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CARBON TRANSPORT IN A BIMETALLIC SODIUM LOOP SIMULATING THE INTERMEDIATE HEAT TRANSPORT SYSTEM OF A LIQUID METAL FAST BREEDER REACTOR

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ABSTRACT

Carbon transport data from a bimetallic sodium loop simulating the intermediate heat transport system of a Liquid Metal Fast Breeder Reactor are discussed. The results of bulk carbon analyses after 15000 hours' exposure indicate a pattern of carburization of Type 304 stainless steel foils which is independent of loop sodium temperature. A model based on carbon activity gradients accounting for this behavior is proposed. Data also indicate that carburization of Type 304 stainless steel is a diffusion-controlled process; however, decarburization of the ferritic 2¼Cr-1Mo steel is not. It is proposed that the decarburization of the ferritic steel is controlled by the dissolution of carbides in the steel matrix. The differences in the sodium decarburization behavior of electroslag remelted and vacuum-arc remelted 2¼Cr-1Mo steel are also highlighted.

INTRODUCTION

Background

The use of 2¼Cr-1Mo steel in sodium heated steam generators is tempered with a concern for its tendency to decarburize in sodium. The loss of carbon from this material has historically been associated with a decrease in strength, and subsequent carburization of austenitic components in the sodium circuit can degrade their properties; therefore, the rate of decarburization of 2¼Cr-1Mo steels and carburization of austenitic steels are key parameters in the design of sodium heated steam generators.

The data used to construct the decarburization rate curve for 2¼Cr-1Mo steels had the following uncertainties:

a) Initial microstructure of the material was not always specified or was inadequate.

b) Test temperatures were higher than those of interest (593-704°C) and mostly the tests were conducted in static sodium.

c) Exposure times were short (less than 3500 hours).

d) The majority of specimen geometries were of the thin foil type exposed to sodium on both sides, not representative of the tubular geometries used in steam generators.

In order to obtain a better design basis for predicting the decarburization of 2¼Cr-1Mo and carburization of austenitic steels in an intermediate heat transport system (IHTS), the Intermediate System Mock-up Loop (ISML) was constructed; the purpose of this report is to describe results obtained to date.

Data Analysis Method

Earlier,[1,4] decarburization of 2¼Cr-1Mo steel in sodium was assumed to be a diffusion control process; thus, the square root of time dependence in the decarburization rate expression

$$K = \frac{M}{\sqrt{t}} \qquad (1)$$

where K = Decarburization rate constant $gm/cm^2sec^{½}$

M = Mass of carbon lost gm/cm^2
t = Time in sec.

As a first approximation, in 1970-72 Krankota and Armijo[1,4] analyzed available decarburization data for 2¼Cr-1Mo steel to yield a straight-line relationship when the calculated decarburization rate constants were plotted versus the reciprocal of exposure temperature. In order to calculate the carbon loss of 2¼Cr-1Mo steel after sodium exposure, the authors[1] assumed that decarburization rate K is invariant with time and projected that a 2¼Cr-1Mo steel steam generator tube would lose about 300 ppm carbon after 210,000 hours at 510°C.

EXPERIMENTAL

Description of ISML

Intermediate System Mockup Loop was designed to simulate an Intermediate Heat Transport System (IHTS) of a Liquid Metal Fast Breeder Reactor (LMFBR).[2] This is accomplished by simulating both the materials temperature and sodium velocity in ISML. The surface area ratio of 2¼Cr-1Mo ferritic and austenitic steels at temperatures above 427°C in ISML closely approaches that found in an LMFBR, i.e., 1:2. Below 427°C, the relative surface area ratio of austenitic to ferritic steel is somewhat higher in ISML. A more detailed description of the loop is given elsewhere.[3]

Materials

a) For decarburization study, tubular (15.9 mm OD) by 2.77 mm wall) specimens exposed to flowing sodium only on the outside diameter were used. Both electroslag remelted (ESR) and vacuum arc remelted (VAR) 2¼Cr-1Mo steel samples were used in the loop. ESR and VAR materials produced from a single air-melted ingot and an added ESR heat were investigated, thus providing a direct comparison of the effect of these two remelting practices on the decarburization behavior of 2¼Cr-1Mo steel.

b) In order to study the carburization of stainless steels both foils and tube materials, including two grades of 304L and 316L, were exposed in flowing sodium.

Chemistries for the loop materials are shown in Table I. Specimens were heat treated according to the details shown in Table II.

RESULTS

Decarburization of 2¼Cr-1Mo Steel

Figure 1 shows a plot of the time dependence of decarburization of 2¼Cr-1Mo steel tubes exposed at 524°C in ISML (M versus $\sqrt{t}$). The data show that the diffusion model for decarburization of 2¼Cr-1Mo steel is not followed. Depending on which set of data is used, the calculated K value for the VAR tubes can vary from 4.4x10^{-8} to 7.9x10^{-8} gr/cm^2-sec^{½}. Figure 1 also shows that for equivalent sodium exposure conditions, the ESR material decarburizes at a slower rate than VAR steel. After 15148 hours at 524°C, the measured carbon losses for ESR and VAR tubes were 100 and 180 ppm, respectively. Furthermore, it is obvious from the figure that the rate of decarburization for both materials is decreasing with time. In order to compare the temperature dependence of decarburization, K values for ESR and VAR tube samples exposed in ISML to 15148 hours are shown on an Arrhenius plot in Figure 2. In this case, the decarburization rate constant was determined by calculating the slope of the line drawn from the data through the origin in Figure 1. Figure 2 confirms that the VAR steel decarburizes at a faster rate than the ESR material. The results further indicate that there is very little temperature dependence in the decarburization rate of VAR material. After 15148 hours at 524°C, the steel lost 180 ppm carbon, while at 343°C the measured loss was 150 ppm carbon. In fact, there is very little difference (25 ppm) between the carbon loss at all temperatures from 3478 to 15148 hours for the VAR material.

It is interesting that the data show the similarities in the decarburization behavior of two heats of ESR steels, indicating that electroslag remelt process render 2¼Cr-1Mo steel similar in its response to decarburizing sodium although the material was supplied by two different vendors. Also shown in the figure are the French decarburization data[5] from Carnacier loop indicating good agreement with data obtained in ISML.

Carburization of the Stainless Steels

Figure 3 shows rate of carburization, M (gm carbon/cm^2) versus $t^{1/2}$ (sec$^{1/2}$), for Type 304 stainless steel foils (Heat M7811) exposed at 438°C in ISML. The figure shows that the carburization of this material can be described by parabolic time dependency for at least up to 5000 hours. Assuming this relationship, the carburization rate constant K (gm/cm^{2}sec$^{1/2}$) for M7811 foils from various temperature regions (350-524°C) of ISML is plotted on Figure 4. The figure indicates that, initially, there is very little temperature dependence of stainless steel in ISML loop. This is very similar to the result of Baque et al. for carburization of stainless steel.[5] However, carbon profile analysis (see below) of samples exposed at higher temperatures (>450°C) for times greater than ∿5000 hours show that stainless steel samples have started to decarburize.

Carbon Profile Analysis

(a) Decarburization

In Figure 5, comparative carbon profiles for ESR tubing exposed at 524°C for 11262 hours are shown. An identifiable diffusion profile is not evident, rather a general decrease in the carbon content of the steel to 400 μm (0.015 in) is seen. The results in Figure 5 are different from data presented by Baque et al. for normalized and tempered 2¼Cr-1Mo steel exposed to flowing sodium at temperatures from 485 to 545°C.[5] Measurable carbon gradients extending up to 2 mm (.08 in) into the samples were shown.

(b) Carburization

Figure 6 shows comparative carbon profiles for 304 stainless steel tubing as-received and after 11262 hours at 438°C. These profiles were determined by emission spectroscopy. After exposure, the stainless steel is shown to be carburized to a depth of approximately 40 μm (0.0015 in). Carbon profiles of several stainless steel samples, with carbon contents ranging from 250 to 670 ppm exposed in ISML between temperatures of 374 to 524°C up to ∿15000 hours, were analyzed by glow discharge and auger electron spectroscopy by Dr. H. Schneider at KFK. The results from these carbon analyses can be summarized as follows:

1) Low carbon Type 304L shows increasing carburization as a function of time. These observations are consistent with Carnacier[5] loop data obtained for 316L alloy, except for similar exposure time and temperature the carbon pickup for 304L in the ISML is less.

2) For exposure temperatures up to 438°C,

the alloys 304 and 316 (both high and low carbon grade) exhibit surface and bulk carburization.

3) The carbon profile data for 304 samples exposed at 524°C for times up to $\sim$15000 hours show a slight decrease in the carbon content up to a distance of $\sim$70 μm from the exposed surface.

Carbide Identification

Transmission Electron Microscopy (TEM) and X-ray diffusion analysis of extracted residues show that carbides present in as-heat treated ESR and VAR 2¼Cr-1Mo steels are essentially in form of $M_{23}C_6$ and M_2C. A typical micrograph is shown in Figure 7.

VAR samples, after exposure at 415°C for 11262 hours, lost all of their matrix carbon in the ferrite.[7] However, some carbide phases were identified in the steel, though a finer dispersion of M_2C was apparent (Figure 8a). It appears that at lower temperatures the breakdown of the carbides has not yet occurred in the VAR material. On the other hand, the ESR 2¼Cr-1Mo steel exposed for 11262 hours at 524°C showed significant formation of M_6C-type carbide near the sodium exposed surface (Figure 8b). This is the most stable carbide in this alloy system.[8-10] Near the interior of the specimen, some M_6C carbides were observed; however, the bulk of the precipitate was M_2C- and $M_{23}C_6$-type carbides. TEM data on ESR material suggest that loss of carbon near the sodium exposed surface assists the formation of M_6C type carbides; furthermore, higher exposure temperature is accelerating this transformation. Since this transformation is predominant near the sodium exposed surface and not a general phenomenon observed throughout the steel implies that carbon and/or nitrogen[11] loss assists in the transformation. The VAR steels exposed at higher temperatures are in the process of being analyzed.

DISCUSSION

Decarburization of 2¼Cr-1Mo Steel

It is apparent from the data presented herein that chemistry and heat treatment will have major effects on the decarburization response of 2¼Cr-1Mo steel in sodium. Subtle differences in chemistry cause the differences in the VAR and ESR data shown in Figure 1. Tyzack and Thorley reported similar conclusions in their review paper on carbon transport in low alloy steels.[12] Hooper[13] suggests that carbide transformations in the steel control the supply of carbon and that trace elements may stabilize one carbide over another; for example, nitrogen stabilizes the M_2C carbide and silicon stabilizes M_6C. Spiers[14] observed that oxygen stabilizes the M_6C carbide, also. Similarly, in analyzing extracted carbide residues from 2¼Cr-1Mo steel samples which were thermally aged and decarburized for 36500 hours at 566°C, Leitnaker et al.[10] found significant concentrations of oxygen associated with the eta carbide.

The data in this report (Figures 1 and 2) further point out the shortcomings of the carbon diffusion model, which assumes parabolic relationship with respect to time for predicting decarburization of the 2¼Cr-1Mo steels tested. It is apparent that after the loss of matrix carbon the carbide decomposition, as suggested by Tyzack and Thorley,[12] becomes the rate controlling step for decarburization of the isothermally annealed 2¼Cr-1Mo steels. It is obvious that the carbides in the steel cannot dissolve rapidly to maintain equilibrium at ferrite/carbide interface (as in the case of plain carbon steel); consequently, time dependence of decarburization ceases to be parabolic. Hooper states that this relationship will be noted for short exposure periods.[13] Nonetheless, ISML data show that further decarburization of the VAR steel is dependent on dissolution of one or more of the carbide types present. Therefore, it is reasonable to assume that this breakdown will depend on either chromium or molybdenum diffusion in the alloy. TEM results on the decarburized ESR steel indicate that molybdenum diffusion is the likely controlling factor, since the eta carbide is a Mo-rich carbide.

Carburization of Austenitic Stainless Steel

Considering the number of variables involved, the carburization of stainless steel presents another complex problem in carbon transport. Figure 3 shows that, initially (up to ∿5000 hours), the diffusion of carbon into the stainless steel is the rate controlling step; however, Figure 4 does not reflect the activation energy for diffusion of carbon into the stainless steel. The data seem to indicate that downstream effect of carbon activity in sodium is influencing the carburization kinetics of stainless steels. The carburization rate of stainless steel is determined by the diffusivity and carbon activity difference between the steel surface and bulk sodium. The activity of carbon in steel surface and sodium is a function of temperature and sample position in the loop. In addition, Katoaka and Matsumoto[15] have observed that an increase in sodium flow velocity (decrease in sodium boundary layer thickness) increases the kinetics of carburization stainless steels, which further complicates the data analysis.

It appears from Figure 4 that, initially (up to ∿5000 hours), a high carbon activity gradient between the sodium and steel is causing increased carburization at lower temperatures. However, as the sodium is heated, the carbon activity in sodium decreases due to downstream effect and, furthermore, the increase in sodium temperature reduces the carburization potential of sodium; consequently, the rate of carburization decreases with increase in temperature. The net results of this phenomenon are causing uniform carburization at all temperatures. This observation is consistent with results obtained at Cadarache[15].after ∿17000 hours of operation.

The most significant observation made after ∿8000 hours of ISML operation is that at temperatures greater than ∿450°C stainless steels have started to decarburize. This observation implies that the carbon activity of sodium in the loop is decreasing with time. This conclusion is consistent with the decarburization data for 2¼Cr-1Mo, which appears to be slowing down considerably with time. The present data are not in agreement with the results obtained at Cadarache,[15] which show that all the stainless steel specimens were still carburizing after ∿18000 hours of operation. This discrepancy can be attributed to the fact that the decarburization of normalized and tempered 2¼Cr-1Mo steels used in the experiment conducted at Cadarache[15] did not slow down with time; hence, the carbon source was never depleted during the experiment. Furthermore, from the present data, admittedly obtained in a small loop, it is not possible to confirm the assumption made by Snyder et al.[16] that the activity of carbon in sodium in a large system will remain constant during the 30 year service life.

CONCLUSIONS

- ESR 2¼Cr-1Mo steels decarburize at a much slower rate than VAR material. Since both materials were remelted from the same ingot and were given identical heat treatments, the large difference in the decarburization kinetics can only be attributed to the presence or absence of minor trace elements.
- The decarburization of ESR and VAR 2¼Cr-1Mo steels with stable initial microstructure is not a diffusion controlled process. Rather, the chemical composition and heat treatment, which establishes the nature of carbides present in these steels, is controlling the rate of decarburization.
- An empirical model for decarburization of 2¼Cr-1Mo steels does not appear feasible. The previous assumption that decarburization rate constant K is invariant with time is not correct. Attempts to calculate long-term carbon loss using a constant K value will lead to an erroneous conclusion.
- The decarburization of ESR 2¼Cr-1Mo steel is accompanied by transformation of carbides initially present in the steel. The initial carbides, such as $M_{23}C_6$ and M_2C, decompose to form a more stable M_6C-type carbide, which is believed to be accelerated by the loss of carbon from the steel.
- The downstream effect of carbon activity in liquid sodium apparently influences the carburization behavior of stainless steel in a flowing sodium loop.
- The carburization results indicate that the activity of carbon in a small bimetallic loop is decreasing with increase in time. The present data do not confirm the assumption that the activity of carbon in a large system will remain constant during the entire service life.
- The transient carbon transport behavior in a bimetallic sodium system should be factored into any assessment of the carburization/decarburization of loop material. It appears that the carbon activity in the loop is slowly changing, and the final steady-state behavior will depend on the balance set up between the sources and the sinks for carbon in the loop.

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TABLE I. CHEMICAL COMPOSITION (WT. %)

Heat	C	Mn	Cr	Mo	Si	P	S	Ni	Cu	Ti	V
ESR 91505*	0.089	.45	2.31	1.0	.26	.007	.004	.05	.05	.01	.01
VAR 91506*	0.110	.43	2.31	1.0	.35	.007	.006	.06	.05	.01	.01
ESR C1005	0.098	.47	2.24	0.95	.18	.01	.008	.19	.10	.01	.01
M7811	0.067	1.9	18.6		.53		10.8				
9T2797	0.047	1.2	18.5		.47		9.58				
8092297	0.065	1.8	17.0	2.4	.45		13.50				
89023	0.062	1.7	18.6		.48		9.6				
421805	0 025	1.6	19.3		.55		11.0				

* These two heats were remelted from the same parent air-melted ingot.

TABLE II. MATERIAL HEAT TREATMENTS

Material	Tube
VAR 91506	AI, 926°C, 30 min ↓ 90 min 704°C, 125 min ↓ RT ↓ Temper, 727°C, 60 min ↓ RT
ESR 91505	Same to VAR 91506 tube
ESR C1005	AI, 926°C, 20 min ↓ 40 min 717°C, 90 min ↓ RT ↓ Temper, 726°C, 60 min ↓ RT
Stainless Steel	Solution Anneal 1066°C, 1 hr ↓ WQ

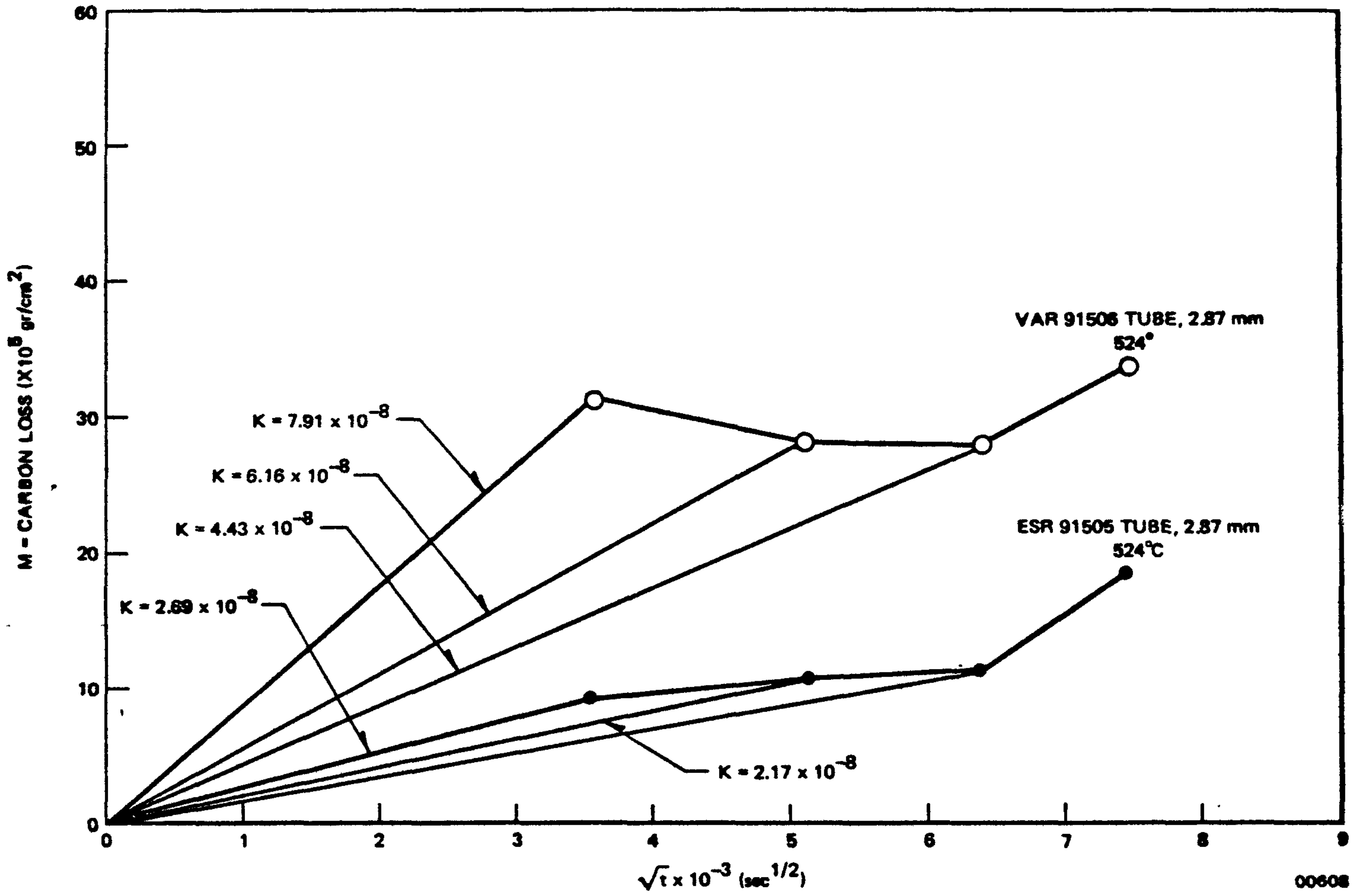


FIGURE 1. TIME DEPENDENCE - DECARBURIZATION OF TUBES

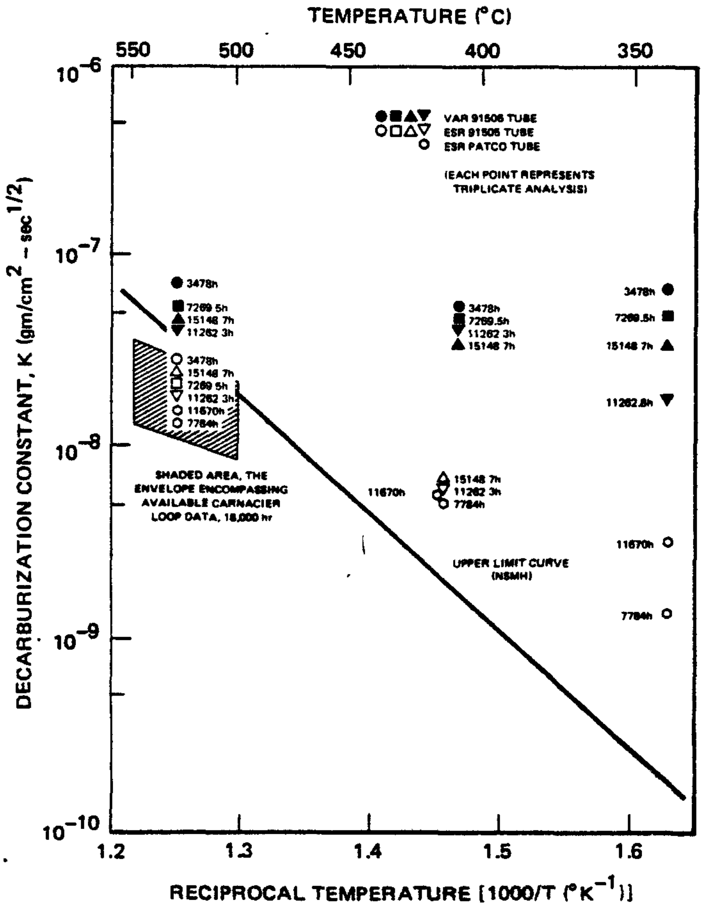


FIGURE 2. ISML DATA AFTER 15148 HOURS

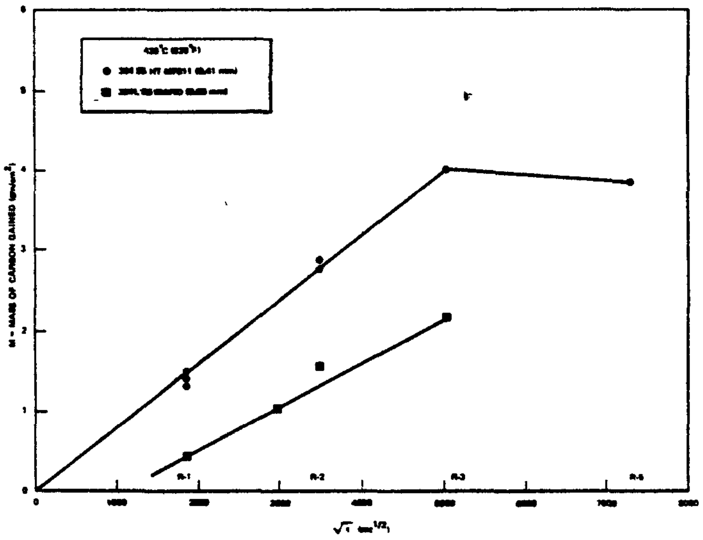


FIGURE 3. M VERSUS $t^{\frac{1}{2}}$ FOR CARBURIZATION OF 304 STAINLESS STEEL IN ISML (FOIL DATA, SH-1, 438°C)

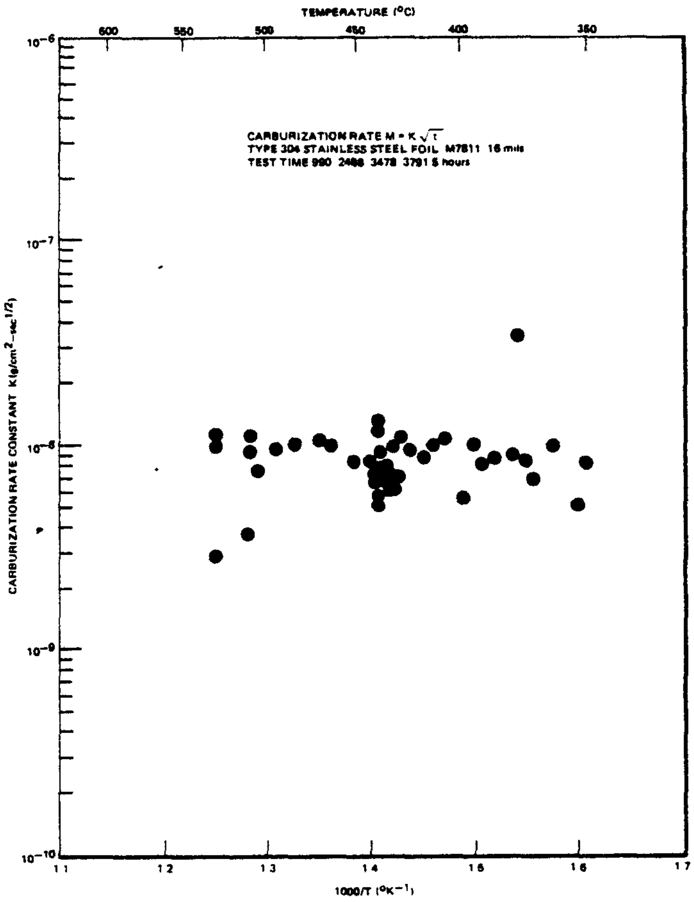


FIGURE 4. RELATION BETWEEN CARBURIZATION RATE CONSTANT & TEMP FOR TYPE 304 STAINLESS STEEL

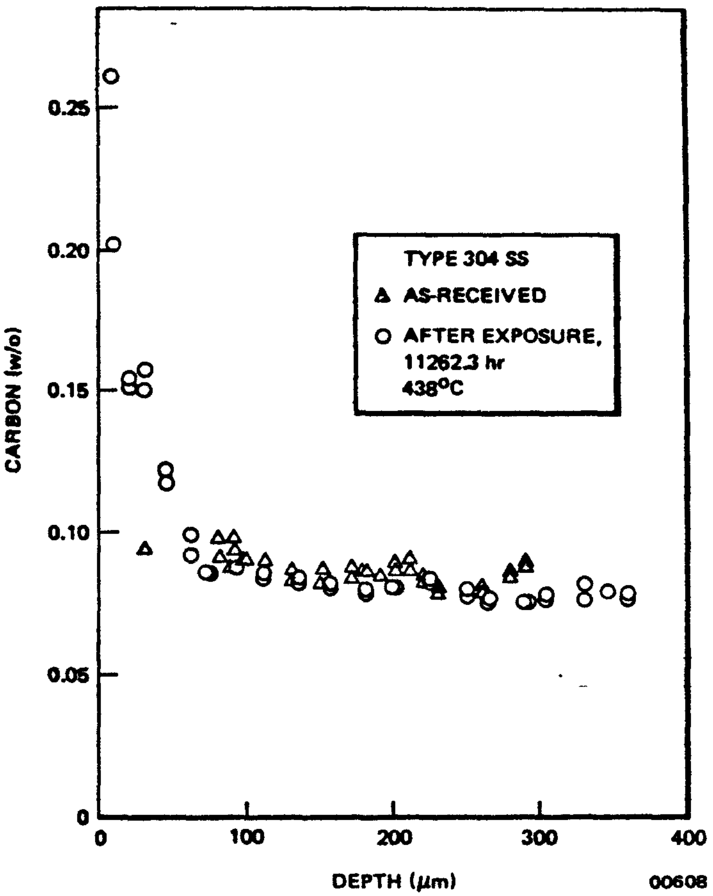


FIGURE 6. CARBON PROFILE OF TYPE 304SS TUBE

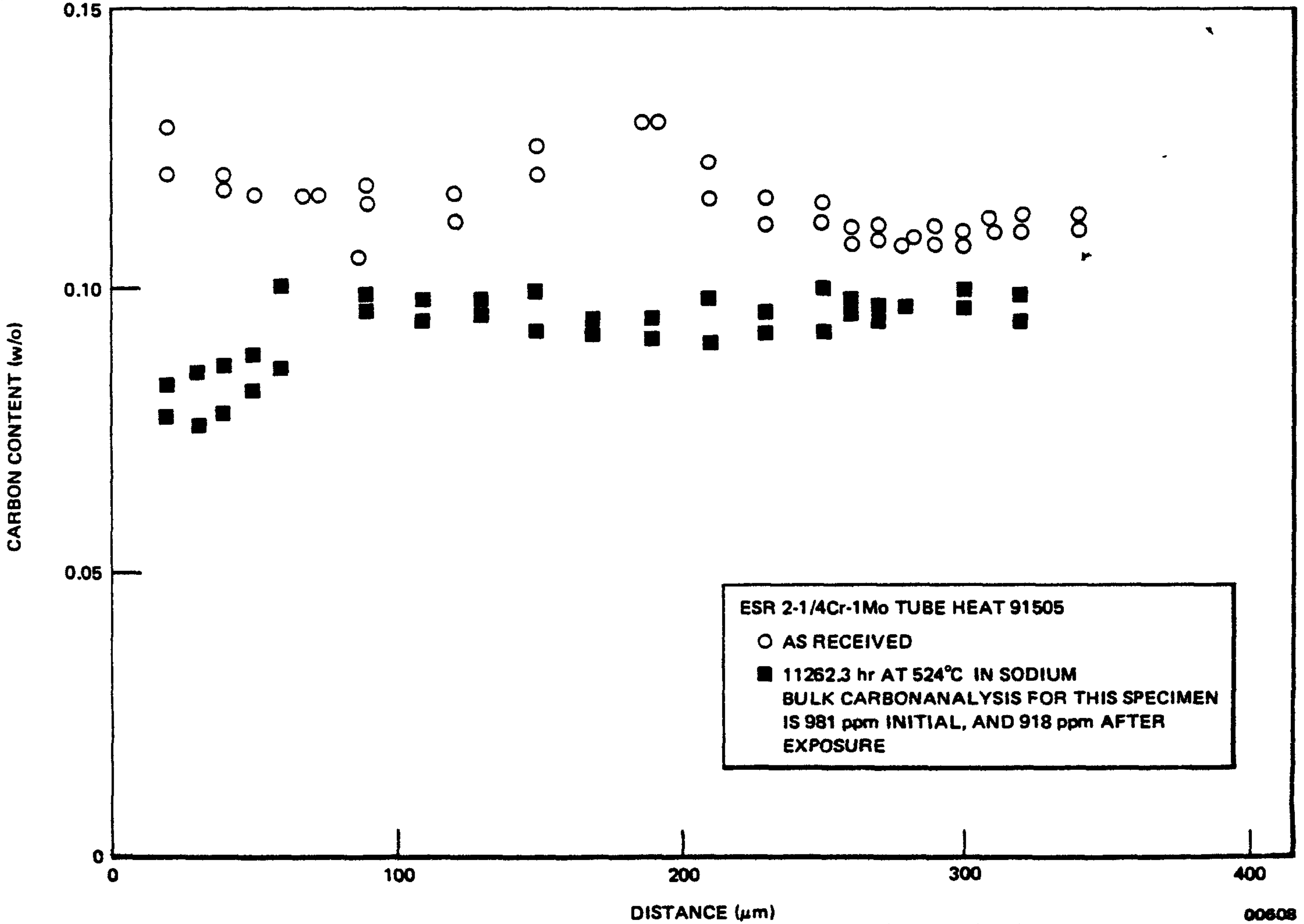
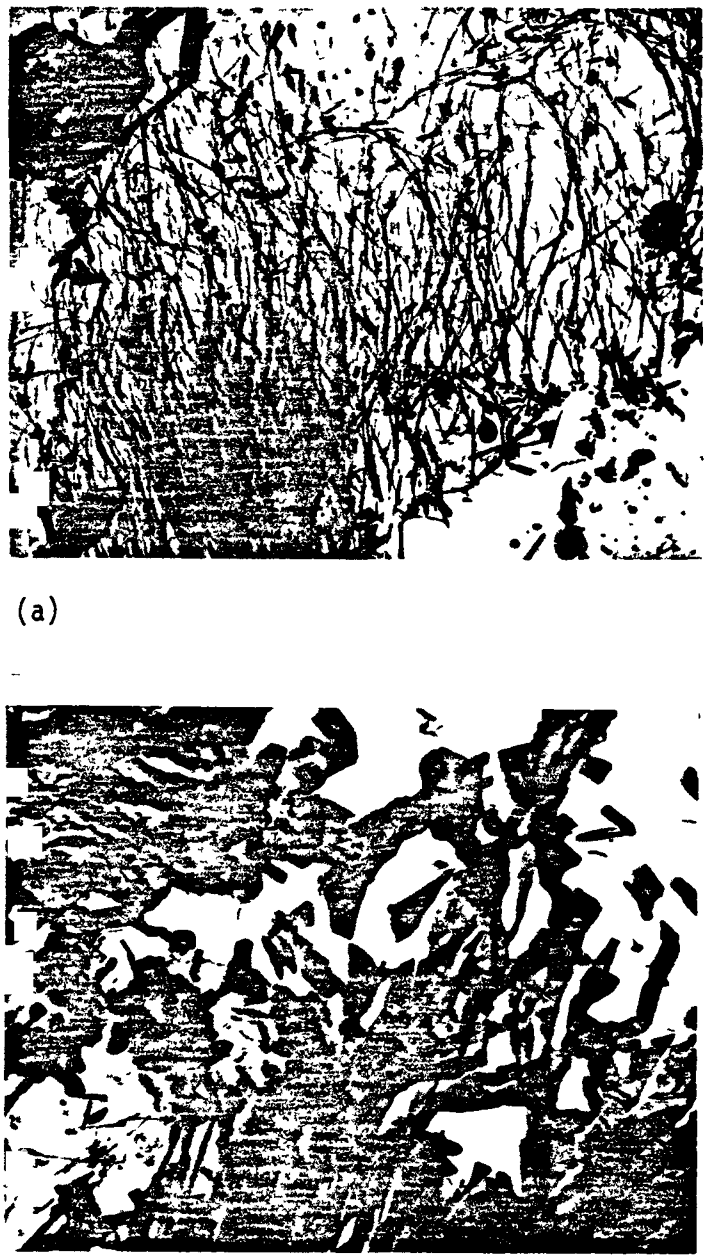
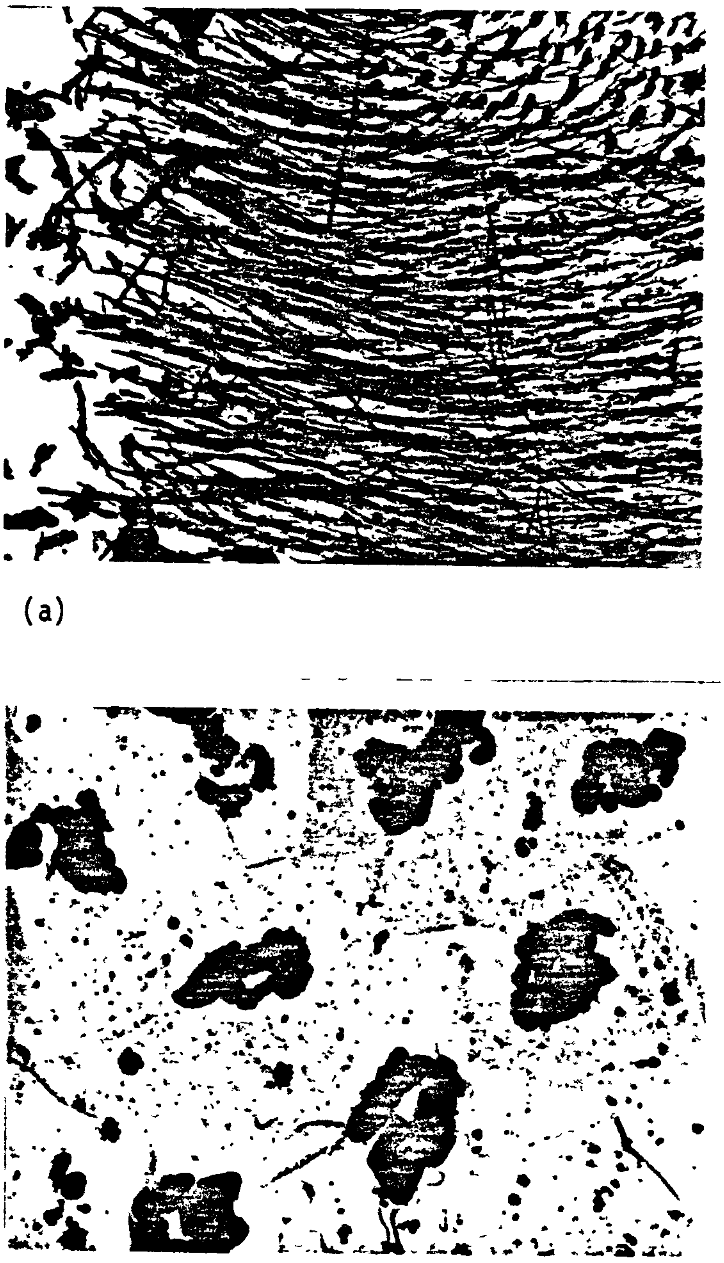


FIGURE 5. CARBON PROFILE ANALYSIS OF 2¼Cr-1Mo STEELS


(a)

(b)

FIGURE 7. TRANSMISSION ELECTRON MICROSCOPY OF AS-HEAT TREATED 2¼Cr-1Mo STEEL
a) M_2C-TYPE CARBIDES IN VAR STEEL
b) $M_{23}C_6$-TYPE CARBIDES IN ESR STEEL 15000X


(a)

(b)

FIGURE 8. a) M_2C-TYPE CARBIDE IN VAR STEEL AFTER 11262 HRS, 415°C
b) M_6C-TYPE CARBIDE IN SURFACE REGION OF ESR STEEL AFTER 11262 HRS, 524°C 15000X