PAPER NUMBER

MASTER

CORROSION/81

The International Corrosion Forum Sponsored By the National Association of Corrosion Engineers / April 6-10, 1981 / Sheraton Centre, Toronto, Ontario, Canada.

CONF-810402--8

LONG-TERM CORROSION OF Cr-Mo STEELS IN SUPERHEATED STEAM AT 482 AND 538°C*

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ABSTRACT

The corrosion of several Cr-Mo ferritic steels was investigated in superheated steam at an operating power plant. Tests were conducted at 482 and 538°C (900 and 1000°F) in a once-through loop for times up to 28,000 h. Chromium concentrations ranged from 2.0 to 11.3%, and the effect of surface preparation on corrosion was investigated.

Only one of many specimens showed evidence of exfoliation at 482°C, but at 538°C exfoliation occurred on at least some of the specimens of most materials; the exceptions were the alloy with the highest chromium content (Sandvik HT-9), one heat of 9 Cr-1 Mo steel with the highest silicon content, and Sumitomo 9 Cr-2 Mo steel, which was in test for only 19,000 h. Parabolic oxidation kinetics adequately described the corrosion process for about the first year, after which corrosion rates were constant and lower than predicted from extrapolation of the initial part of the penetration versus time curves. With chromium concentrations between 2 and 9%, corrosion behavior was independent of chromium content, and corrosion

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*Work sponsored by U.S. Department of Energy, Office of Advanced Nuclear Systems and Projects, Gas Cooled Reactor Programs Division, under contract W-7405-eng-26 with the Union Carbide Corporation.

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was only slightly less with Sandvik HT-9. Corrosion was nearly independent of surface preparation, but in two cases the presence of mill scale on the surface prior to steam exposure seemed to retard oxidation in steam.

INTRODUCTION

The low-alloy ferritic Cr-Mo steels have been used extensively in superheaters and reheaters of fossil-fired power plants, but few quantitative measurements have been made of their oxidation rates in superheated steam. It is well established, however, that the oxidation rates of these materials are considerably lower in steam than in hot combustion gases, and consequently there has been little practical reason to investigate steam-side corrosion. On the other hand, when a liquid metal or an inert gas is used to transport heat to superheaters and reheaters, as in some types of nuclear reactors, steam corrosion constitutes the principal means of tube degradation, and a knowledge of oxidation behavior in steam is essential to establish realistic corrosion allowances. Scaling rate data would be helpful additionally in nonnuclear systems in estimating the onset of exfoliation and for determining an optimum schedule for cleaning superheaters and reheaters, if necessary.

Most of the studies on the oxidation of Cr-Mo steels have relied on the measurement of scale thicknesses on the steam side of superheater tubes or on corrosion specimens removed from power plants. Based on such data Effertz and Meisel[1] and Manning and Metcalfe[2] concluded that the growth in oxide thickness with time was adequately described by a parabolic oxidation law. Eberle and Kitterman[3] examined the scaling behavior of similar alloys at 593 and 649°C (1100 and 1200°F) using the same technique but over shorter periods. Their data indicated that parabolic oxidation kinetics prevailed for only about six months, following which the rate became constant. Grobner et al.[4] also noted a transition from parabolic to linear kinetics in steam oxidation studies. In another study Eberle et al.[5] exposed several Cr-Mo steels to steam at 527/554°C (980/1030°F) and determined oxide thickness after 36,000 h. They correlated their single time exposure with 7300-h data obtained at 538°C (1000°F) assuming parabolic kinetics.

With data obtained under the conditions described above, each data point represents a separate specimen that is destructively examined. Inherent in this approach are the assumptions that specimen-to-specimen variation is small and that oxide is not lost throughout the test period. Since specimens are removed at different times from operating power plants over extended periods (up to 1000,000 h), it is also questionable whether conditions (steam purity and temperature) remain constant throughout the test as assumed.

Shorter term tests (up to 14,000 h) of Cr-Mo alloys were conducted in 538°C steam by McCoy and McNabb[6] under controlled conditions with specimens that were weighed several times during the test. Their data showed a decrease in the rate of weight gain throughout the test in all cases. Log-log plots of weight gain versus time produced straight lines with an average slope of 0.36, significantly less than the 0.5 indicative of parabolic behavior. In tests conducted by Hurst and Cowen,[7] ferritic Cr-Mo steels corroded at decreasing rates at 475°C (887°F) for up to 12,000 h, but at 550°C (1022°F) the rates became constant after 8000 h and were higher than predicted from extrapolation of the early parabolic data. In some cases spalling was noted after 6000 h at the higher temperature.

Thus the data in the literature on corrosion rates of ferrous alloys in steam do not provide a clear picture of the effect of exposure time. Something approaching parabolic kinetics seems to prevail initially, but when or if a transition to linear kinetics occurs has not been unambiguously established. Furthermore, most of the available data were obtained at temperatures in excess of those presently recommended for the use of low-alloy steels in power plants. The purpose of this investigation was to obtain quantitative oxidation data for several Cr-Mo steels in superheated steam over extended periods so that the data could be confidently extrapolated to longer times. Such data are needed in the design of nonfossil power plants such as liquid-metal- or inert-gas-cooled nuclear reactors.

EXPERIMENTAL

The tests were carried out in an Inconel 617 nonrecirculating loop at the Bartow Plant of the Florida Power Corporation. The loop used 45 kg (100 lb) of steam per hour from the superheater of the plant. Figure 1 shows the loop with electric heaters in place before the insulation was installed. Steam, cooled slightly below 482°C (900°F), entered the loop from the top. As it passed through the electrically heated piping, its temperature was increased to 482°C by the time it reached the first autoclave (long pipe, fifth from top in Fig. 1). After leaving the first autoclave, the steam passed through additional electrically heated pipes to raise its temperature to 538°C before entering the second autoclave (bottom pipe, Fig. 1). The steam from the second autoclave was condensed and discarded. The 48-mm-ID (1.9-in.) autoclaves had flanged openings on each end for insertion and removal of test specimens. The nominal steam velocity past the test specimens was 1.5 m/s (5 ft/s), and the loop pressure was 10.5 MPa (1525 psi).

Steam at the Bartow Plant was raised from boiler water that contained 10 to 30 ppm phosphate and hydrazine (0.01 to 0.02 ppm in the feedwater) and had a pH of 9.5 to 10.5. The steam condensate had a pH of 8.6 to 9.0, contained less than 0.4 ppm ammonia, and had a specific resistivity greater than 2500 Ωm.

Most of the specimens were flat rectangular strips 73 × 13 × 1.6 mm (2 7/8 × 1/2 × 1/16 in.) and had a 4.8-mm-diam (3/16-in.) hole near each end for mounting, but a few had slightly different dimensions. Most of the specimens were ground on all surfaces using a 100-mesh belt grinder, but some were annealed or pickled. A few were cut axially from heavy-walled pipe so that one surface on the specimen was the inner wall of the pipe. This surface was covered with mill scale which was not disturbed during preparation of the specimen; all other surfaces of these specimens were ground. All specimens were washed with soap and water, rinsed in acetone, and weighed before testing. The specimens were stacked on stainless steel bolts and separated from each other by narrow stainless steel washers. The stacks of specimens were then placed in stainless steel boats for insertion in the autoclaves. At scheduled intervals the specimens were removed and weighed. Most of the specimens were returned to test but some were removed for destructive examination, and these were usually replaced with new ones of the same type. The loop operated for a total of 28,339 h.

Some of the specimens were metallographically mounted and polished to characterize the oxide and others were chemically descaled in Clarke's solution[8] (concentrated HCl containing 20 g Sb_2O_3 and 50 g $SnCl_2$ per liter). The amount of metal oxidized was calculated from weight gain assuming that all the corrosion product remained on the specimen and that the composition of the corrosion product was known. Weight gains were then converted to penetrations assuming uniform oxidation. The oxidation products were assumed to be $Cr_2O_3 \cdot FeO$, $Mo_2O_3 \cdot FeO$, and $Fe_2O_3 \cdot FeO$. Independent measurements of the quantities of metal oxidized were obtained in some cases from weight loss measurements on specimens descaled in Clarke's solution.

Table 1 lists the compositions of the alloys tested. In most cases the specimens were machined from standard mill products, but in three cases experimental electroslag remelt (ESR) heats of 9 Cr alloys were used.

RESULTS

All alloys initially developed black scales that were composed of two distinct layers plus a third layer in some cases. Except for one specimen, those exposed at 482°C retained all their scale throughout the entire test, but at 538°C the scale on some of the specimens began to exfoliate after several thousand hours. Weight gain measurements at both temperatures indicated parabolic oxidation kinetics for about the first year, followed by a constant rate for the remainder of the test. This point is graphically illustrated by plots of weight gain versus time on linear coordinates for representative specimens. To show specimen-to-specimen variability, we made similar plots for several specimens of each alloy and tabulated the corrosion rates calculated from the slope of the straight-line portion of the curves and the intercepts obtained by extrapolation of the straight line to time zero.

2 1/4 Cr-1 Mo Steel

These specimens were machined from mill-annealed plate and all surfaces were ground. Subsequently, some specimens were annealed (732°C for 2 h, furnace cooled) and some pickled. All three surface conditions were tested simultaneously. Within the reproducibility of the data, there were no significant differences in weight gains experienced by the specimens with the different surface treatments or in the tendency of the scale to exfoliate. Only one specimen lost oxide at 482°C. The oxide on this specimen had developed a few blisters by 10,000 h and appreciable spalling had occurred by 16,000 h. At 538°C a few specimens exhibited exfoliation by 12,000 h, and with increasing exposure both the number of specimens showing loss of oxide and the area on a specimen undergoing exfoliation increased. However, the amount of oxide lost on all exfoliated specimens except two was so small that weight gains continued to increase with exposure time. It should be noted that some specimens of each heat treatment retained their oxides for the entire 28,339 h.

Figure 2 shows representative weight gain versus time curves for specimens with different surface treatments. Although there is slight variation in the data between individual specimens, only a single curve has been drawn for each temperature. Table 2 shows corrosion rates and penetrations for four specimens with each surface treatment and illustrates the agreement among specimens regardless of surface treatment.

Figure 3(a) shows a cross section through an intact oxide, and Fig. 3(b) is a similar view through one that had undergone spalling. Figure 3(a) illustrates the two-layered oxide typical of those formed on Cr-Mo steels in superheated steam. The scale shown in Fig. 3(b) is composed of multiple layers, indicating that at some time the initial two-layered scale became detached from the metal, a new two-layered scale formed, and the layers subsequently joined.

9 Cr-1 Mo Steels

Four different heats of 9 Cr-1 Mo steel were tested (Table 1): one air-melted heat and three experimental heats of ESR materials. These materials were tested only with ground surfaces. At 482°C all specimens retained their oxides, but at 538°C only the air-melted material (heat 316381A) remained completely free of exfoliation. Some specimens of all heats of the ESR materials began to lose oxide after 12,000 h, but heat 91887 showed less tendency to spall than the others.

Figure 4 shows weight gain versus time curves, Table 3 gives calculated corrosion rates and initial penetrations for representative specimens of each material, and Fig. 5 shows cross sections of typical scales. In contrast to the scale formed on 2 1/4 Cr-1 Mo steel, the oxide formed at 538°C on all the 9 Cr-1 Mo alloys was characterized by a clearly distinguishable third layer at the oxide-metal interface. The third layer has been observed before and has been referred to as an inner oxidation zone.[9] Ion microprobe analysis showed that the metal composition of the inner oxidation zone was the same as the middle layer (or inner layer) for 2 1/4 Cr-1 Mo steel; both contained chromium and molybdenum in the same volume concentration as the substrate metal, whereas the outermost layer contained only iron.

The exposure of one specimen of heat XA-3177 at 538°C for 24,965 h produced a small blister that contained a few cracks but was basically intact. This specimen was placed in a mold that was evacuated before the epoxy resin was added so that the epoxy filled the void between the adherent oxide and the detached oxide. Figure 6 shows a cross section through the blister, and Fig. 7 is an enlargement of both the detached oxide and the adherent oxide under it. Although both oxides consisted of two distinct layers, the outer layer of the detached oxide appears lighter in color and more porous than the corresponding layer on the attached oxide. Interestingly, the lighter phase, while irregular, stops at the interface between the pure magnetite and the chromium- and molybdenum-containing layer, suggesting that the presence of the latter two elements in the oxide inhibited the formation of the lighter phase. However, a very thin layer of the lighter phase appears to exist on the bottom of the chromium- and molybdenum-containing layer. The light-colored oxide was also noted on scales formed on 2 1/4 Cr-1 Mo and 9 Cr-1 Mo steel (heat XA3178) that had at some time been separated from the metal [see Figs. 3(b) and 5(c)]. Armitt et al.[9] reported that the light phase in such scales is Fe_2O_3 (hematite). Examination of the detached scale shown in Fig. 7 as well as that on 2 1/4 Cr-1 Mo steel with a normal 2θ diffractometer scan using copper radiation and a graphite crystal diffracted beam monochrometer showed that the light phase in our oxides was also hematite.

Sumitomo 9 Cr-2 Mo Steel

Two groups of specimens were machined from the wall of a short length of heavy-walled pipe. One of the "flat" surfaces of one group of specimens was the concave interior surface of the pipe that was covered with mill scale. Five specimens of this type were tested at each temperature. A second group of specimens was machined from the interior of the pipe wall and all their surfaces were initially ground. Four specimens with the ground surfaces and three additional ones that had been heavily pickled after grinding were tested at each temperature.

All the specimens were placed in test at the same time and were exposed for 19,345 h. Under any set of conditions the reproducibility of weight change was good (no greater than ±6% from average), and average values are presented in this case. All specimens gained weight at decreasing rates during approximately the first year and then corroded at a constant rate. Exfoliation was not found at either temperature. Specimens with mill scale on one face before exposure showed average weight gains of 46.4 and 119.2 g/m^2 at 482 and 538°C, respectively, after 19,345 h. Values for the specimens without the mill scale were 52.2 and 116.0 g/m^2, independent of whether the surfaces had been ground or pickled. Thus the weight gains indicated no significant effect of the mill scale. The character of the oxide formed on the oxide-free surfaces was identical to that noted on the 9 Cr-1 Mo specimen shown in Fig. 5(a). The final oxide on those surfaces with prior mill scale was slightly different in that the interface between the inner and outer layers was less distinct than in the oxide on the ground or pickled surfaces. This is illustrated in Fig. 8, which shows the oxides formed on specimens exposed for 19,345 h at 482°C.

Analysis of the weight gain versus time curves for the ground and pickled surfaces yielded corrosion rates of 4.5 and 8.3 µm/year at 482 and 538°C, respectively, and intercepts of 8.2 and 19.8 µm; these values are comparable to those for 2 1/4 Cr-1 Mo and 9 Cr-1 Mo steels.

Sandvik HT-9

Specimens of this alloy initially installed in the loop were from heat 451738 (Table 1) and all had ground surfaces. Later, specimens of the same heat of the alloy with as-received (mill annealed and pickled) surfaces were installed in the loop, and later still, specimens machined from the walls of two pipes (heats 451774 and 454191) were added. In the latter two cases the inner wall of the pipes which was covered with mill scale formed one of the flat surfaces of the specimen. Specimens machined from the interior of the wall of one of the pipes (heat 454191) were also tested. All specimen surfaces were ground and some were heavily pickled before test.

All specimens completely retained their scales under all conditions. Figure 9 shows weight gain versus time plots of ground specimens at 482 and 538°C that were tested for 28,339 h, and Table 4 shows corrosion rates and intercepts for other ground specimens placed in test at different times. The annealed specimens of the same heat were in test for a shorter time but showed the same type of behavior as those with ground surfaces (Table 4).

A distinct inner oxidation zone in addition to the two-layered oxide existed on specimens exposed at 482°C, but at 538°C only an occasional hint of such a zone was apparent (Fig. 10). This behavior was opposite to that of the 9 Cr alloys, where an inner oxidation zone was apparent at 538°C but not at 482°C.

Specimens from heat 454191 with mill scale on one face had distinctly lower weight gains after 19,345 h than those with all ground surfaces: 34.2 versus 44.1 g/m^2 at 482°C and 58.0 versus 78.0 g/m^2 at 538°C. Assuming that the ground surfaces on those specimens with mill scale initially on one face developed oxide to the same extent as on those specimens with all surfaces ground, the surfaces with mill scale gained only 19.6 and 28.5 g/m^2 at 482 and 538°C, respectively. Those specimens with mill scale from heat 451774 showed weight gains almost identical to similar specimens with mill scale from heat 454191, and cross sections through the oxides showed similar thicknesses. The oxide formed on surfaces that initially had mill scale on them did not have a sharp interface between the outer and inner oxide layers as did the 9 Cr-2 Mo steel specimens (Fig. 8).

With Sandvik HT-9 the effect of pickling was not clear. Pickled specimens (heat 454191) gained the same weight as those with ground surfaces at 482°C but gained 13% more weight at 538°C.

Measurements of Corrosion Product Scales

Cross sections of several specimens of all alloys were polished and examined. In all cases the characteristic two-layered oxide was found, and as indicated earlier, an internal oxidation zone was also present in some cases. Ion microprobe analysis across the oxides showed that the internal oxidation zone and the inner layer contained chromium and molybdenum in the same volume concentration as the alloy, whereas the outer layer contained neither and was essentially pure magnetite. Our observations are in agreement with those of all others who have investigated the composition of steam-formed scales on Cr-Mo alloys.

We also measured the thicknesses of the inner and outer oxide layers on the polished cross sections. For a given alloy there was no significant difference in the ratio of outer to inner oxide thickness as a result of either temperature or exposure time. This latter point is especially significant because if oxide were lost, the outer layer would probably have been preferentially dissolved or eroded away and the ratio would have decreased with time. The ratios noted for the different alloys are shown in Table 5. Within the standard deviations there were no significant differences in the ratios among the alloys. The internal oxidation zone that existed in some cases (482°C for Sandvik HT-9 and 538°C for 9 Cr-1 Mo steels) was not included in the inner oxide thickness measurement. Had it been included, the ratio would have been near unity. The significance of the ratio in terms of oxidation mechanisms is not readily apparent. However, Effertz and Meisel[1] noted that the demarcation line between the outer and inner layers on Cr-Mo steels occurs at a position corresponding to 40 to 60% of the total scale thickness, and our values are within this range.

We have assumed that weight gain is a reliable measure of the amount of metal oxidated so long as visible exfoliation of the oxide has not occurred. An indication that such is the case is shown in Fig. 11, where total oxide thickness (excluding the inner oxidation zone) is plotted versus weight gain. Since each oxide thickness was measured from a photomicrograph (as shown in Figs. 3, 5, and 10) that surveys only one point along the long axis of the specimen, the fit of the data points to the line as drawn is satisfactory. Furthermore, there appears to be no major difference in the thickness-to-weight-gain ratio among the alloys. The dashed line in Fig. 11 represents oxide thickness as a function of weight gain if the corrosion product were stoichiometric Fe_3O_4 of theoretical density (5.2 Mg/m^3). The experimental points lie on the average about 10% above this line, primarily resulting from obvious porosity in the scale, which increased as the scale thickened.

Further confirmation of the validity of weight gain as a measure of corrosion was obtained by defilming several specimens in Clarke's solution and determining the weight of oxide and the amount of metal oxidized on each specimen. Assuming that the metal oxidized to stoichiometric $Fe(Cr)_3O_4$, the weight of oxide actually formed was compared with the amount expected. The average amounts of oxide found were 93% for 2 1/4 Cr-1 Mo steel, 94% for Sandvik HT-9, and 91% for the ESR 9 Cr alloys. On one 2 1/4 Cr-1 Mo steel specimen that had lost some oxide, only 89% of the oxide expected was found. Attempts to descale air-melted 9 Cr-1 Mo steel specimens resulted in heavy attack of the base metal while appreciable amounts of scale remained on the specimen. All the descaled weight losses included some base metal loss; however, by removing the specimens from the descaling solution at the first exposure of bare metal (as evidenced by formation of hydrogen bubbles), loss of base metal was held to a minimum. Because the oxide scales were quite uniform in thickness (except where exfoliation had occurred), exposure of bare metal began only at the end of the descaling process (except for the air-melted 9 Cr-1 Mo alloy). Although slight, attack on the base metal was sufficient to account for the indicated less than 100% oxide retention. Nevertheless, the data clearly indicate that Cr-Mo steels exposed to steam form magnetite $[Fe(Cr)_3O_4]$ scales that are retained on the surface until exfoliation occurs.

DISCUSSION

Our data show clearly that all the Cr-Mo steels that we investigated oxidized at a decreasing rate [weight gain proportional to $(\text{time})^{1/2}$] for about the first 8000 h and then became constant. We exposed a minimum of seven specimens of most alloys at each temperature, and in all cases the behavior was the same until exfoliation began. The constant rates fell below extrapolation of the initial parabolic curve; that is, the behavior was directly opposite to the break-away phenomenon that is often observed in other systems. The transition from parabolic to linear kinetics did not occur at a given oxide thickness. The time of transition was approximately the same at 482 and 538°C, although the oxide was substantially thinner at the lower temperature. Furthermore, we detected no change in the character of the oxide before or after transition; that is, the composition and apparent compactness of the oxide and relative thickness of the inner and outer oxide layers remained unchanged despite the transition in growth kinetics.

The growth of oxides on Cr-Mo steels in steam is generally believed to result from both the outward migration of iron ions to the surface, where they react with water molecules, and the inward diffusion of oxygen ions to the metal-oxide interface, where they react with the metal.[1] Since the solid state diffusion rates of chromium and molybdenum ions are much smaller than that of iron ions, they are oxidized in place. Consequently, the interface between the two layers marks the original surface of the steel. This mechanism accounts for parabolic kinetics, but it does not explain the transition to a constant corrosion rate. Unfortunately, our data also shed little light on the reason for the transition.

Some of the specimens of 2 1/4 Cr-1 Mo steel and ESR 9 Cr-1 Mo steels underwent exfoliation at 538°C, but no specimen of the air-melted 9 Cr-1 Mo steel or the Sandvik HT-9 showed any signs of spalling. The chromium content of the latter alloy was 11.4%, a value approaching that necessary to give it a stainless character, which perhaps accounts for its slightly lower corrosion rate. On the other hand, corrosion rates experienced by the air-melted 9 Cr-1 Mo, 9 Cr-2 Mo, the ESR 9 Cr alloys, and 2 1/4 Cr-1 Mo steel were similar, yet only the air-melted 9 Cr-1 Mo and the 9 Cr-2 Mo steels remained free of exfoliation. (The latter alloy was only in test for 19,345 h.) The fact that Cr-Mo alloys with chromium contents between 2 and 9% behave about the same in steam has been noted by several investigators,[1,2,7,9] some of which have concluded that within this range silicon is more important than chromium in determining corrosion behavior. Although we did not specifically investigate the effect of silicon content, it is interesting to note that of the alloys tested, the air-melted 9 Cr-1 Mo steel had the highest silicon concentration (0.46%), followed by Sumitomo 9 Cr-2 Mo (0.29%), 2 1/4 Cr-1 Mo steel (0.22%), and the ESR 9 Cr alloys (0.08 to 0.21%). Thus our data suggest that a high silicon level retarded the onset of exfoliation but, within the range examined, had little effect on the corrosion rate prior to exfoliation.

Usually as the oxide thickened beyond some level, the voids increased in number and size and frequently concentrated at the metal-oxide interface or between the two oxide layers. Even at 538°C this behavior was not evident until after many thousands of hours, and at 482°C it was not observed even after 28,000 h except for the one specimen of 2 1/4 Cr-1 Mo steel referred to earlier. Our data, as well as that of McNary,[10] generally indicate that when spalling occurred the separation was at the oxide-metal interface followed by the formation of a new two-layered oxide. The cause of the separation is not altogether clear, although differential expansion between the metal and oxide during cooling is suggested as one reason.[10] It has been stated that the formation of a hematite layer on the outer oxide surface enhances spalling because the mismatch between expansion coefficients of oxide and metal is greater with hematite than with magnetite.[9] In our tests the only times we saw significant amounts of hematite on top of magnetite were after separation had occurred, indicating that the hematite was a result of the separation rather than a cause of it. This indicates that with adherent oxides the flux of ferrous ions at the steam-oxide interface preserves the magnetite structure, but once the oxide becomes detached from the steel the magnetite can be oxidized to hematite. It was previously noted that regions of faster duplex oxide growth often contained less Fe_2O_3 than slower growth regions,[9] and the above explanation is consistent with this observation.

Armitt et al.,[9] in a review of the corrosion of steels in power plants and in experimental programs in the United Kingdom, noted that oxides on ferritic steels often show degradation by "through scale" cracking and by accelerated oxidation associated with multiple laminations in the inner layer. We also noted multiple laminations, usually when spalling had either occurred or was imminent, but only rarely were cracks found perpendicular to the surface. Our data indicate that at random locations the oxide, which was under compression as a result of cooling, buckled from the surface to form a blister; a new oxide then formed on the metal, and at least in the vicinity of the blister these oxides grew together. In this regard our data are consistent with McNary's explanation of the formation of multiple laminations.[10]

Armitt et al.[9] further noted that voids are frequently found in scales formed in power plants but that scales grown in the laboratory contain few voids. The oxides formed isothermally on our specimens contained few voids until after many thousands of hours, usually not until spalling was about to begin, and then numerous voids were apparent. On the other hand, experiments conducted with 2 1/4 Cr-1 Mo steel in which a high heat flux existed across the corroding surfaces showed numerous voids even in the early stages of oxidation.[11,12] Furthermore, oxides formed under these conditions appeared to be much less firmly anchored to the substrate than those in our isothermal tests. Comparison of isothermal results with those obtained with a high heat flux across the corroding surface suggests that under otherwise similar conditions a high heat flux produces in a short time the same type of oxide degradation that only occurs after much longer times without heat flux.

Although we do not have a rational kinetic model to explain our results, our data show that until exfoliation occurs all the alloys we investigated had long-term steam oxidation rates at 482 and 538°C significantly lower than predicted on the basis of extrapolation of short-term data. This fact, combined with the absence of exfoliation at 482°C (except in one case), is particularly significant for liquid-metal- and inert-gas-cooled nuclear reactors, where recent trends have been toward operating temperatures in the range of these experiments. Furthermore, from an oxidation standpoint, there is no reason to choose an alloy with greater than 2 1/4% Cr or to be concerned about surface treatment; between 2 1/4 and 9% Cr there were no significant differences in corrosion rates or surface treatments. Sandvik HT-9 (11.4% Cr) exhibited slightly lower corrosion rates at 538°C than the other alloys, but even in this case surface treatment had no major effect.

SUMMARY

A variety of Cr-Mo steels containing from 2.0 to 11.4% Cr were exposed to superheated steam at 482 and 538°C for times to 28,000 h. In all cases the alloys oxidized at decreasing rates for about the first year, after which the rates became low and constant. Even at 538°C, continuing oxidation rates did not exceed 11 μm/year (0.5 mpy) and most were below that level. At 482°C corrosion rates generally ranged between 3 and 4 μm/year (0.12 and 0.16 mpy) after the initial period of higher oxidation rates. Except for slightly less corrosion on the alloy with the highest chromium content (Sandvik HT-9), all materials exhibited similar oxidation rates at each temperature. At 538°C exfoliation was noted with some of the alloys, but Sandvik HT-9 and one air-melted heat of 9 Cr-1 Mo steel with a relatively high silicon content remained free of exfoliation throughout the test.

ACKNOWLEDGMENTS

We wish to express our appreciation to personnel of the Florida Power Corporation for allowing us to conduct the tests at the Bartow Power Plant and for their support and cooperation. We also gratefully acknowledge O. B. Cavin for the x-ray determinations and M. D. Allen for preparation of the metallographic specimens. We also appreciate the efforts of M. R. Sheldon for editing and S. G. Frykman for preparing the report for publication.

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Table 1. Composition of Test Materials

Steel Designation	Heat Number	Composition[a] (wt %)								
		C	Cr	Mo	Ni	Mn	Si	V	W	Nb
2 1/4 Cr-1 Mo	84042-53	0.11	2.01	0.98		0.54	0.22			
9 Cr-1 Mo	316381A	0.08	8.79	1.00	0.38	0.34	0.46			
9 Cr-1 Mo	XA-3177[b]	0.09	9.58	0.80	0.08	0.44	0.17	0.15	0.46	0.11
9 Cr-1 Mo	XA-3178[b]	0.10	9.52	1.55	0.16	0.50	0.21	0.30		0.14
9 Cr-1 Mo	91887[b]	0.10	9.22	1.01	0.08	0.38	0.08	0.22		0.15
Sumitomo 9 Cr-2 Mo	—[c]	0.04	8.80	2.06	0.13	0.50	0.29			
Sandvik HT-9	451738	0.19	11.4	1.00	0.50	0.50	0.26	0.27	0.49	
Sandvik HT-9	451774[c]	0.20	11.2	0.97	0.51	0.50	0.32	0.29	0.51	
Sandvik HT-9	454191[c]	0.18	11.3	0.93	0.50	0.52	0.35	0.29	0.51	

[a] Balance iron.

[b] Electroslag remelt heats. Specimens supplied by Combustion Engineering Corporation.

[c] Specimens supplied by General Atomic Company.

Table 2. Penetrations and Corrosion Rates for 2 1/4 Cr-1 Mo Steel in Superheated Steam Calculated from Weight Gain—Time Curves

Test Time (h)	Surface Preparation	Penetration Calculated from Extrapolation of Weight Gain—Time Curves (μm)		Corrosion Rate After First Year (μm/year)	
		482°C	528°C	482°C	538°C
28,339	Ground	13.9	18.3	3.0	9.8
27,835		13.6	21.4[a]	3.3	11.0[a]
26,711		13.6	21.0	3.6	9.3
25,288		11.9	15.6[b]	3.8	11.3[b]
28,339	Annealed	14.2	19.3	3.2	8.8
27,835		13.9	20.7[c]	3.4	9.1[c]
25,288		12.2	21.7	3.0	9.5
23,267		8.5	23.7	3.8	5.9
28,339	Pickled	16.3	21.0	3.0	7.8
27,835		15.9	14.9[d]	3.8	11.4[d]
26,719		13.5	24.1	2.9	8.6
25,288		11.5	18.3	3.2	10.0

[a] 18,235 h.

[b] 20,334 h.

[c] 26,719 h.

[d] 23,267 h.

Table 3. Calculated Penetrations and Corrosion Rates for 9 Cr Steel Specimens with Ground Surfaces in Superheated Steam

Total Test in Time (h)	Heat Number of Test (alloy)	Penetration Calculated from Extrapolation of Weight Gain—Time Curves (μm)		Corrosion Rate After First Year (μm/year)	
		482°C	538°C	482°C	538°C
28,339	316381A[a]	11.9	18.2	3.2	5.1
27,835	316381A[a]	11.3	19.6	2.9	5.0
26,719	316381A[a]	10.6	18.2	3.3	5.1
23,267	316381A[a]	9.0	16.6	3.5	6.5
23,267	XA-3177[b]	9.6	21.6	4.0	6.7
23,267	XA-3178[b]	9.6	21.9	4.0	7.1
23,267	91887[b]	10.0	24.5	4.4	8.7

[a] Individual specimens.

[b] Average of three specimens.

Table 4. Calculated Penetrations and Corrosion Rates for Sandvik HT-9 Specimens Exposed in Superheated Steam

Total Test in Time (h)	Heat Number of Test (alloy)	Penetration Calculated from Extrapolation of Weight Gain–Time Curves (μm)		Corrosion Rate After First Year (μm/year)	
		482°C	538°C	482°C	538°C
28,339	451738[a]	10.6	14.3	2.7	3.7
27,835	451738[a]	11.0	15.3	3.0	4.1
26,719	451738[a]	10.3	12.6	3.0	4.2
23,267	451738[a]	9.0	14.9	3.2	4.5
20,334	451738[b]	6.8	12.3	3.1	4.6
19,345	454191[c]	7.1	10.5	3.6	7.0

[a] Individual specimen with ground surface.

[b] Average of three specimens with annealed surfaces.

[c] Average of three specimens with ground surfaces.

Table 5. Ratios of Outer and Inner Oxide Thicknesses on Different Alloys

Alloy	Number of Measurements	Average Ratio $\left(\frac{\text{Outer Oxide}}{\text{Inner Oxide}}\right)$	Standard Deviation
2 1/4 Cr-1 Mo steel	20	1.40	0.16
9 Cr-1 Mo steel[a]	18	1.27	0.08
9 Cr-1 Mo steel[b]	15	1.31	0.08
Sandvik HT-9	24	1.37	0.22

[a] Air-melted heat 316381A.

[b] ESR heats XA-3178, XA-3178, and 91887.

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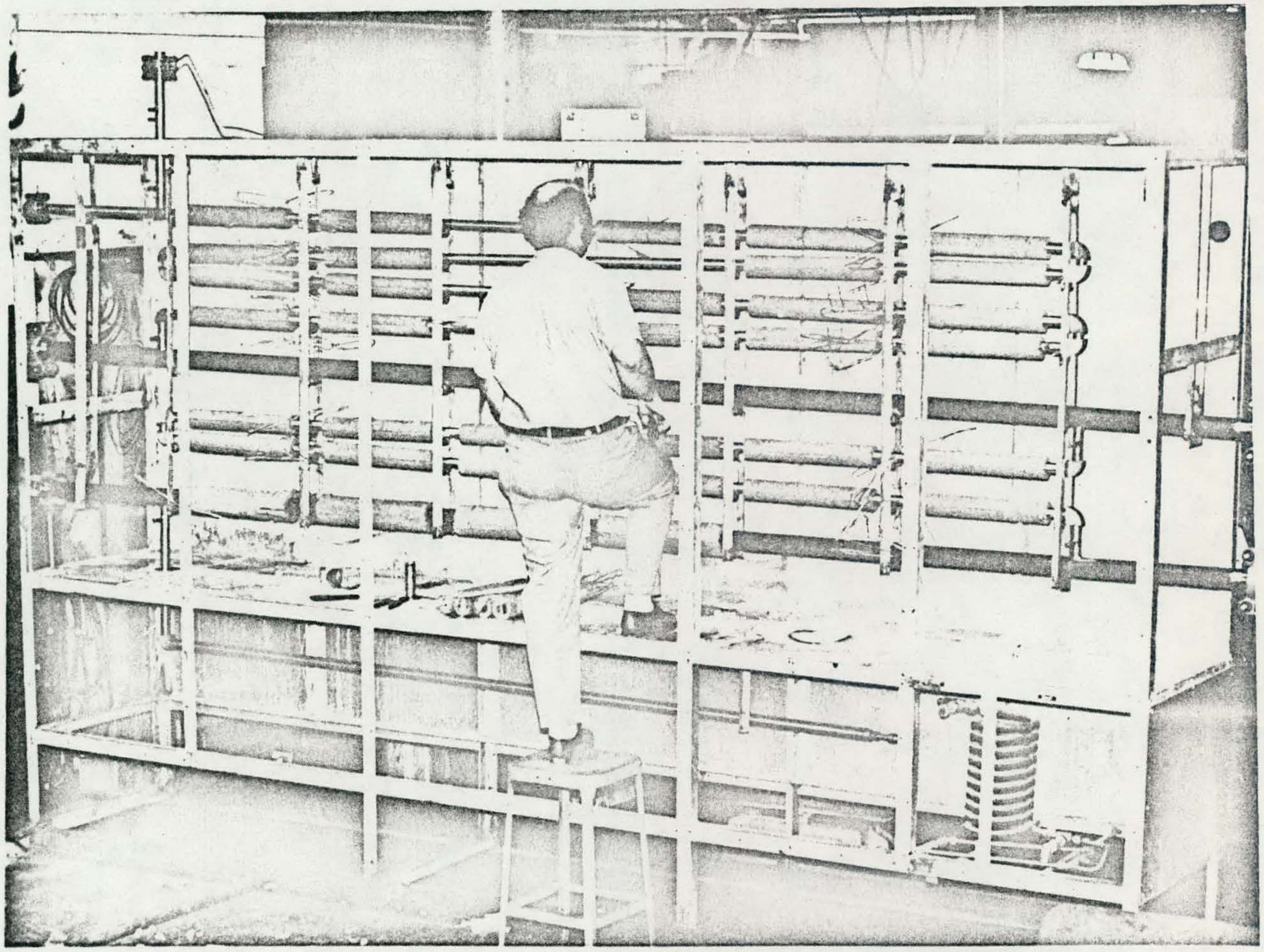

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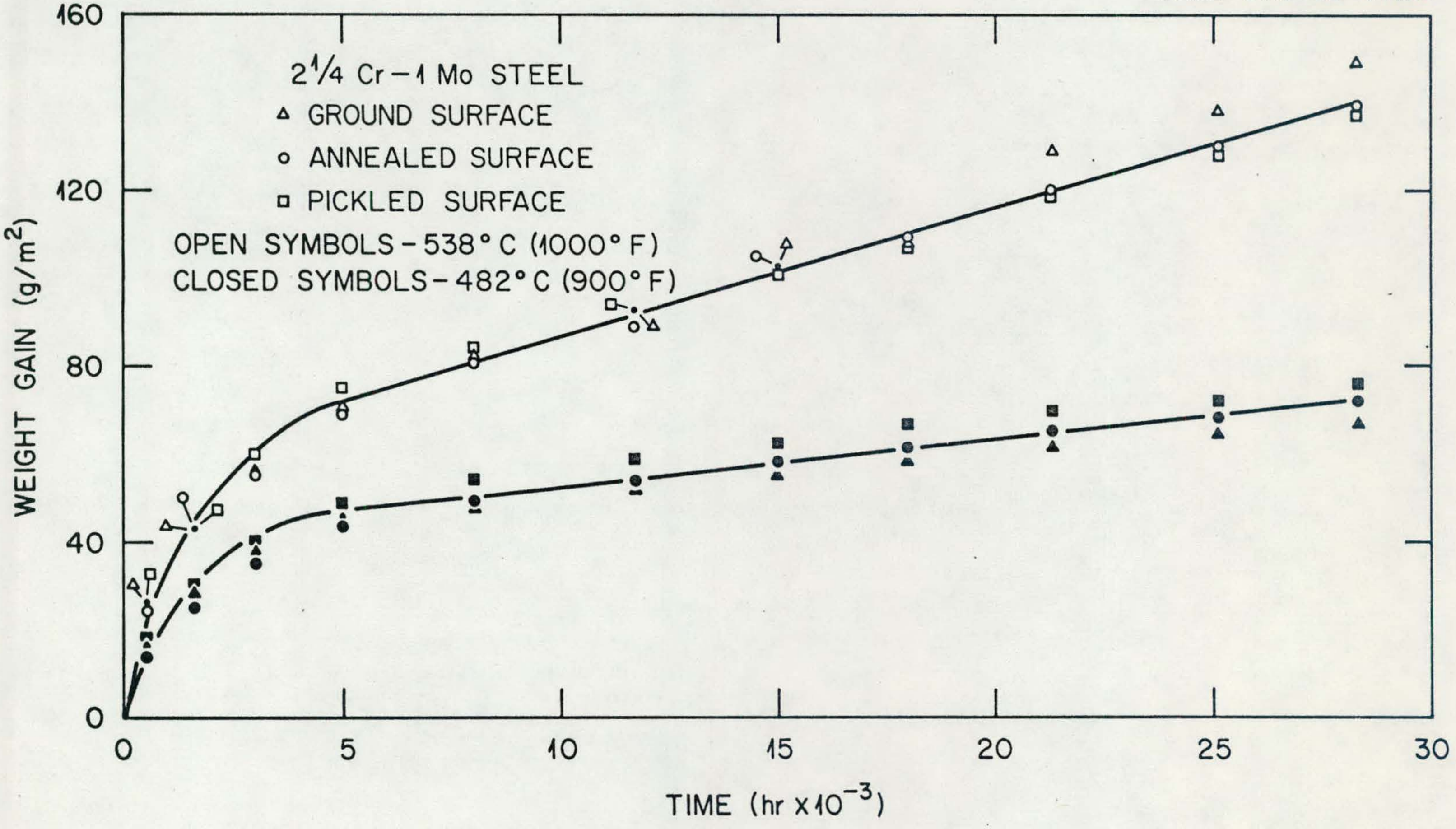

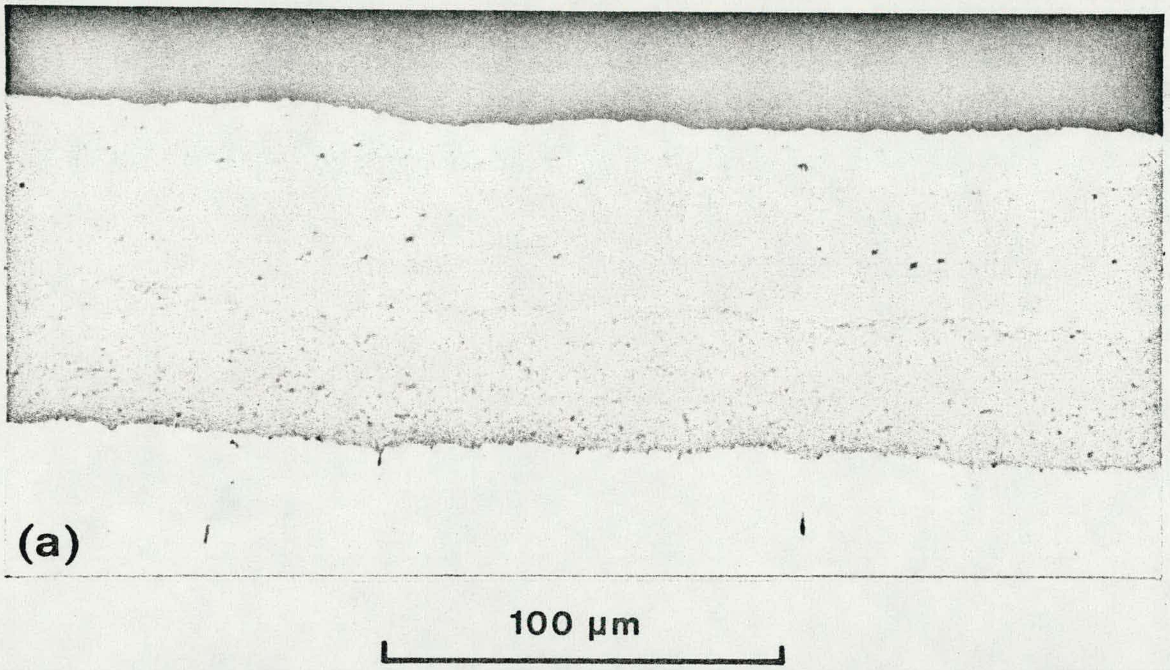
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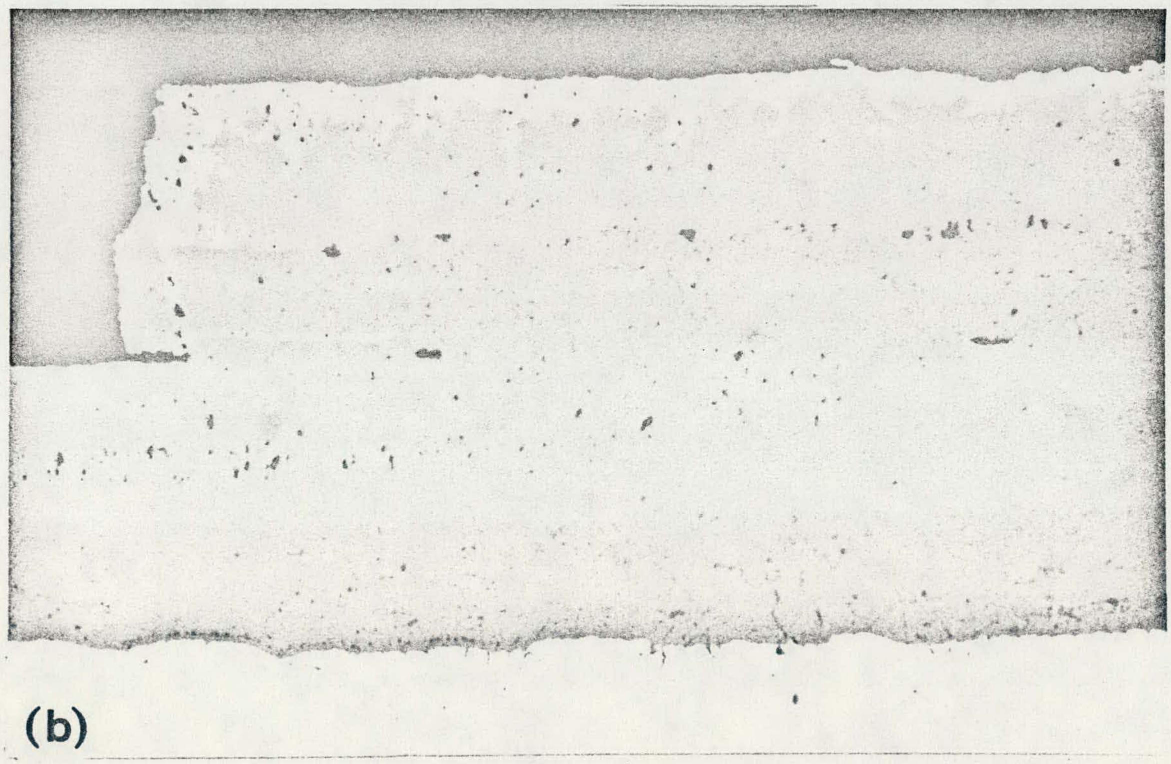
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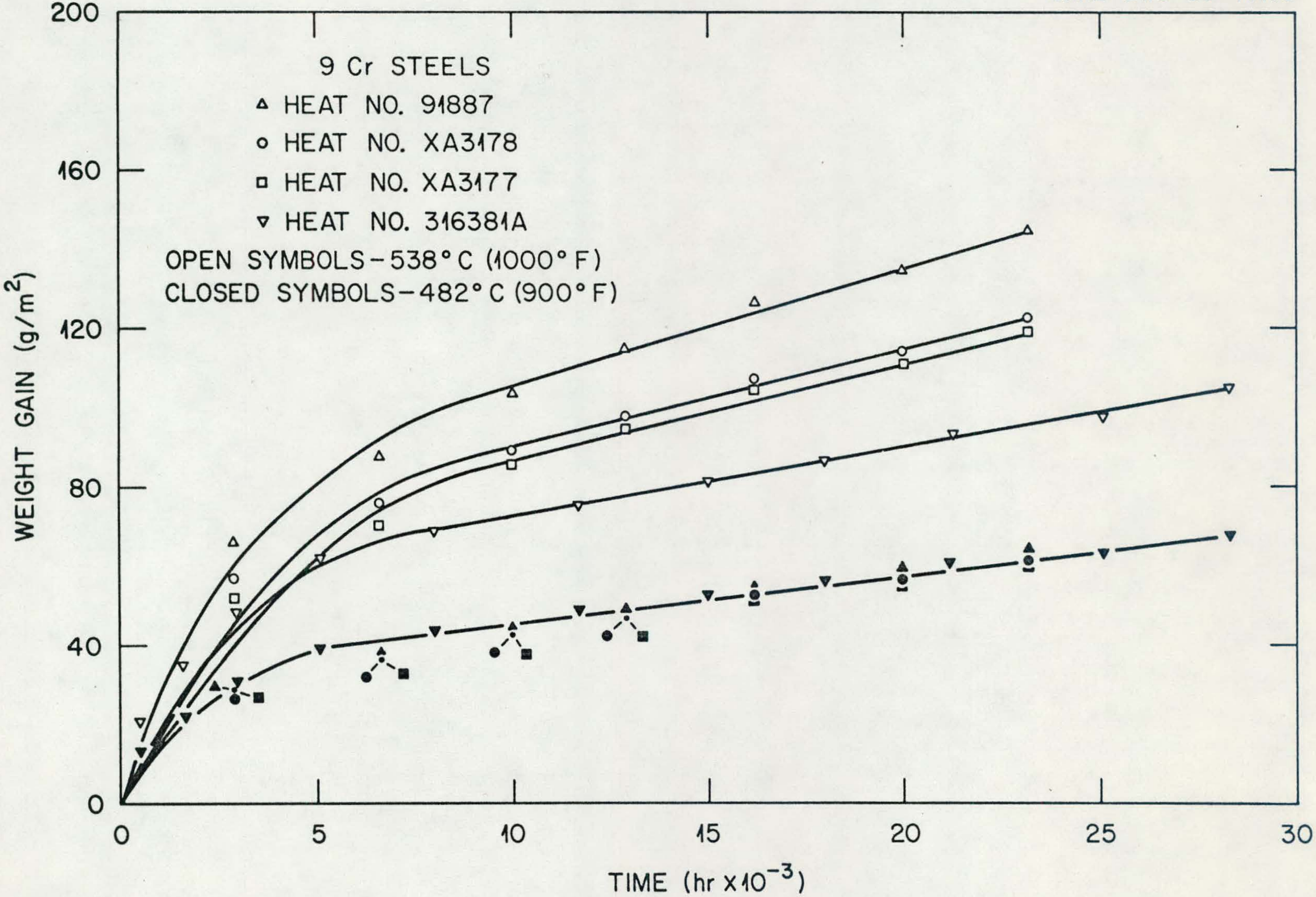

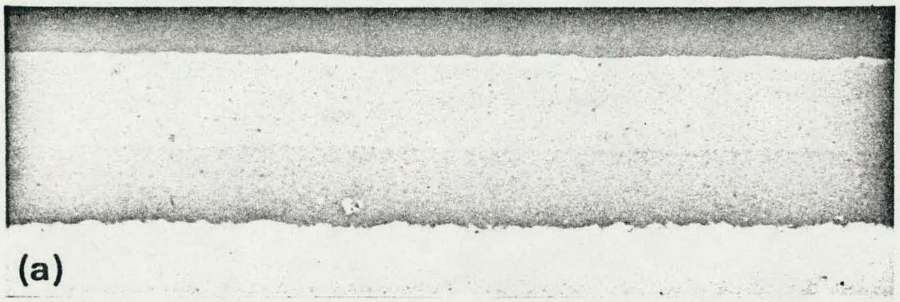

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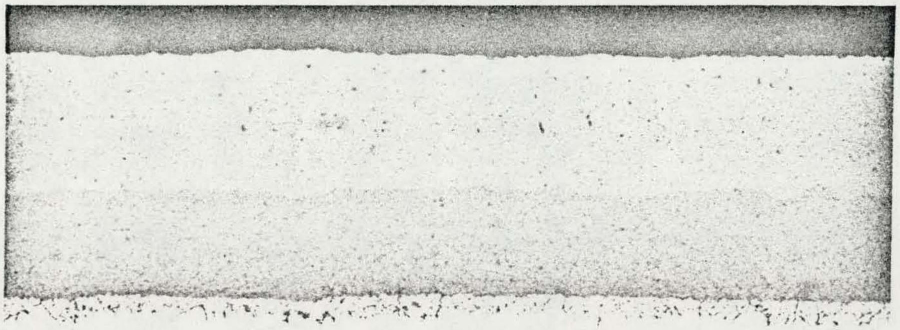

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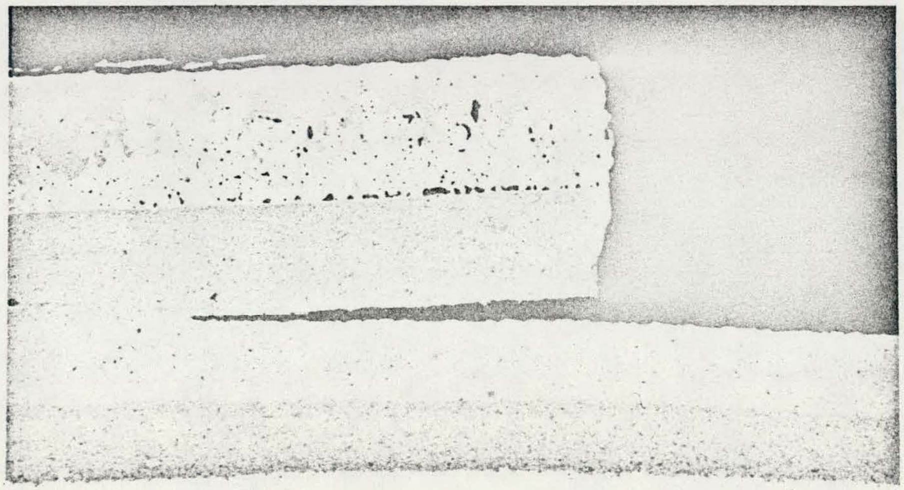

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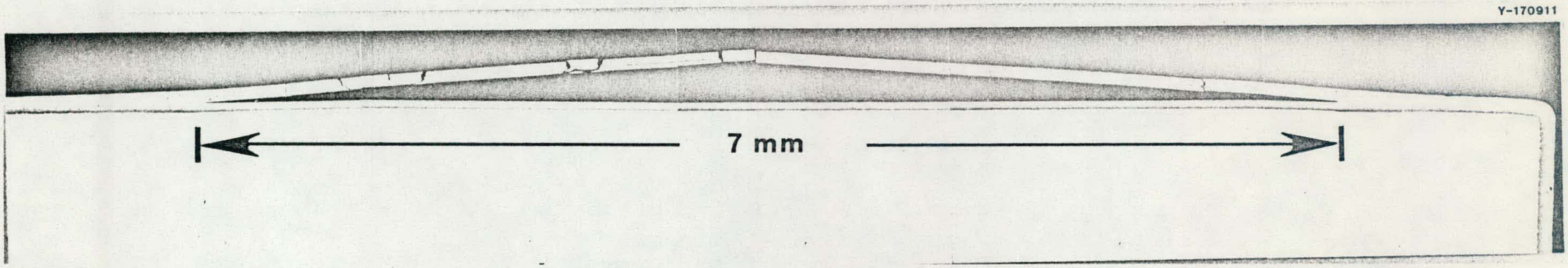
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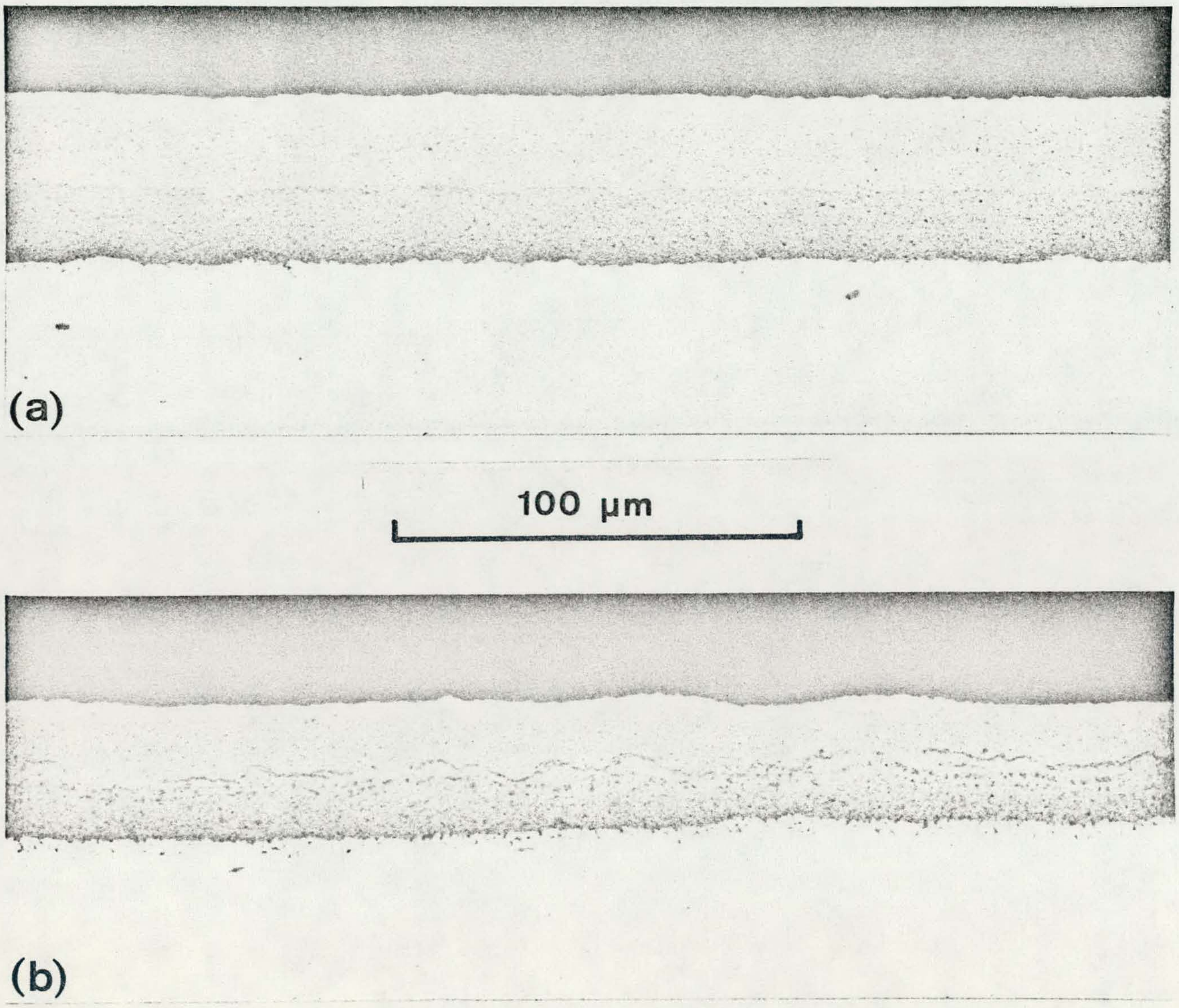
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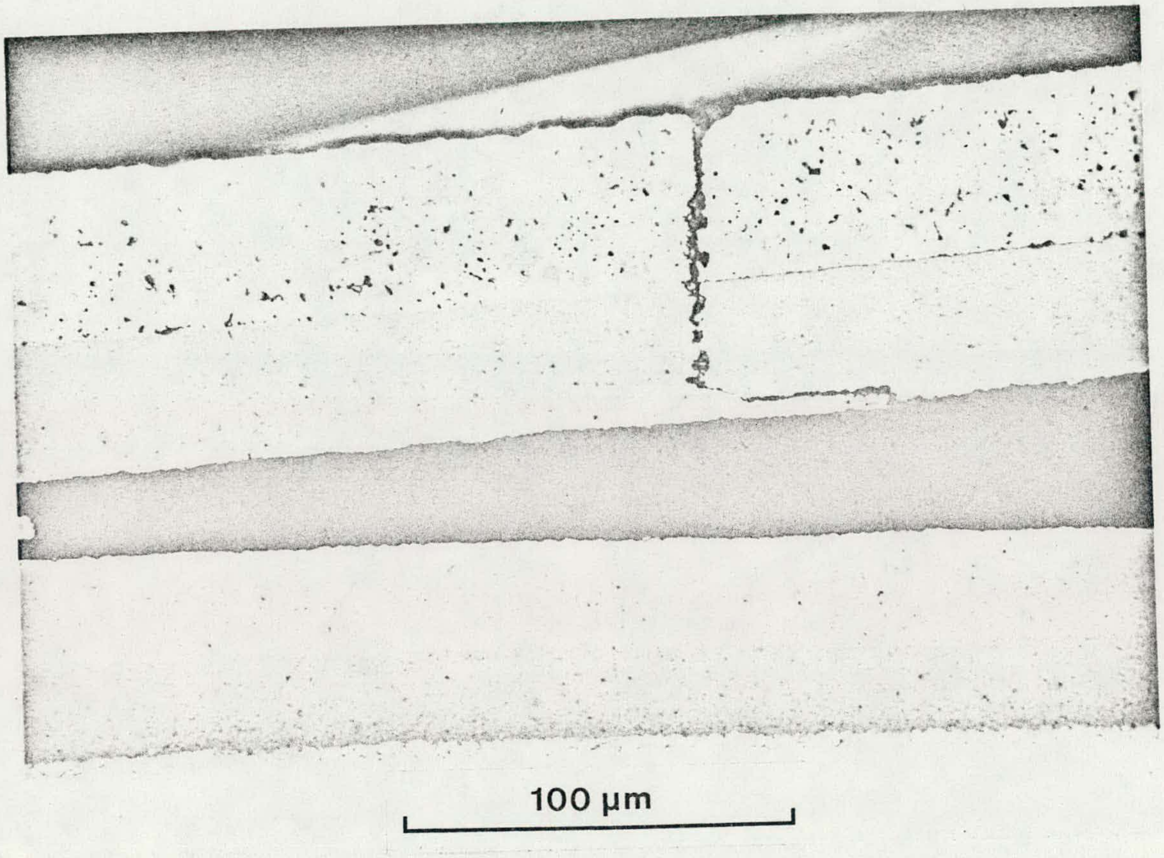
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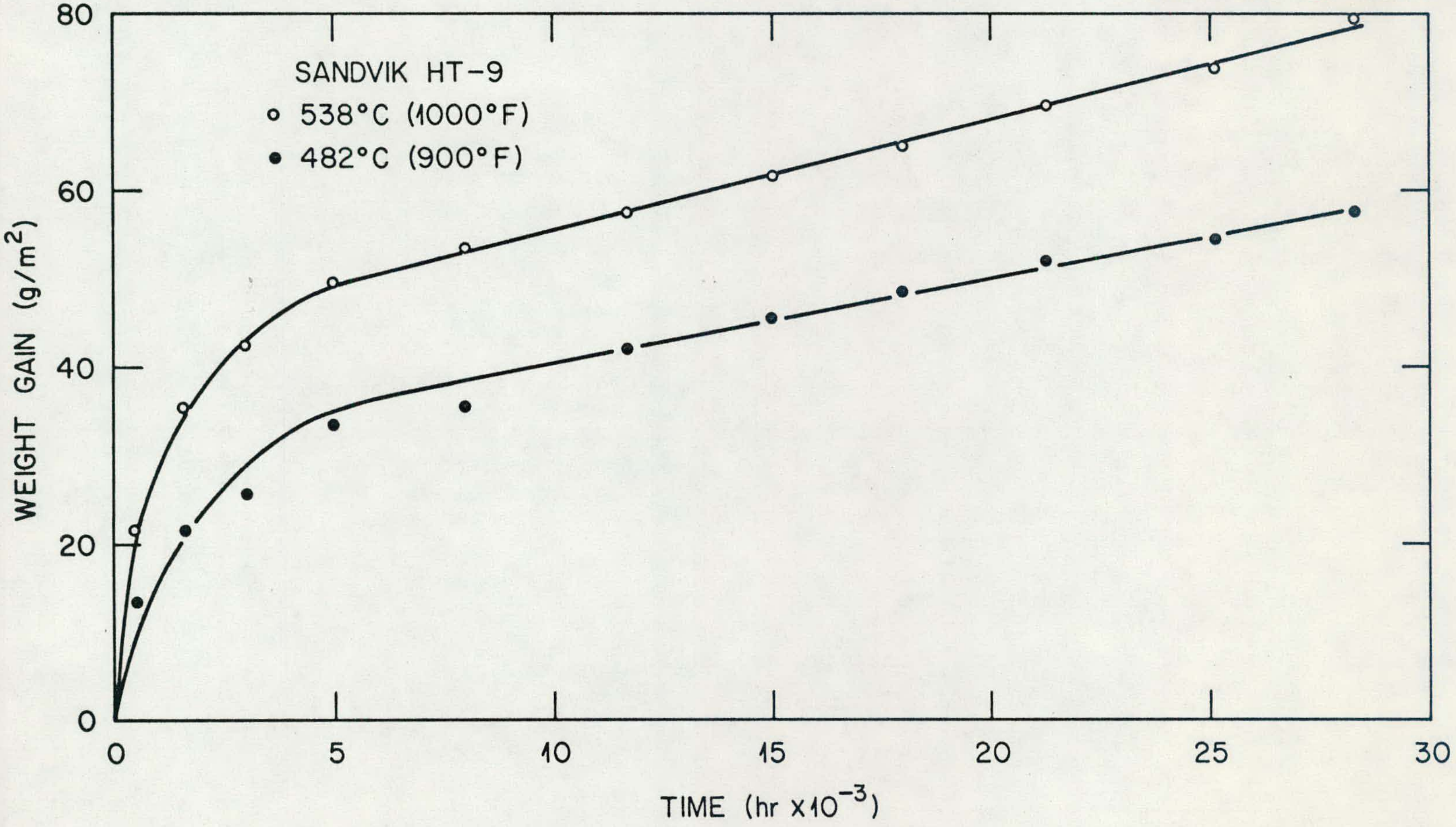

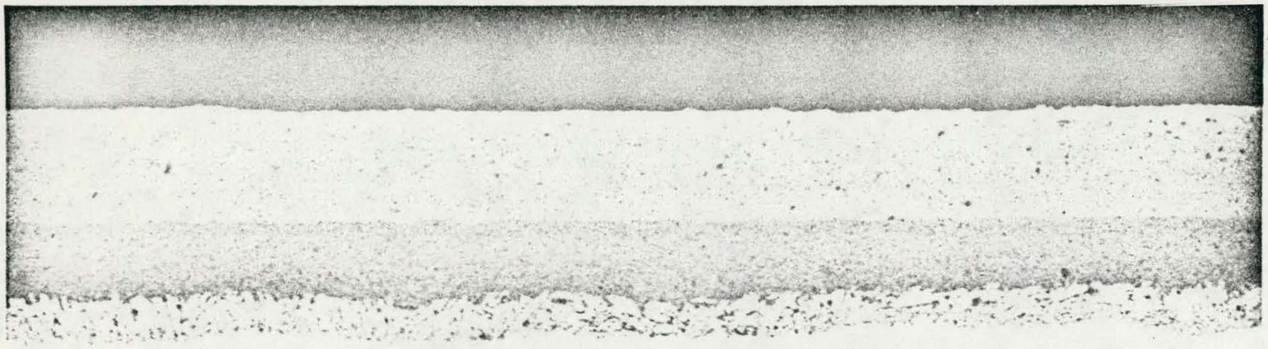

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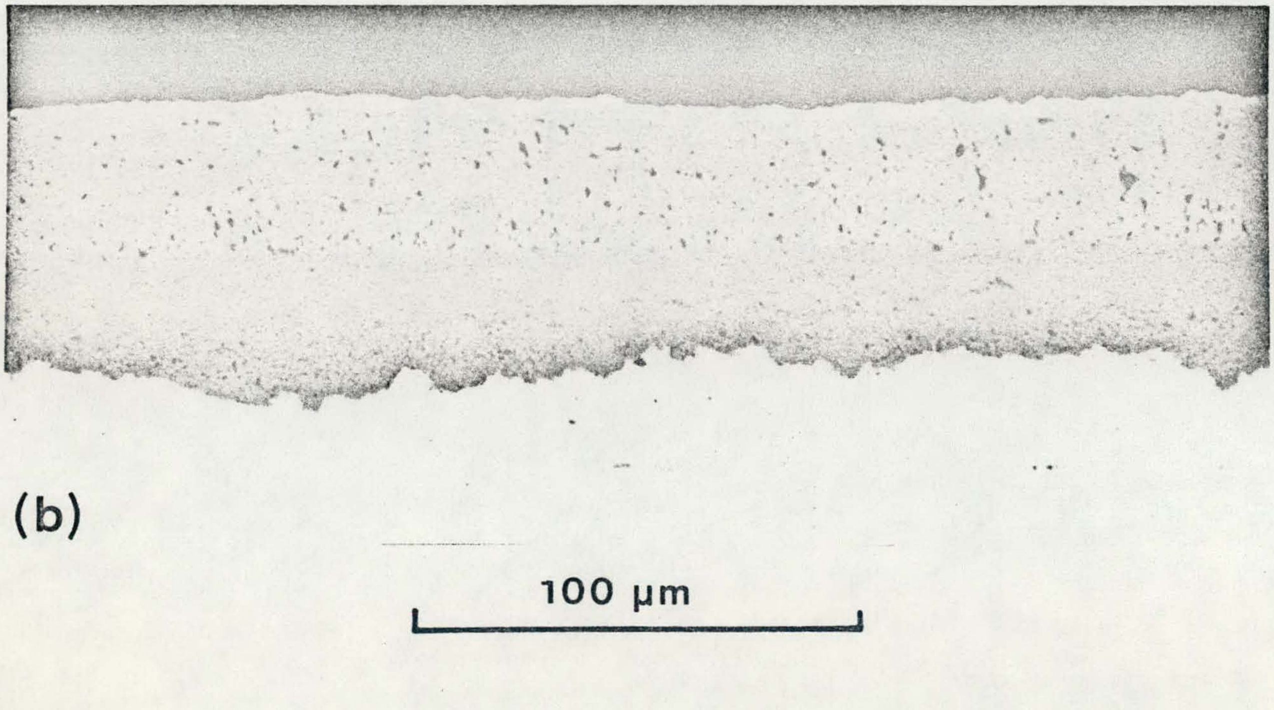

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