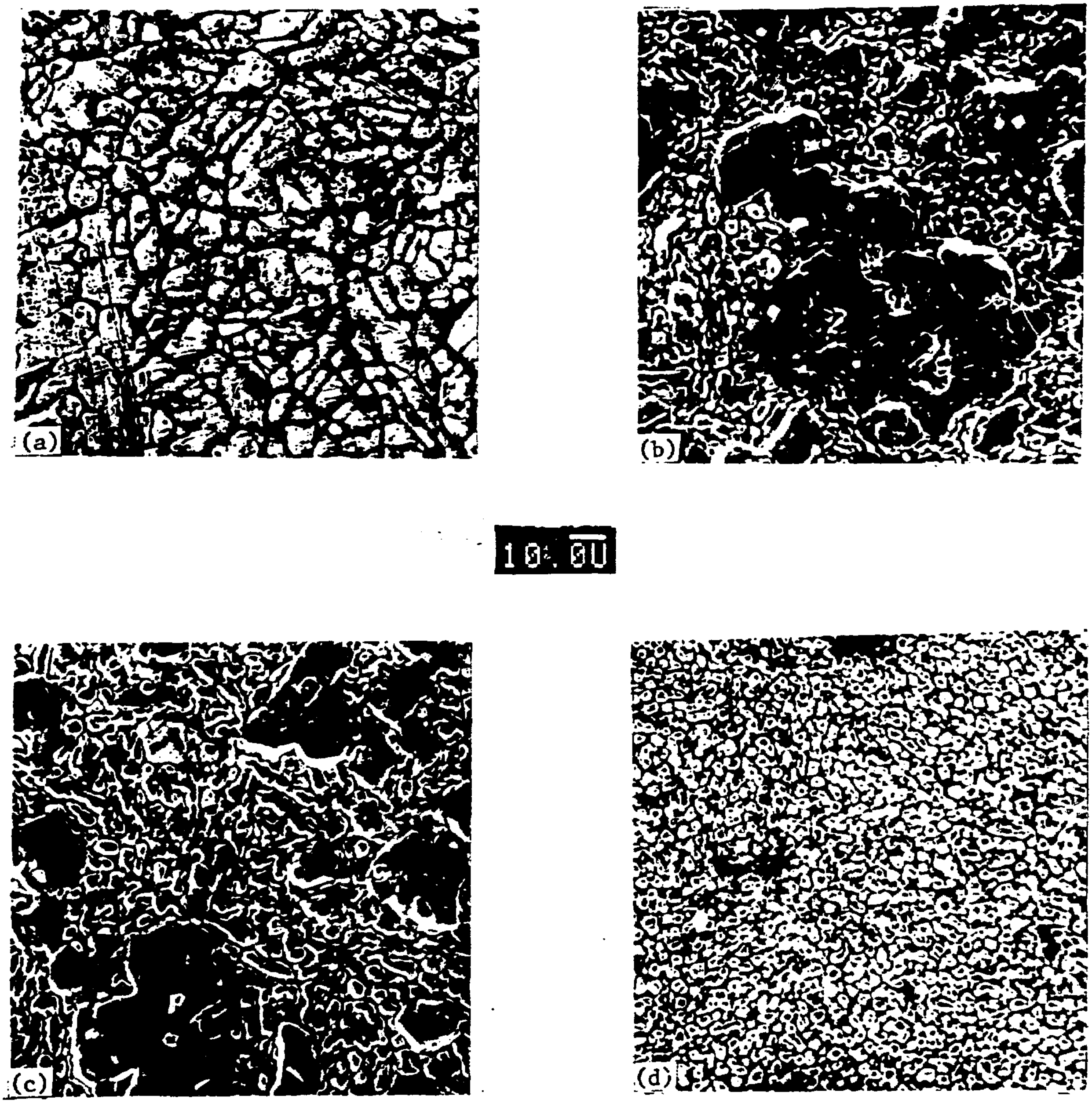



Fe-12Cr-1MoVW steel in thermally convective Li
WEIGHT LOSS (g/m²)
EXPOSURE TIME (h)
0
5
10
15
20
0
2000
4000
6000
8000
10000
T_max = 600°C
T_max = 500°C


(a)
(b)
10.0U
(c)
(d)

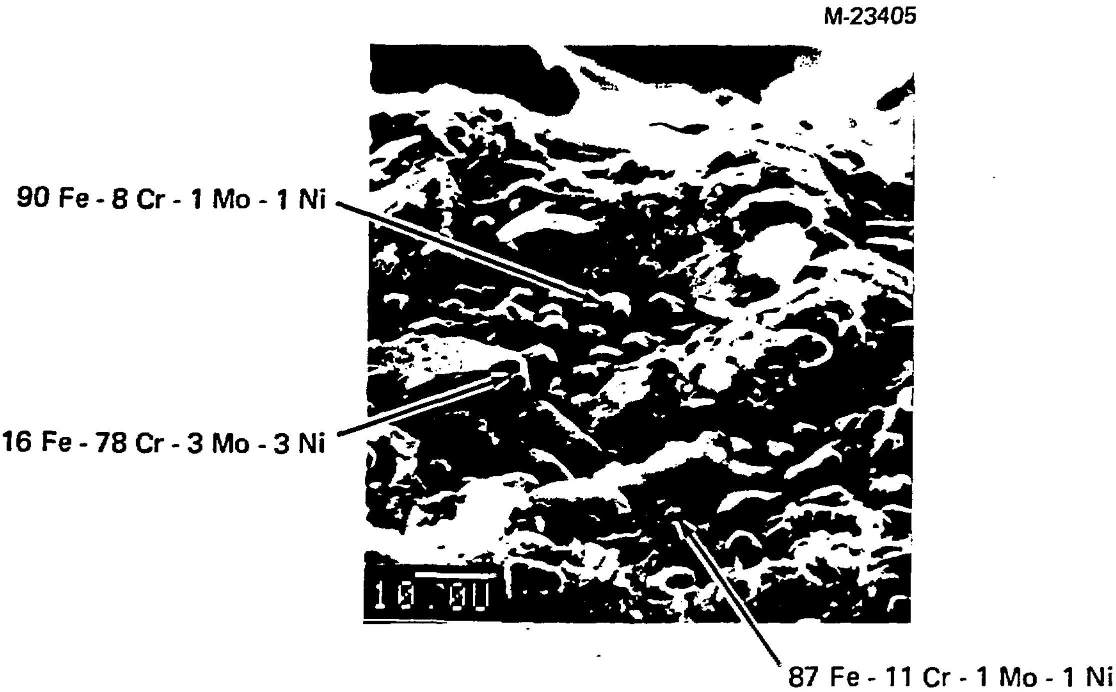
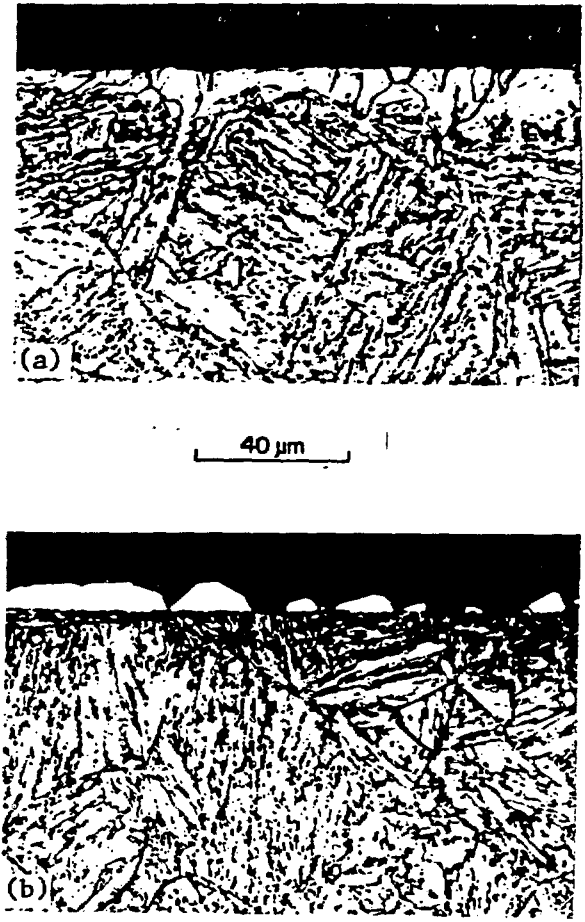


Fig. 4. Scanning electron micrograph of 12 Cr - 1 MoVW steel exposed for 6962 h to thermally convective lithium at about 560°C; approximate compositions in wt % were obtained by energy dispersive x-ray analysis and represent average of data taken from several surface features of similar type.


(a)
40 µm
(b)