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TUBING WASTAGE IN FLUIDIZED-BED COAL COMBUSTORS (GRIMETHORPE PFBC TUBE BANK "E")

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TUBING WASTAGE IN FLUIDIZED-BED COAL COMBUSTORS
(Grimethorpe PFBC Tube Bank "E")

By
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TUBING WASTAGE IN FLUIDIZED-BED COAL COMBUSTORS[1]
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1.0 ABSTRACT

Samples of evaporator tubing from Tube Bank "E" of the Grimethorpe pressurized fluidized-bed combustion (PFBC) facility in the UK were examined in the third of a series of studies being conducted at Lawrence Livermore National Laboratory (LLNL) under sponsorship of the U.S. Department of Energy's Morgantown Energy Technology Center (METC). The program is being conducted to identify the mechanism or mechanisms responsible for metal loss (wastage) of in-bed carbon-steel evaporator tubes in bubbling-bed coal combustors.

Results of examination suggest that bed conditions were less aggressive than in previous experiments in this combustor; however, tubing wastage was observed in some samples. Observations made on these tubes are consistent with the hypothesis of tubing wastage proposed in reports of previous LLNL studies conducted under this program that the dominant cause of metal loss is exfoliation of the normally-protective oxide scale by impacting bed particulates. Good correlation was also observed with trends noted earlier that microstructure of the tubing steel plays a role in its wastage response.

2.0 EXECUTIVE SUMMARY

This report describes results of the third in a series of examinations of samples of in-bed evaporator tubing that were removed from operating fluidized-bed coal combustors (FBC) of the bubbling-bed type. These examinations are being conducted by LLNL in collaboration with METC to determine the mechanism or mechanisms responsible for metal loss (wastage) and to identify tubing characteristics or combustor operating conditions that influence tubing wastage in these types of combustors.

The samples examined in the study described in this report were from the most recent experiments conducted at Grimethorpe and were provided by Foster-Wheeler Development Corporation (FWDC), a collaborator with UK governmental agencies in the design and operation for the series of test runs using Tube Bank "E."

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[1]Work performed under auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory, in collaboration with Morgantown Energy Technology Center, under Contract No. W-7405-ENG-48.

Six samples were submitted by FWDC at the request of METC for LLNL study. These represented various tubing compositions and surface modifications that had been made to deflect or resist metal wastage. The tubes were removed from several bed locations. The samples included: (a) an unfinned and uncoated carbon steel tube, (b) an unfinned carbon steel tube having a chromized surface, (c) a finned and uncoated carbon steel tube, (d) a finned and uncoated tube of chromium-molybdenum low-alloy steel (2-1/4% Cr-1% Mo), and (e) two finned and studded tubes of austenitic stainless steel (Type 347H) and 2-1/4% Cr-1% Mo alloy-steel, respectively.

The general impression from examinations of these samples was that the fluidized-bed conditions to which these tubes were exposed during the 1,300 hour test period were less aggressive than for previous runs of the same Grimethorpe PFBC unit. This impression is based upon the glazed appearance of the oxide scale in wastage-susceptible regions of some tubes, suggesting a more gentle abrading or scouring bed action in contrast to the scenario, deduced from observations of previously-submitted samples, of an aggressive and repetitive impacting of hard bed material upon the undersides of the tubes.

Differences in surface appearance between samples of this latest series of Grimethorpe runs and previous runs of the same and other combustors could be due to a number of things, including a different mode of bed fluidization, differences in the size, mass or hardness of bed particulates, and differences in fluidizing velocity, bubble formation or bed-streaming tendencies and, of course, a different tube bank.

Despite observations suggesting possibly less aggressive conditions within the combustor, tubing wastage did occur in some tubes. This may have been a function of localized bed conditions, as finned tubes (including an alloy-steel tube) exhibiting wastage were from upper locations in the bed, while the unfinned carbon steel tube that resisted wastage was from the bottom row of the combustor bed.

All observations made on these tubing samples were consistent with the earlier-proposed wastage mechanism hypothesis that the dominant cause of metal loss is exfoliation of the normally-protective oxide scale caused by impacting bed material of the right size, mass, and hardness. Also, there was good correlation with earlier observations that microstructure of the tubing steel plays a role in its wastage response. The tube exhibiting the most wastage (a finned carbon steel tube) had a banded microstructure and higher hardness at elevated temperatures. A tube exhibiting minimal wastage was a carbon steel tube with no surface coating or modification (no fins or studs) having a chemical composition identical to that of the finned tube experiencing wastage, non-banded microstructure that appeared more homogeneous, and its elevated temperature hardness was the lowest of the group of samples tested.

Minimal wastage was also observed on the carbon steel tube having a chromized surface. However, the 1,300-hour combustor exposure probably was insufficient to assess long-term wastage resistance of such coated materials in these environments.

Three of the carbon steel tubes were determined to be from the same mill heat and, therefore, had the same chemical composition. Because of this, it was not possible to correlate chemical composition with wastage response among this group of samples, independent of microstructural effects. The three steels developed virtually identical scales in laboratory oxidation tests at 450 C in still air, despite microstructural differences. But thinner scale developed on a specimen from the Cr-Mo alloy steel tube sample. This suggests that while effects of chemical composition upon scale formation appear to be discernible in laboratory tests in still air, test environments approching the complexity of that of actual combustors may be required for evaluating the apparently more subtle effects of microstructural variables.

3.0 INTRODUCTION

The examinations described in this report were conducted on samples of evaporator tubing from experiments at the Grimethorpe PFBC facility designated as Tube Bank "E." This tube bank was the product of a collaborative design exercise between the British Coal/Central Electricity Generating Board (CEGB) project (UK) and FWDC (USA). It is the third in a series of studies that LLNL has been conducting in collaboration with DOE-METC and the second study of tubes from Grimethorpe.

4.0 PURPOSE

The work is being done to identify the mechanism or mechanisms responsible for metal loss (wastage) that has occurred in in-bed evaporator tubing of fluidized-bed coal combustors. The approach has been to examine samples of actual in-bed evaporator tubes that have been exposed to FBC environments. The studies have included affected (wasted) and unaffected tubes from various tube banks, tubes from different locations of a given tube bank, as in this study, and representing varying degrees of wastage. The primary purpose of this work is to formulate a plausible and coherent explanation of the wastage mechanism or mechanisms that is consistent with observed behavior and operating experience. A secondary purpose is to identify tubing metal characteristics or compositions that resist metal loss in these environments, if it is found that such variables affect tubing wastage. The goal is to develop information that will be useful to combustor designers and operators in minimizing wastage of in-bed evaporator tubes.

5.0 BACKGROUND

METC requested that representative samples from Grimethorpe Tube Bank "E" be included in the LLNL program, as the initial study in the series was of samples from Tube Banks C and C-2 of Test Series 2 of the Grimethorpe PFBC. All tubes submitted for examination in that earlier study (1-2) had experienced wastage, although higher-alloyed tubes modified through addition of longitudinal flow-disrupter fins at four locations 90 degrees apart around their periphery exhibited less wastage than unmodified carbon steel tubes. Those earlier Grimethorpe tubes had an outside diameter of about 35 mm with a wall thickness of about 4.5 mm; the unprotected (non-finned) tubes were of carbon steel and the finned sample was of 2-1/4% chromium-1% molybdenum (2-1/4% Cr - 1% Mo) alloy steel.

Tubes for the second series in this LLNL program (3) were from two tube banks of the Tennessee Valley Authority (TVA) atmospheric fluidized-bed combustion (AFBC) 20 megawatt Pilot Plant in Padukah, Kentucky. Those tubes were of carbon steel, had unmodified peripheries, and were of larger diameter (about 54 mm outside diameter) and thicker wall (about 6 mm) than previously examined Grimethorpe tubes.

6.0 MATERIALS AND PROCEDURES

6.1 Tubing Samples

For the third series of examinations, six short lengths of steel evaporator tubing were received at LLNL on March 15, 1988 from FWDC, Livingston, New Jersey, and identified as "Second Generation PFBC System, R&D Contract DE-AC21-86MC 21023, FWDC 9-41-3448 R210 Tube Samples." Table 1 lists the sample identifications, combustor locations, tube configurations, and steel specification limits. Details on sample removal, handling and packaging procedures used for these samples are included in Reference 4 and is reproduced in its entirety in the Appendix.

From information provided by FWDC (4), the samples represented tubes that had been exposed to three consecutive experimental runs of 500, 500, and 300 hours, respectively (1,300 hours total operating time), with the first and third runs using UK coal having a 0.2% chlorine content. Figure 1, excerpted from Reference 5, is an elevation view of Tube Bank "E" showing overall tubing layout and locations of the tubes submitted for study.

To assess materials behavior and measure metal loss, the tube bank was constructed such that the 1.4 meter useful length of each tube contained three lengths of tubes of precisely-machined outside diameter welded together. The different materials in each platen were arranged in such a way that each material of interest was exposed to a representative range of combustor temperatures and bed erosivities (5). Consequently, for materials assessment purposes, each length might include three different materials. Diameters of the as-machined external surfaces (before combustor exposure) were not provided to LLNL with the samples.

Figures 2 through 7 show as-received appearance of the six tubing samples (photographically reduced by about 45%). In each figure, the four views from left to right represent successive 90 degree clockwise rotational steps (as viewed from above) to show the complete periphery of each tube. The reference position at zero ("O degree", corresponding to the indicated arrow stamped on the tube at the time it was removed from the tube bank) represents the top, or 12:00 o'clock, position of the horizontally-oriented tubes in the combustor. The bottom, or 6:00 o'clock, position corresponding to the usual site of greatest metal loss is indicated in the photos as 180 degrees of rotation from the zero (or arrow location) position. Tubes 2C7, 8C1, and 13T7 had shallow machined surface grooves in a helical configuration around the periphery and along the length of the tube. These were reportedly for the purpose of visually monitoring extent of metal loss during combustor operation.

Two of the sample tubes submitted, No. 11S5 and No. 12T8, had closely-packed studs attached to the external tubing wall, between longitudinally-oriented flow-disrupter fins, in the quadrant of the tube periphery that was positioned downward in the combustor (corresponding to the region where metal loss usually is greatest). The studs almost entirely obscure the fireside surface of the tubing in the region of principal interest and restrict access by analytical instruments, preventing meaningful comparisons with the other tube samples (see Figures 5 and 6). Therefore, these two tube samples had to be excluded from most of the examinations described in this report.

Accordingly, for the most part, this study was confined to the four tubing samples identified as: (a) 2C7, (b) 8C1, (c) 9C5, and (d) 13T7. All but one, 13T7, were of the same grade of medium-carbon steel, SA-210, Grade C (6); with 13T7 being of SA-213 (T-22), a 2-1/4 % Cr - 1% Mo steel, with carbon steel fins.

6.2 Examination Methods

6.2.1 Visual Inspection. Before other inspection procedures were begun, as-received appearance of the six samples was documented photographically using both black and white and color film (the black and white photos are shown in Figures 2 through 7, a set of color prints are available upon request from LLNL). Transverse cross-sections were also made and ground to a smooth finish to reveal tubing profiles. Figure 8 shows the four non-studded samples (zero, or arrow, location is at the top of all these full-scale photos). External (fireside) surfaces were examined visually using a stereoscopic microscope at magnifications up to about 20x to observe general surface features, textures, coloration, presence and appearance of scales, and overall condition.

Although metal loss data and dimensions of the tubes at the time of installation in the combustor were not provided with the tube samples, attempts were made to estimate extent of tube wastage through measurements of as-received tubes. These are, of course, subject to error because of scale buildup (tending to increase wall thickness) and overall surface roughness. However, two types of measurements were made to obtain an approximation of the extent of tubing wastage. One method was to measure wall thickness at two locations 180 degrees apart; the other was to measure outside diameter of the tubing at two locations 90 degrees apart.

One wall thickness measurement made on each tube was at the topside, corresponding to the "arrow" location, and the other at the bottom side, or 180 degrees around the tube periphery from the first measurement. These were made using a vernier caliper with knife-edged, parallel measuring surfaces permitting accurate measurements on the cylindrical tubes, and were made on tubing segments that had cutting burrs removed but with surface scales intact on both fireside and waterside tube surfaces. Accordingly, the wall thickness measurements included the thickness of any surface scale that was present on the as-received tubing samples.

Outside diameter measurements were made at two locations: (a) from 12:00 o'clock to 6:00 o'clock locations, and (b) from the 3:00 o'clock to 9:00 o'clock locations. This provided two outside diameter measurements, one in the direction of the usually dominant wastage (from about 5:00 to 7:00 o'clock region) and the other where wastage has not generally been severe. For finned tubes, these measurement locations are the only ones not covered by fins or fillet welds.

Extent of metal loss was estimated by calculating differences between the sets of measurements. The differences were considered to be metal loss that occurred during the 1,300 hour operational period. The values were normalized to metal loss per thousand hours of operating exposure by multiplying the actual numerical differences by 0.77 (1,000/1,300).

It is recognized that the resulting values (considered to be "metal loss") are subject to error due to inclusion of scale thickness and buildup of surface deposits in the measurements. Regions not subject to wastage or the eroding effects of bed material would be expected to have wall thicknesses greater than that of the tubing wall at the start of the combustor run before any scale had formed on the tube. Similarly, in areas of the tube subject to wastage or scale loss due to impacting bed material, measured wall thickness would be less, merely because scale thickness was not included in the measurement.

However, because three of the tubes were of the same alloy (medium carbon steel) and all were in the same combustor and, presumably, subject to the same conditions affecting scale formation; wall thickness measurements and corresponding metal loss calculations made as described above were believed to offer a reasonable basis for comparing wastage response among tubes in a given combustor.

Scanning electron microscopy (SEM) was used to characterize and compare surface features on both a macro and micro scale, corresponding generally to: (a) those regions where maximum metal loss would be expected to occur (undersides, from about 5:00 o'clock to 7:00 o'clock location as oriented in the combustor), and (b) those of minimal metal loss (from about 10:00 o'clock to 2:00 o'clock locations). Metallographically mounted and polished cross-sections were also examined using SEM techniques to observe scale morphology and thickness, scale-interface features, extent of any preferential attack, and microstructural characteristics.

The specimens were prepared using the same techniques as previously reported (7). These included precautions to avoid contamination of sample surfaces with cutting fluids and polishing media, and polishing of cross sections without water to avoid the possibility of leaching water-soluble species. Special preparation techniques, described in the previously-cited report, were required to preserve the integrity of the friable surface scales. Mounted and polished cross sections, where SEM examinations of scales and scale interfaces were desired, were pre-sputter-coated with a thin conductive layer of either carbon or a gold-palladium alloy.

6.2.2 Chemical Analysis. These determinations were, generally, of two types: Surface analyses to identify chemical compositions of scales were conducted within the SEM using energy-dispersive spectroscopy (EDS) instrumentation. Also, chemical analyses were run on the tubing steels using standard methods to determine their compositions. These were run on clean samples cut from the tubes and after waterside and fireside surfaces had been dry-machined to a depth sufficient to remove all traces of scale, coatings, and weld deposits (from fin attachment).

6.2.3 Hot-Hardness Testing. Determinations of indentation hardness at elevated temperatures were conducted on tubing specimens that had been prepared similarly to those used in determining all-metal (surface-deposit-free) chemical compositions. The tests were carried out on 1/2 inch long peripheral segments cut from 3/8 inch wide transverse slices from the as-received tubing samples that had first been machined clean of all traces of surface scales, deposits, and weld metal. Before hardness testing, these segments were surface-ground to obtain flat uniform samples with parallel surfaces to facilitate obtaining accurate hardness indentations.

After cleaning the tubing specimens, they were hardness tested (Rockwell B scale) at room temperature, and duplicates (separate specimens) were tested at elevated temperatures at intervals of 100 degrees F (56 C) from 400 degrees F (204 C) through 800 degrees F (427 C) and at 840 degrees F (450 C). The specimens were heated in the testing apparatus to the desired test temperature and held for thermal equalization purposes at least 5 minutes at that temperature before testing. Protective argon atmosphere was circulated throughout the test chamber during all elevated temperature hardness tests. Hardness determinations were made on one specimen of each tube sample at each temperature, with at least 5 indentations for each set of conditions.

6.2.4 Oxidation Tests. Specimens from each tubing sample were also subjected to laboratory oxidation tests to observe if differences in microstructure or chemical composition of the tubing samples would affect oxidation behavior (scale and growth kinetics) at elevated temperature. Machined tubing segments free of scale and other contaminants were placed in individual porcelain boats and heated in still air to 450 C (840 F) in a laboratory electric oven and held at that temperature for 100 hours. After furnace-cooling to room temperature, cross-sections were prepared for examination by optical metallography and SEM.

7.0 RESULTS

7.1 Surface Characterization

7.1.1 Visual Observations. With minor exceptions, most tubes had the same coloration and hue, which varied somewhat around the periphery of the tube from the purplish-black color characteristic of magnetite (Fe_3O_4), a product of high temperature oxidation of iron, to various shades of reddish-tan, characteristic of FBC residues. In general, upper, or "protected," areas of the tubes had reddish-tan deposits while those subject to abrasion by bed material had darker coloration characteristic of Fe_3O_4 or iron sulfide (FeS). Tips of fins and surfaces of studs more often had lighter-colored reddish-tan deposits, possibly as a result of higher temperatures that would be expected at these locations because of their remoteness from the water-cooled tube wall.

Tubes of this group of samples from Grimethorpe Tube Bank "E" exhibited a surface feature not observed in previous samples, and that was a polished or glazed surface on some tubes and some regions of tubes. This was most apparent on tube sample No. 8C1 (see Figure 3), but also was observed on tube sample No. 13T7 and, to some extent, on tube sample No. 2C7. The region of most prominent glazing was along the undersides of tube samples Nos. 8C1 and 13T7. Tube 2C7 had a higher luster at the top side and somewhat along the sides, but it was not a polished and glazed surface.

The most highly glazed scale on tube sample 8C1 was quite friable, thin, and readily flaked off the tube surface (see Figure 3). This was not evident on the glazed underside surface of tube sample No. 13T7, as surface deposits on this tube appeared to be adherent, with no signs of flaking off; however, it was not as highly glazed and had a slightly different color and could have had minor microstructural differences.

Of all tubes submitted for examination within this group, only tube sample No. 2C7 had a surface whose texture resembled that of wasted surfaces examined in previous studies, and this surface was at the underside of this finned tube. See Figure 2 (180 degree location).

As noted in Table 1, three of the tubes submitted for study had been grooved in a helical pattern around their peripheries. These grooves are clearly evident in some photos of the as-received tubes (Figures 2 and 3) but they are probably not discernible in Figure 7 although they were distinguishable in some regions of the actual tube of Figure 7 (13T7) during visual examination.

These grooves provide a readily available reference for determining if the surface suffered wastage during its life in the combustor. This is clearly demonstrated in tube sample No. 2C7 (Figure 2) where the reference grooves are clearly evident in one region (0 degree location) and missing altogether in another (180 degree location). They were clearly visible around the entire periphery of tubing sample 8C1. On sample 13T7 they were most distinguishable on the more highly polished underside but were also distinguishable on the two sides. However, apparently because of adherent scalar deposits at the topside, they were obliterated from view. The topside surface of sample 13T7 was much duller and rougher than the other surfaces and those of the other two tubes (8C1 and 2C7), and appeared to be comprised of adherent and agglomerated particulates that had not been subject to the same scouring or abrading action of bed material as the other tubes.

The tube that had the chromized surface, sample No. 9C5, had a surface appearance that differed from all the others, except along the topside where its coloration and, to some extent, texture resembled some of the others. For the most part, the chromized tube had a dull, metallic, silvery color and a fairly rough texture (in comparison to surfaces of samples 8C1 and 2C7, and most surfaces of 13T7).

The two studded tubes, 11S5 and 12T8, had slightly different surface appearance and coloration from one to the other, possibly a reflection of their different compositions. The 11S5 tube was Type 347H steel, 12T8 was 2-1/4% Cr - 1% Mo steel, with fins on 11S5 of the same alloy as the tube but of carbon steel on 12T8; studs on both were of the same alloy, a ferritic stainless steel.

Tube 11S5 had a reddish-orange-colored adherent deposit along the sides and covering most fin surfaces, but of a darker and more purplish shade at the topside. The surfaces of the steels appeared lighter in color than the sides of the tube and the deposits on the studs appeared powdery or finely mottled. In some locations where the tube had been contacted with other objects, the reddish-brown deposits appear to have been chipped off, revealing a dark-colored underlayer that resembled Fe_3O_4.

The other studded tube, 12T8, had fins of about the same color as that of 11S5, but regions between the fins were mostly purplish-black, resembling Fe_3O_4. Surfaces of the studs had the same appearance as those of sample 11S5.

Results of wall thickness and outside diameter measurements are listed in Table 2. In reviewing these results, it is worth noting that, of the four tube samples shown, tube 13T7 had a thicker wall to start with. The tabulation shows that indicated metal loss (that is, a measured difference in wall thickness of as-received tubes) occurred in all tubes, although the chromized tube showed very little difference in wall thickness measurements. Greatest "metal loss" based upon wall thickness measurements occurred in samples 2C7 (finned, carbon steel tube) and 13T7 (finned, 2-1/4% Cr - 1% Mo steel tube). Indicated metal loss of the unfinned carbon steel tube 8C1 was substantially less than that of the two finned samples. In all cases, the thinner wall was at the underside, as observed in previously-examined FBC tube samples.

For some tubes, indicated metal loss calculated from outside diameter measurements was different from that derived from wall thickness measurements. Although values for the two methods were nearly the same for tube 8C1, the finned tubes differed more, with a major difference noted in tube 13T7. Possibly, this is a reflection of the thicker granular deposit at the topside of this tube that would indicate a thicker-than-actual tube wall in the wall thickness measurement (resulting in higher values for indicated metal loss) and a larger-than-actual outside diameter (resulting in smaller differences in outside diameter measurements, suggesting less-than-actual metal loss).

Since this was the only tube of the group having the thicker starting wall (roughly 9 mm thick), there are no others to serve as a basis for comparison. Tubes 2C7 and 8C1 were both of the same type of steel and both had nearly identical wall thickness measurements at the topside, even though their surface scales differed in appearance, suggesting that the metal loss values for these two are probably in the proper order and represent a correct relative indication.

The tube having a chromized surface, 9C5, had nearly identical tube wall thickness measurements from top to bottom, although thicker than samples 2C7 and 8C1, probably due to thickness of the chromizing layer. The larger dimension for the vertically-oriented outside diameter for this tube probably is a reflection of non-uniformity in original thickness of the chromizing layer and not indicative of metal wastage along the sides of the tube.

7.1.2 Micromorphology. Scales and/or deposits were observed in SEM examinations on all fireside surfaces of all tubes, with the possible exception of sample 9C5 (having the chromized surface); although even that sample had a scale or deposit within crevices between protruding chromium irregularities in the surface layer. Typical appearance of surfaces in both wastage-susceptible (generally 5:00 o'clock to 7:00 o'clock location) and non-wastage-susceptible regions (generally 11:00 o'clock to 1:00 o'clock location) is shown in Figures 9 through 12, all photographed at the same magnification (200x).

As noted earlier, fireside surfaces of these tube samples had a more glazed or polished-appearing texture, in contrast to those of previous series of examinations conducted under this program. This was visually evident in the as-received tubes and persists at higher magnifications, as well. This is apparent in Figures 9 through 12 in the overall lack of textural detail in most surfaces.

Sample 2C7 (Figure 9) was the only tube sample of the group having a surface that outwardly resembled the coloration and texture of wasted surfaces in previously-examined samples. From tube wall measurements described earlier, it is evident that the lower surface (underside, as the horizontally-oriented tubes were positioned in the combustor) did experience metal loss or wastage. As noted in previous studies, the wasted surface is not typical of that produced by erosion alone, as a scale or deposit is present on the affected surface, as shown in Figure 9 (wastage-susceptible region). The upper surface of the same tube, however, was smoother with a glazed or finely burnished appearance.

In tube sample 8C1 (Figure 10), textures of the two regions were reversed from that of sample 2C7. At high magnifications, the upper (or non-wastage-susceptible) region had a rougher-appearing texture than the lower (or wastage-susceptible) region. In fact, the surface debris or deposit on the lower portion of tube 2C7 had generally the same appearance as that on the upper portion of tube 8C1. As shown in Figure 3, the lower portion of tube 8C1 had a highly polished, or smoothly glazed, surface; although this was on a very thin (approximately 1 to 2 mils thick), friable, black, slightly magnetic, layer of what appeared to be high-temperature oxide or sulfide scale (probably composed of Fe_3O_4 and FeS). Figure 10 (wastage-susceptible region) shows a location where the smoothly glazed deposit (darker appearance) had flaked off revealing the substrate or a substrate deposit (lighter appearing area).

In SEM examinations, the surface appearance of finned tube 13T7 more nearly resembled the unfinned 8C1 tube in that the non-wastage-susceptible region had a rougher texture than the wastage-susceptible underside. But, while the underside of 13T7 visually appeared shiny and glazed, higher magnifications in the SEM showed it to be not as smooth and featureless as the underside surface of tube 8C1.

The surface of the unfinned chromized tube 9C5 revealed a roughly-pebbled texture with adherent debris in-between. The higher protrusions - particularly at the underside - appeared burnished, shiny, and smooth.

7.1.3 Chemical Analyses. During SEM examinations of fireside surfaces of the as-received tubing samples, determinations of chemical compositions of the regions examined were made using EDS instrumentation on the SEM. Elemental detectability of this analytical method is limited to cations and elements generally heavier than aluminum. Therefore, analytical results do not include such elements as carbon and oxygen, two principal and probable constituents of these surface scales. To assure sufficient averaging over a reasonably representative surface area, the EDS determinations were made in the SEM at magnifications of 50x (or at about one-fourth that of Figures 9 through 12).

Analytical determinations were made on both non-wastage-susceptible and wastage-susceptible regions of each of the four tube samples. The analytical spectra obtained are shown in Figures 13 through 16. Each figure contains spectra for both non-wastage-susceptible and wastage-susceptible regions.

For all samples, concentrations of all elements (other than iron) were greater in the non-wastage-susceptible regions. Also, in some samples, more such elements were detected in those same regions. With a few exceptions, the same elements were found on all samples, although their concentrations differed somewhat from sample to sample. The detectable elements identified were: aluminum, silicon, sulfur, chlorine, potassium, calcium, titanium, chromium, manganese, and iron.

The low elemental concentrations in the wastage-susceptible region of the surface deposit on the finned carbon steel tube 2C7 probably are due to the relatively thin scale in this region (see Figure 13). This is believed to be a result of scale loss from abrasion by bed material for, as noted earlier, this surface was the only one of this series of samples that had a typically wasted appearance.

Similarly, while the non-wastage-susceptible region of this tube had higher elemental concentrations than the wastage-susceptible region, it was relatively low in elemental concentrations. Again, the surface scale in this region was very thin, although apparently not the result of wastage processes, but probably related to temperature and chemical activity in the region of the combustor where this tube was located (see surface appearance in Figure 2, zero degree location). This non-wasted region of the tube had detectable levels of potassium and calcium, not detected on the wasted surface, in addition to aluminum, silicon, sulfur, manganese, and iron, which were detected on both wasted and non-wasted surfaces. A low concentration of chlorine was present on the wasted surface although it was not detected on the non-wasted surface.

On carbon steel tube sample 8C1 (non-finned tube), elemental concentrations, once more, were higher in the non-wastage-susceptible region (tube topside) than at the wastage-susceptible underside (see Figure 14); however, concentrations at the topside were much higher than in the corresponding region of tube sample 2C7, described previously. This is probably due to the heavier surface deposit at the topside region of tube 8C1 (see Figure 3).

The wastage-susceptible bottom-side of this tube had detectable concentrations of aluminum, silicon, sulfur, manganese, iron, potassium and calcium - the same elements and in about the same concentrations as were observed at the <u>topside</u> of finned carbon steel tube 2C7, previously described. However, at the protected topside of tube 8C1, there were considerably higher concentrations of these same elements and, in addition to these, there also were detectable levels of phosphorus, chlorine, titanium, and chromium. Because of the thinness and friability of the glossy layer of scale on the underside of sample 8C1, most of it had flaked off the sample being examined in the SEM; but EDS analyses of remaining fragments revealed a chemical composition similar to that of the immediate substrate shown for the wastage-susceptible region of Figure 14. The major differences between the two layers were in the somewhat higher concentrations in the outer scale of aluminum, silicon, sulfur, potassium and calcium, and a trace amount of titanium; otherwise, the two were very similar.

Although surfaces of tube sample 9C5 were predominantly of chromium (as it had a chromized surface), the same general trend of higher elemental concentrations at the protected topside persisted in this sample, as well. As shown in Figure 15, EDS spectra for both regions are similar, except for higher concentrations at the protected topside. As in sample 2C7, a trace of chlorine was detected in the wastage-susceptible region but not in the other.

In tube sample 13T7 (a 2-1/4% Cr-1% Mo steel finned tube) too, the scale on the protected topside was higher in concentrations of the various elements characteristic of the FBC environment (see Figure 16). Presence of chromium in the fireside scale of this tube is, no doubt, traceable to the 2-1/4% chromium content of the tube steel itself. The significantly higher calcium level at the topside is probably due to pebbly deposits of combustor residues observed in this region of the sample.

Similarity in chemical composition of scales on these tube samples is not unexpected, as they saw the same exposure in the same combustor at the same time, although in different locations. Also, the observation of higher elemental concentrations at the protected topsides is understandable as it is less subject to impingement of bed material and its spalling and abrasive effects on the surface scale. Absence of these conditions would produce thicker scale and, in turn, higher indicated elemental concentrations.

A few observed anomalies are worth noting: One is detection of chromium in the topside scale of tube sample 8C1 (a carbon steel tube), and at about the level that was detected in the Cr-Mo steel tube sample 13T7. The other was detection of chlorine in the wastage-susceptible (underside) region of two of the samples, 2C7 and 9C5, that was not observed in the usually more heavily concentrated topsides.

7.2 Cross-Section Examinations

7.2.1 Scale and Interface Characterization. With few exceptions, continuous scales were observed on all fireside tube surfaces. The scales were sometimes layered and/or textured and frequently cracked or broken away from the tube substrate. The portion of the scale nearest the tube usually was dense and had a slate-gray appearance resembling magnetite (Fe_3O_4). The thinner outer layers often were more porous and reddish-brown in color, resembling hematite (Fe_2O_3), although there were variations in scale texture, density, and color, from tube to tube and from one location of the tube to another - probably reflecting localized bed compositional variations. As observed in surface examinations, scales were thicker at the protected topside than at the bottom-side, which is subject to upward impingement of bed particulates. The outer surfaces of most tubes were relatively smooth; this was apparent visually and in the SEM examinations previously described.

Tubes examined in other studies conducted under this program sometimes had evidence of mechanical deformation of the metal substrate in wastage-susceptible regions, and particularly those experiencing the most severe wastage. This condition was not observed in any of these tube samples, despite careful high-magnification examinations of cross-sections of susceptible surfaces. In fact, only one tube, 2C7, had a surface that outwardly resembled wasted regions of tubes of previous studies, and no metal deformation was observed in this region.

Figure 17 shows optical photomicrographs of cross-sections of two regions of tube sample No. 2C7 at the same magnification. Both are tube surfaces between fins and fin welds and represent the wastage-susceptible underside and the non-wastage-susceptible topside, respectively. It is apparent that the wastage-susceptible underside has much less scale than the protected topside. Examinations at higher magnification revealed a fairly continuous scale at the wastage-susceptible underside, although shrinkage of the plastic mounting medium used to encapsulate the cross-section during metallographic preparation had separated the scale from the substrate in most regions. As noted above, no metal deformation was observed along the wastage-susceptible underside, although this region of this tube sample was the only one of the four samples examined that was typical of wasted surfaces of FBC tubes studied previously.

Cross-sections of tubing sample No. 8C1 showed differences in surface scale from one region to another, as shown in Figure 18. The scales had about the same thickness although, at the topside, it was more prominently layered and appeared denser than at the bottom-side, which had a more granular appearance. Layers of the topside scale had a tendency to delaminate.

Tube sample No. 9C5 had the chromized surface and this introduced a number of peculiarities that were unique to that sample. These are best observed at lower magnifications (see Figure 19-A). The chromium outer layer closely follows irregularities in the metal substrate that existed before chromizing (and before FBC exposure). There is a decarburized zone about two grains wide along the outer periphery of the substrate. But, immediately beneath the chromium layer, and sandwiched between the chromium layer and the decarburized zone, is a continuous band of what appears to be carbide. This apparently originated from the steel substrate (the decarburized zone) and diffused outward - because of affinity of carbon for chromium - toward the chromium layer during exposure to elevated temperatures in the FBC. It is likely that at least some of this layer is chromium carbide. It is not known whether the carbon migration occurred during the chromizing treatment or during FBC exposure, but it probably was the latter in view of the prolonged period of exposure at an elevated temperature well within the range where this reaction is known to occur.

As shown in Figure 19-B, there is little difference in appearance of tubing cross-sections of the two fireside surface regions of this tube sample (9C5). There are fine granular deposits within depressions and crevices on both surfaces, with somewhat thicker deposits at the protected topside.

Figure 20 shows the appearance of surface scales at the two regions of interest for tube sample No. 13T7. The lighter cast in the photomicrograph showing the wastage-susceptible region is due to the presence of a very thin sputter-coated conductive metallic layer that was deliberately deposited upon the metallographically-prepared sample to facilitate SEM examination. Scale in both regions is similar in thickness and texture, and is considerably thicker than in other samples.

This may be a result of the fact that the 13T7 tube is of 2-1/4% Cr-1% Mo steel, whereas the other three tubes are of essentially unalloyed medium-carbon steel. It might be expected, however, that in the same environment the carbon steel tubes would form a thicker scale than the low-alloy steel. It is possible that it does but that adhesion of carbon steel scale to the substrate, or its cohesive strength, may be inferior to those of alloy steel scale. It is also apparent that the fireside surface of scale at the underside is very flat and uniform, while that at the protected topside is more irregular.

<u>7.2.2 Microstructure</u>. Microstructures of polished and etched cross-sections of the four tubing samples are shown in Figures 21 through 24. The same magnification was used for all to assist in making comparisons. Although the three tubing samples of Figures 21 through 23 were of the same steel type and chemical compositions, their microstructures have considerably different appearance, indicating different thermomechanical history.

While the grain size of tubing samples 2C7 and 8C1 is similar, the pearlite is arranged in segregated bands in 2C7 but appears to be more uniformly distributed in 8C1. Pearlite lamellae in 2C7 are fairly distinct, whereas most have become spheroidized in 8C1. However, closer examination over a range of magnifications suggests that the microstructures of 8C1 and 2C7 may previously have been the same, but subsequent thermomechanical processing resulted in disintegration, in sample 8C1, of the pronounced pearlite lamellae and eventual spheroidization.

In tube sample No. 9C5, grain size is much larger and the pearlite lamellae are partially spheroidized. In tube sample No. 13T7, a low-alloy steel, the pearlite has become substantially decomposed and is nearly completely spheroidized. The level of non-metallic inclusions in the four tubing samples is generally the same.

7.3 Chemical Compositions of Tubing Steel

Table 3 shows results of chemical analysis conducted on the four tubing samples. From the values obtained, it appears almost certain that the three carbon steels of tube samples No. 2C7, 8C1, and 9C5 originated from the same heat of steel. Nevertheless, from the microstructures shown and described earlier, it is apparent that the various tubes saw different thermomechanical processing conditions along the way, possibly while being prepared for and during combustor service. Duplicate samples of 2C7 and 8C1 were re-analyzed several months apart under different identifying numbers and, as shown, the recheck confirmed that the tubes have nearly identical chemical compositions.

7.4 Hot-Hardness Survey

Average indentation hardness values obtained for three of the tube samples (2C7, 8C1, and 13T7) are plotted in Figure 25. These three tube samples were selected for hardness determinations because meaningful wastage data were available for these samples. Tube 9C5 was not included because it had a chromized surface which influenced wastage behavior and, therefore, would interfere with attempts to correlate combustor response with metallurgical characteristics of the steel substrate.

As shown in Figure 25, there is a difference in hardness between the two carbon steels 2C7 and 8C1, despite their nearly identical chemical compositions. Steel from tubing sample 2C7 had consistently higher hardness than 8C1 over the entire temperature range evaluated, and its response over the test temperature range had a somewhat different profile with peaks at intermediate temperatures; while 8C1 progressively decreased in hardness with increasing temperature. The differences in hardness for tubing sample 13T7 are not necessarily significant as it is not a carbon steel but a Cr-Mo alloy grade.

7.5 Laboratory Oxidation Tests

This type of test was first conducted in this program for the series of tubing samples from the TVA 20 megawatt AFBC pilot plant (8). Its purpose was to determine if observed compositional and microstructural differences between the two steels of principal interest in that study would affect oxidation response in a simple atmosphere of still air in contrast to scale formation and its subsequent wastage occurring within the complex FBC environment.

If so, it would assist in understanding how differences in those steels may have influenced their combustor response; for they did differ in wastage behavior within the combustor, although in two different tube banks and different combustor runs at different times. It was believed that if differences in scale formation were observed in simple laboratory tests, then it may be possible to more readily identify the controlling parameters because of the fewer environmental variables involved. And, if laboratory tests were found to provide reliable indications of FBC scale-forming behavior as a function of tubing composition and microstructure, such tests would provide an effective means for evaluating these differences without the need for screening tests in an operating FBC.

Of course, in the previous study of TVA tube samples, a number of differences in both chemical composition and microstructure, were identified between the tubing steels, as well as in their wastage response. In tubes of the present study, however, it has already been established that the carbon steels used in three of the four samples probably were from the same heat of steel. Although their chemical compositions are essentially identical, some differences in microstructure have been noted.

Despite the similarity in the three steels, it seemed useful to conduct laboratory oxidation experiments, as before, in an attempt to determine whether their microstructural differences affected scale forming characteristics and correlated with their FBC wastage response. As described earlier, their difference in wastage behavior (0.3 mm/1,000 hours for tube 2C7 vs. 0.1 mm/1,000 hours for tube 8C1) was not as dramatic as experienced by the two steels in the TVA 20 megawatt AFBC pilot plant tube banks (0.3 mm/1,000 hours vs. 0.03 mm/1,000 hours; see Reference 3, Table 1).

As shown in Figures 26 through 29 for steel from the four tubing samples, thickness of scale that formed at 450 C in still air in the laboratory was virtually the same for the three carbon steels having the same composition (samples No. 2C7, 8C1, and 9C5). Scale that formed on steel from tube sample 13T7 (2-1/4% Cr-1% Mo steel) was considerably thinner (Figure 29).

8.0 DISCUSSION

Results of these examinations of FBC evaporator tubes submitted for LLNL study suggest that bed conditions associated with Tube Bank "E" had been less aggressive than for previous experiments in the Grimethorpe PFBC. Surface appearance and textures of these tubes indicate a more gentle abrading action of the bed, at least in some regions, that tended to polish and glaze the protective oxide scales instead of exfoliating it. This appearance may indicate a different fluidization mode, differences in size, mass or hardness of bed particulates, or differences in fluidizing velocity, bubble formation or streaming tendencies. Absence in these samples of the surface deformation observed in some of the previously-examined samples is an additional indication of less aggressive bed conditions.

These observations tend to confirm the conclusion of an earlier LLNL report that, in the absence of intervening mechanical forces that cause localized loss of protective oxide scale, in-bed evaporator tubes should have long life in these environments (9). One of the tubes with the best response, sample No. 8C1, was a plain carbon steel tube, without fins or other surface modification to afford wastage resistance, and this sample had the most highly glazed surface at the wastage-susceptible underside of all the tubes examined - indicating that the scale will remain intact and the tube unwasted if mechanical forces are insufficient to cause the scale to exfoliate. This tube had been located at the bottom row of the combustor, near its center, and this may have had some effect on its response.

The tube with the chromized surface (sample No. 9C5) had essentially no discernible wastage and appeared to be unaffected by its exposure in the combustor. However, such a relatively brief exposure as 1,300 hours may not be sufficient to establish long-term survivability of a protective coating in these environments.

Despite indications of generally less aggressive conditions for this set of tubing samples, there was evidence of significant wastage in some samples, particularly along the underside of tubing sample No. 2C7, and this was a *finned* carbon steel tube from Row 7, near the top of the bed and not far from a wall. Estimated wastage rate from tube wall measurements of this sample was about 0.3 mm per 1,000 hours of FBC exposure. This roughly compares with the wastage rate experienced in the second tube bank of the TVA 20 megawatt AFBC pilot plant, which was considered excessive (10).

Tubing sample 13T7, a Cr-Mo steel tube that also was finned and located in the same row as tube No. 2C7, next to the opposite wall of the combustor, also experienced wastage according to tube wall measurements made on the as-received sample. However, surface appearance of the wastage-susceptible region more closely resembled the underside of 8C1 and not that of 2C7, in that it appeared to have been abraded to a glossy surface condition although not so highly polished as the underside of 8C1.

Nothing was uncovered in the study of this group of tubing samples that cast doubt on validity of the previously-proposed tube wastage mechanism. That is, that wastage of in-bed FBC carbon steel evaporator tubes occurs predominantly through exfoliation of the normally-protective oxide scale, probably by impacting bed materials. All indications in this study tend to support this hypothesis.

In regions not directly exposed to upward impingement of bed particulates, scales appear thick and protective. At exposed undersides, where wastage has occurred, scales are thinner and the interface more irregular. Scale at the undersides of wastage-resistant tubes is glazed, apparently from abrasion or scouring by relatively soft bed material. And, as observed in previous studies, wastage of in-bed evaporator tubes in FBCs does not appear to be caused or aggravated by chemical effects such as sulfidation or grain boundary attack.

Although three of the four tubes examined in the present study had the same chemical composition and appeared to have come from the same heat of steel, some microstructural differences were observed, and it is useful to consider what effects, if any, such variables may have had on wastage response of these tubes. In the following discussions on this aspect, it is important to review and understand the findings of previous studies (11) as they are relevant here, and technical discussions of these effects will not be repeated here.

In the previous study of TVA samples, it was observed that the steel experiencing lowest wastage rate in the FBC was metallurgically different from that experiencing significant wastage. There were differences in both chemical composition and in microstructure. In chemical composition, the steel of the wastage-resistant tube had residual trace amounts of aluminum (0.06%), chromium (0.12%), nickel (.05%), and molybdenum (0.03%), among others; while levels of these residuals in the steel of the wastage-susceptible tube were virtually nil, although the steels had essentially the same carbon contents.

Indications are that the steel used for tube samples 2C7, 8C1, and 9C5 of the present study came from the same mill heat. When its composition is compared to those of tubing steels of the previous study, we find it to more closely resemble that of the wastage-*susceptible* steel (of the TVA tubing study) - with one exception, and that is in chromium content. The chromium residual of the three steels of this study was 0.09%, not much below the 0.12% of the wastage-resistant TVA steel tube. Otherwise the three steels are about the same in residual content as the wastage-susceptible TVA steel (principally in aluminum, nickel, and molybdenum).

The key to the effectiveness of a chromium residual in producing surface characteristics that resist FBC wastage is believed related to whether the steel had been thoroughly deoxidized during the steelmaking process. Aluminum deoxidation is viewed as important, and probably critically so, in producing a wastage-resistant tubing steel. In the three steels of this study, residual aluminum was very low (more than an order of magnitude lower than the wastage-resistant tube from TVA). It is thought that aluminum deoxidation is essential in providing a metallurgically-neutral or inert microstructural matrix (low oxidation potential) for obtaining optimal response from other micro-alloying residuals such as chromium, nickel and molybdenum. Without a co-present aluminum residual the effects of these other residuals in modifying the scale-forming properties of the steel are believed to be very substantially reduced. This is evident in tube sample No. 13T7, a Cr-Mo alloy steel, but without evidence of having had aluminum deoxidation. That tube experienced wastage despite its flow-breaker fins and alloy content.

In the previous study of tubing samples from TVA, there also were microstructural differences between wastage-resistant and wastage-susceptible steels. That is, the wastage-resistant steel had a more homogeneous microstructure, while there was pearlite banding in the wastage-susceptible steel. Also, there were fewer non-metallic inclusions in the wastage-susceptible steel, believed to be a reflection of the steelmaking process used.

Although inclusion levels of the three steels of the present study were nearly identical, as would be expected of material derived from the same heat, they were lower than that of the wastage-resistant TVA tubing steel. And the tubing sample of the present study that experienced the most wastage (No. 2C7) had a banded microstructure (see Figure 21), as did the wastage-susceptible steel in the TVA study. The microstructure of the wastage-resistant steel of this study (No. 8C1) more nearly resembled that of the wastage-resistant steel of the TVA study. That is, it was not banded but was homogeneous and the pearlite was partially spheroidized.

In indentation hardness tests at elevated temperatures, there is good correlation with previous observations; expressed in simple terms - wastage-resistant steels are softer at elevated temperatures. As shown in Figure 25, wastage-resistant steel from tubing sample 8C1 had lower hardness - from room temperature and over the entire testing range - than the other two samples of material that experienced higher rates of wastage. This same trend was also observed in the previous study of TVA samples.

It is also of interest to note that the elevated temperature hardness profile of sample 8C1 somewhat resembled that of the wastage-susceptible TVA steel, particularly at higher temperatures. However, the wastage-resistant TVA steel was even softer than sample 8C1 of this study. These indications do not refute earlier conclusions but are believed to be merely reflections of differing response to differing FBC conditions. It must be recalled that there was a marked difference in aluminum residuals in samples 8C1 and the wastage-resistant TVA steel.

The laboratory oxidation tests carried out in still air developed practically identical scales on the three steels of essentially identical composition, but thinner scale on the Cr-Mo steel. Scale thickness in the laboratory tests did not correlate, however, with that observed on actual tubes exposed to FBC conditions. But it is apparent that compositions and morphology of scales formed in the combustor are different from those formed in still air in the laboratory. In laboratory tests there were no products of combustion, and no coal or sorbent in the test environment and no physical contact of bed material or any other substance with the surface of the metal sample.

It was observed that scale formed in the combustor on low-alloy steel tube sample 13T7 was thicker than that formed on the carbon steels (see Figures 17, 18 and 20). Besides, the scale had different texture and appearance. It is possible that these differences are traceable to the steel's alloy content (chromium and molybdenum) in producing a more adherent or coherent scale than formed on plain carbon steel, accounting, therefore, for its greater thickness. Growth rate, also, may be involved; but probably is not a dominant factor in explaining the greater thickness of scale on sample No. 13T7. Steel from this tubing sample had the thinnest scale after a 100-hour exposure in still air at 450 C in the laboratory.

From results of examinations of evaporator tubing samples in this study, it appears that microstructural differences in tubing steels of the same chemical composition can influence FBC wastage response. As observed in the previous study of TVA tube samples, a wastage-susceptible tube had a banded microstructure and higher indentation hardness at elevated temperatures; whereas wastage-resistant steel had a more homogeneous microstructure and lower indentation hardness at elevated temperature. The microstructural differences observed in this study in different steel tubes of identical chemical composition are, no doubt, a reflection of thermomechanical processing differences and, perhaps, differences in thermal history within the FBC.

It is of interest to note that at least some aspects of the microstructural effect upon scaling behavior appear to be confined to FBC environments, as the same steels (viz. 2C7 and 8C1, having different wastage response in the combustor) developed scales of virtually identical thickness and morphology in still air in the laboratory at 450 C. Scales formed in the FBC will, obviously, not be pure oxides of iron but will also contain sulfur, silicon, aluminum, calcium and other elements characteristic of the FBC environment. Scales formed in air in the laboratory will not be subject to these extraneous impurities or to the impacting and abrasion of foreign particulates.

At this stage of our understanding of the FBC wastage process, it is not known if growth rate is the dominant scaling factor, or whether physical or chemical properties of the scale itself, or its adhesive or cohesive qualities in resisting the exfoliating effects of impingement of bed particulates, are governing. In any event, it appears that steels of identical chemical composition but of varying microstructure form virtually-identical-appearing scales in still air; yet, experience differing wastage response under FBC conditions.

Chemical composition of the steel substrate does, however, have an effect upon scale growth rate in laboratory oxidation tests in still air at elevated temperatures, as the scale on the Cr-Mo steel sample was markedly thinner than that on the unalloyed carbon steel samples exposed to the same test environment for the same time. Nevertheless, the finned-tube sample of this steel (13T7) was not as wastage-resistant as an unfinned carbon steel tube sample (8C1), suggesting that lower scale growth rate in still air, per se, is not a reliable indicator of probable behavior in FBC environments.

It is worth noting in this regard that, despite the alloy content of sample 13T7, its scale/substrate interface did not resemble that of the wastage-resistant steel of the TVA study, where a zone of apparently complex intermetallics or spinel had formed that may have served not only as a barrier to outward diffusion of iron species and to inward diffusion of oxygen, but also as a protective shell against scale-exfoliating damage inflicted by impinging bed material (12). Therefore, it appears that residuals such as chromium, molybdenum, and nickel - *in the absence of thorough deoxidation (as indicated by an aluminum residual)* - are not particularly effective in influencing FBC tubing wastage.

The next step planned for this program is to prepare a series of experimental steels in the laboratory for the purpose of confirming the effects on scaling behavior of microalloying residuals and microstructure in tubing steels. In light of findings of the present study, use of laboratory oxidation tests in still air as an evaluation tool may necessarily be restricted to effects on scale growth rate and interface phenomena. For, while microstructural effects may influence FBC wastage response, they were not discernible in the formation of scales on steels at elevated temperatures in lab tests in still air.

It seems likely, then, that laboratory evaluation of experimental steels will be restricted to studying compositional effects upon scale forming behavior. Evaluation of microstructural effects upon FBC wastage response will apparently require exposure to actual FBC conditions. However, pending information from initial tests, there may be an inter-relationship between microstructural and compositional variables that may be discernible under laboratory conditions, as it was in the two TVA steels, and this will be determined during evaluation of the experimental steels.

9.0 CONCLUSIONS

1. The appearance of fireside surfaces of these tubing samples suggests that, in general, the fluidized-bed conditions to which they were exposed during the 1,300-hour operating period in Tube Bank "E" were less aggressive than those of previous runs in the same combustor. This may be due to differences in any number of operating variables including a different fluidizing mode, differences in the size, mass or hardness of bed particulates, or differences in fluidizing velocity, bubble formation or bed streaming tendencies.

2. Notwithstanding these general indications, there was evidence of a significant degree of tubing wastage in some samples, particularly on finned samples located near the top of the bed and near a wall. All observations of tubing wastage and its probable mechanism are consistent with the hypothesis developed in previous LLNL studies that metal loss occurs principally through exfoliation of the normally-protective oxide scale, probably by impacting bed particulates.

3. Three of the tubes submitted for study were of the same chemical composition of steel, although they differed in microstructure. In laboratory oxidation tests, these developed scales of virtually identical thickness and morphology; however, in the combustor, they experienced differing degrees of wastage, consistent with microstructural observations of earlier studies. These differences in scale formation in the two environments are thought to be related to differences in compositions of the scales as a result of differences in chemical activity of the environments.

4. On the basis of these observations it appears that, because of differences in scales formed in laboratory air and in the combustor, the influence of microstructure may not be discernible in simple oxidizing environments at elevated temperatures, although compositional effects are apparently discernible in such laboratory tests.

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Table 1

SAMPLES OF EVAPORATOR TUBING FROM GRIMETHORPE TUBE BANK "E"

Tube Ident.	Platen	Row	Surface Configuration	Materials
2C7	2	7	Grooved and finned	Tube: SA-210 steel(Grade C) Fins: AISI 1020 steel
8C1	8	1	Grooved	Tube: SA-210 steel (Grade C)
9C5	9	5	Chromized	Tube: SA-210 steel (Grade C)
11S5	11	5	Finned and Studded	Tube: SA-213 steel (Type 347H) Fins: Type 347 stainless steel Studs:Type 430 stainless steel
12T8	12	8	Finned and Studded	Tube: SA-213 steel (T22) Fins: AISI 1020 steel Studs:Type 430 stainless steel
13T7	13	7	Grooved and Finned	Tube: SA-213 steel (T-22) Fins: AISI 1020 steel

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Compositions of Steels Noted Above
(Specification Limits, not Chemical Analyses)

Chemical Compositions[1] (maxima, unless indicated otherwise)

Type/Grade	Fe	C	Mn	P	S	Si	Cr	Ni	Mo	Cb+Ta
SA-210/C	Bal.	0.35	0.29-1.06	0.048	0.058	0.10[2]	--	--	--	--
SA-213 (347H)	Bal.	0.04-0.10	2.00	0.040	0.030	0.75	17.0-20.0	9.0-13.0	--	[3]
SA-213 (T-22)	Bal.	0.15	0.30-0.60	0.030	0.030	0.50	1.90-2.60	--	0.87-1.13	--
Type 430	Bal.	0.12	1.00	0.040	0.030	1.00	16.0-18.0	--	--	--
AISI 1020	Bal.	0.18-0.23	0.30-0.60	0.040	0.050	--	--	--	--	--

Notes: 1 - Weight %
2 - Minimum
3 - Cb+Ta content not less than 8 times the carbon content and not more than 1.00%

Table 2

APPARENT WASTAGE RATES DERIVED FROM MEASUREMENTS ON AS-RECEIVED TUBES

Wall Thickness Method

Sample No.	Wall Thickness (mm) Top	Wall Thickness (mm) Bottom	Indicated Metal Loss (mm)	Apparent Wastage Rate (normalized to 1,000 hours) mm/1,000 hrs	Apparent Wastage Rate (normalized to 1,000 hours) mils/1,000 hrs
2C7	7.53	7.12	0.41	0.31	8.02
8C1	7.52	7.39	0.13	0.10	2.54
9C5	7.68	7.66	0.02	0.015	0.38
13T7	9.03	8.68	0.35	0.26	6.8

Outside Diameter Method

	Outside Diameter (mm) Horizontal	Outside Diameter (mm) Vertical			
2C7	50.38	50.12	0.26	0.20	5.08
8C1	50.65	50.55	0.10	0.08	2.03
9C5	51.09	51.47	-0.38*	*	*
13T7	50.54	50.50	0.04	0.03	0.76

* Invalid indications, measurements show vertical diameter to be greater than horizontal. See text for explanation.

Table 3

RESULTS OF CHEMICAL ANALYSIS OF TUBING SAMPLES

Element	Chemical Analysis (weight %)[1,2] Sample No. 2C7 Original	Sample No. 2C7 Recheck	Sample No. 8C1 Original	Sample No. 8C1 Recheck	Sample No. 9C5	Sample No. 13T7
Al	0.005	<0.005	0.005	<0.005	0.005	<0.005
B	<0.0005	0.0009	<0.0005	0.0006	<0.0005	<0.0005
Ca	<0.005	0.003	<0.005	0.005	<0.005	<0.005
C	0.26	0.26	0.27	0.26	0.24	0.12
Cr	0.09	0.09	0.09	0.09	0.09	2.24
Ce	<0.01	<0.005	<0.01	<0.005	<0.01	<0.01
Cb	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Cu	0.12	0.13	0.12	0.13	0.12	0.11
Fe	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
La	<0.01	<0.005	<0.01	<0.005	<0.01	<0.01
Mg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mn	0.81	0.90	0.82	0.90	0.80	0.43
Mo	<0.005	<0.005	<0.005	<0.005	<0.005	0.95
Ni	0.02	0.03	0.02	0.03	0.02	0.03
N	0.011	0.010	0.011	0.011	0.007	0.005
O	0.004	0.005	0.004	0.004	0.004	0.005
P	0.018	0.022	0.018	0.020	0.018	0.021
Si	0.25	0.27	0.26	0.27	0.26	0.32
S	0.013	0.016	0.014	0.016	0.012	0.010
Ti	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
W	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
V	0.009	--	0.01	--	0.009	0.009
Zr	<0.005	--	<0.005	--	<0.005	<0.005

Notes: 1. Dash indicates not analyzed

2. All analytical samples taken from mid-wall of the tubing sample to assure a region chemically unaffected by scale, welds, or combustor environment.

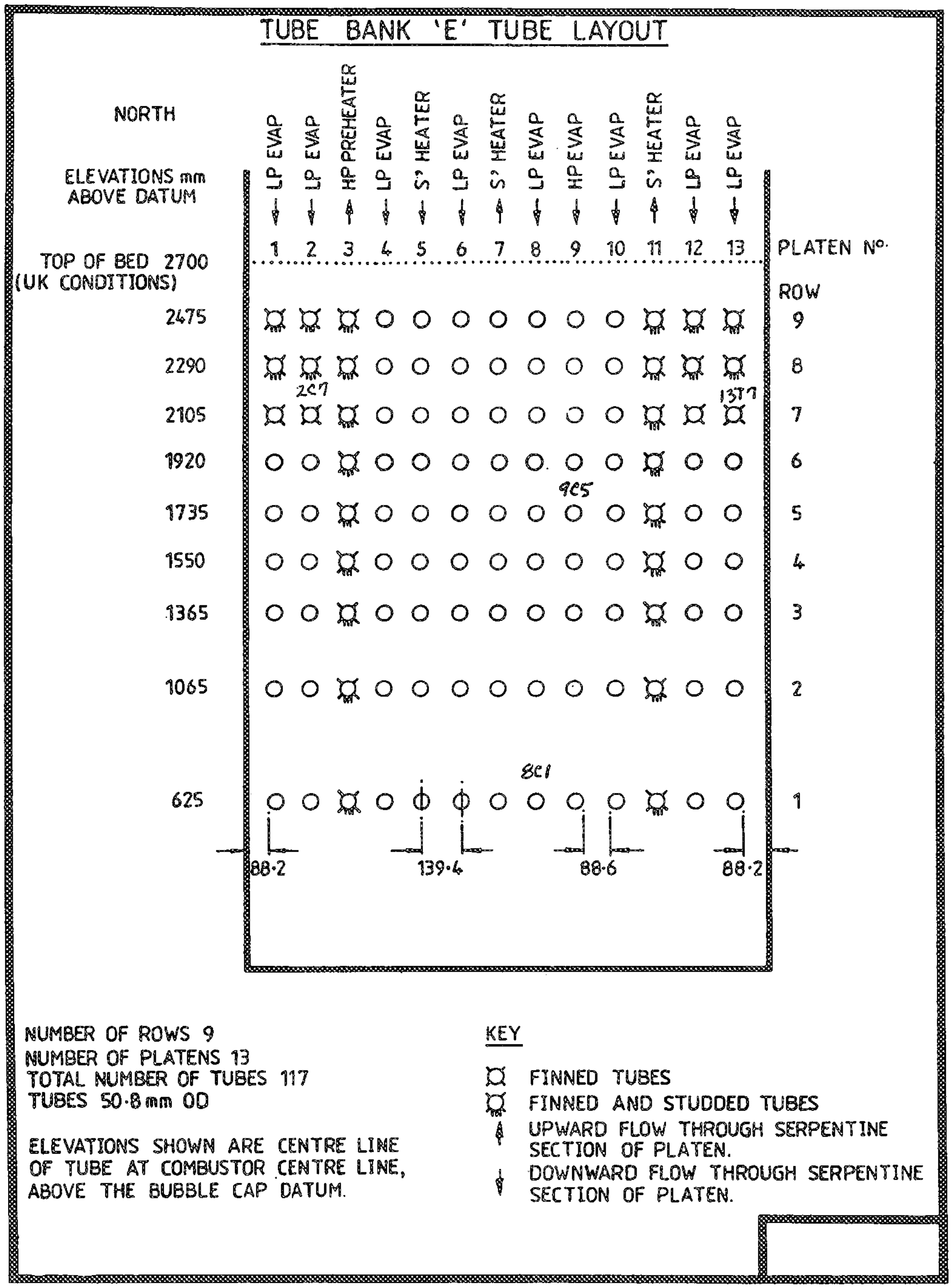
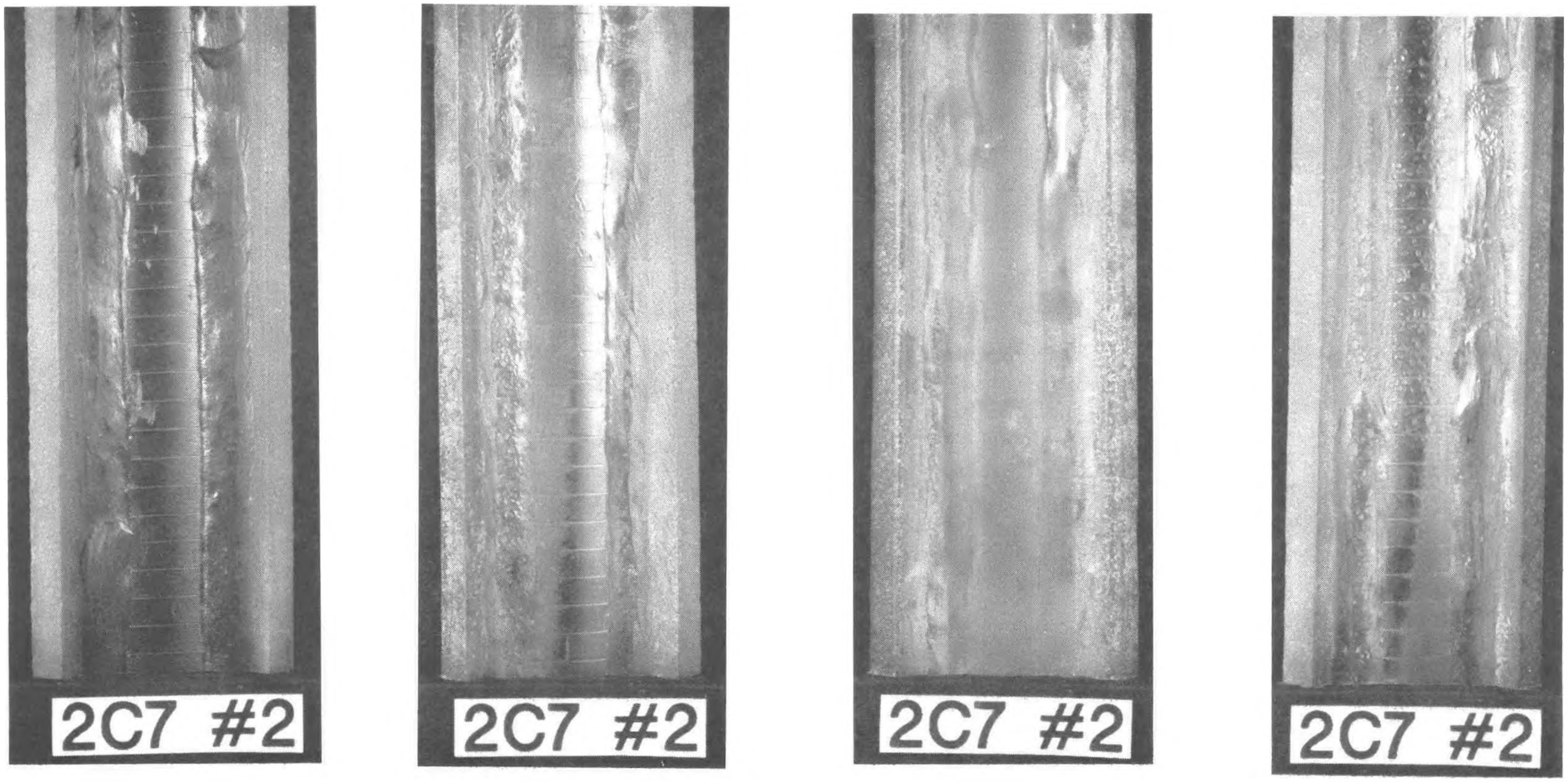


FIGURE 1

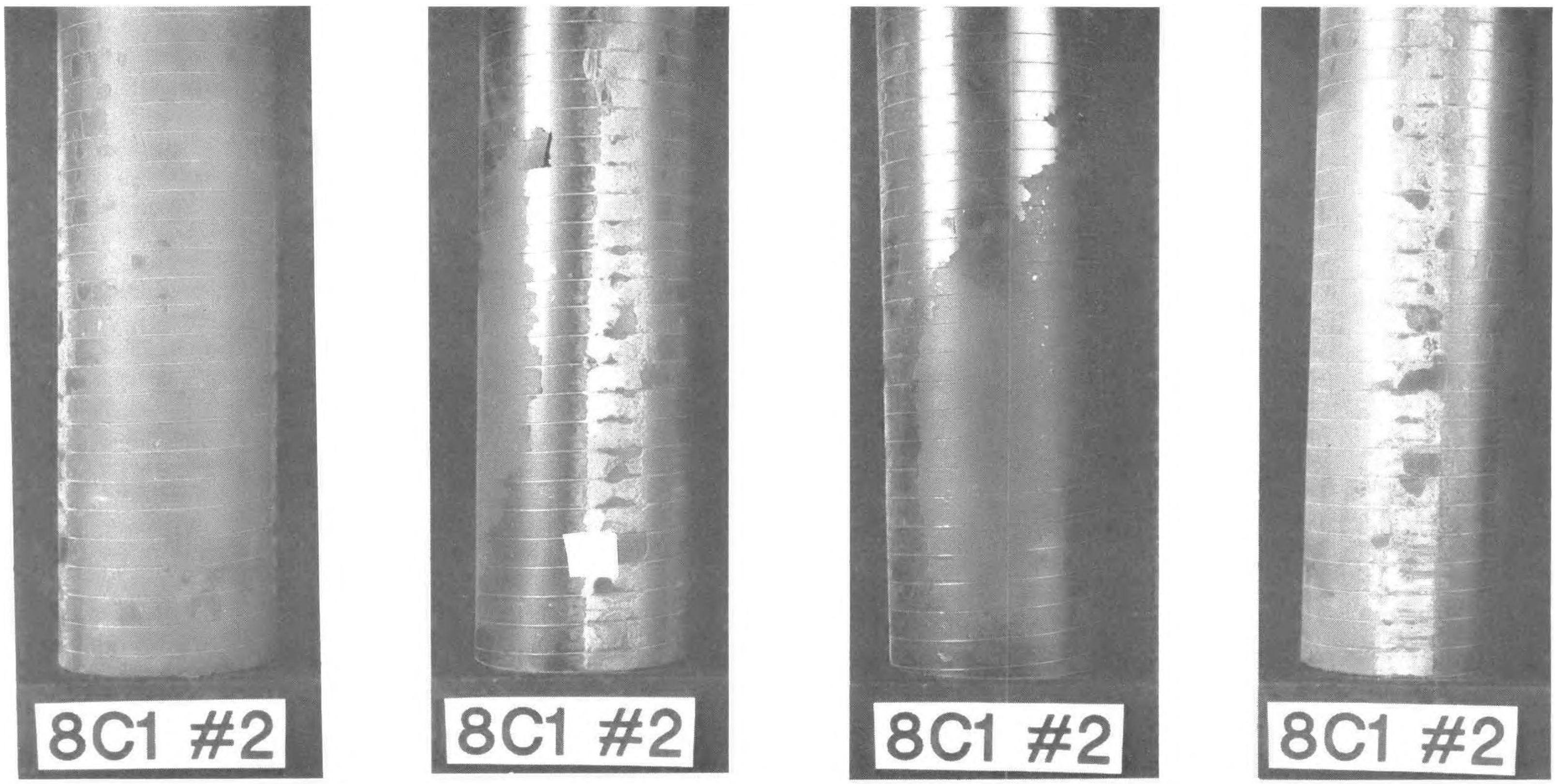
Schematic of Tube Layout for Grimethorpe Tube Bank "E"



0 Degree Position | 90 Degree Position | 180 Degree Position | 270 Degree Position

FIGURE 2

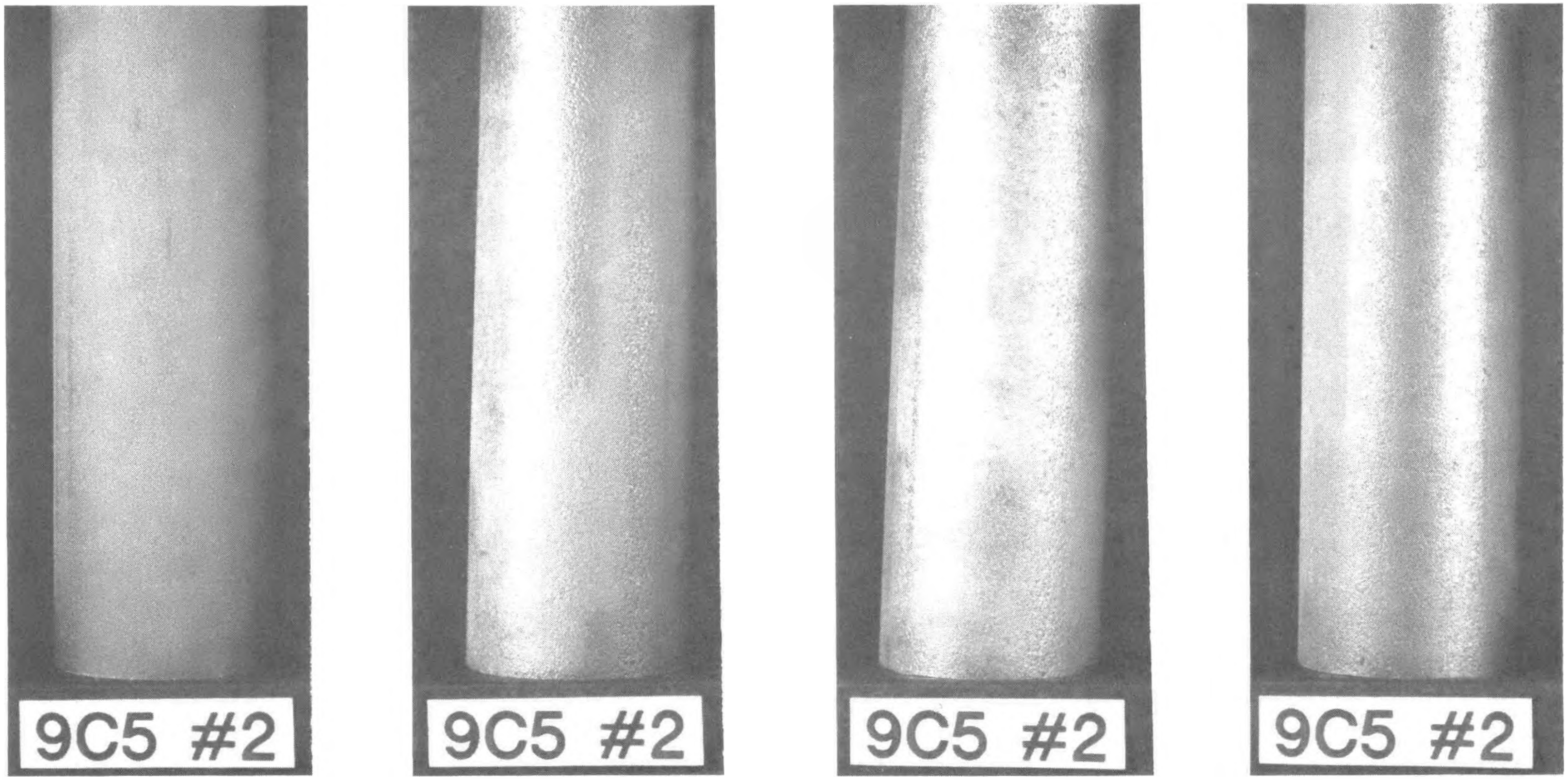
Appearance of As-Received Tubing Sample 2C7



0 Degree Position | 90 Degree Position | 180 Degree Position | 270 Degree Position

FIGURE 3

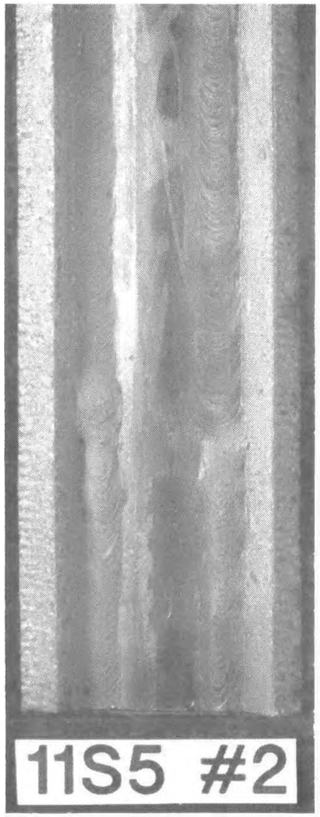
Appearance of As-Received Tubing Sample 8C1



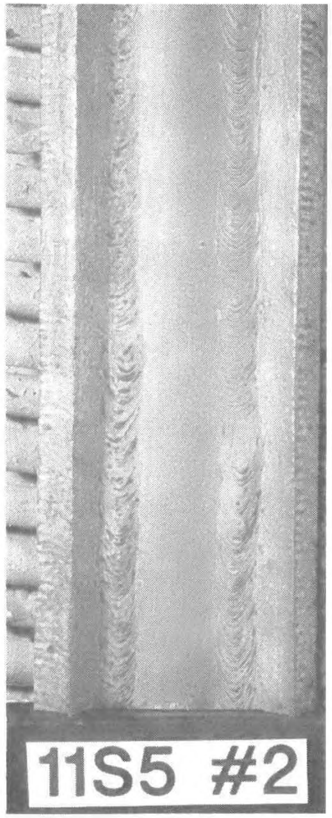
0 Degree Position | 90 Degree Position | 180 Degree Position | 270 Degree Position

FIGURE 4

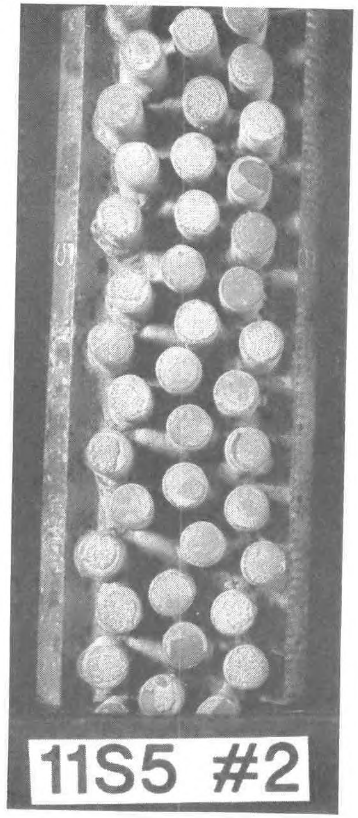
Appearance of As-Received Tubing Sample 9C5



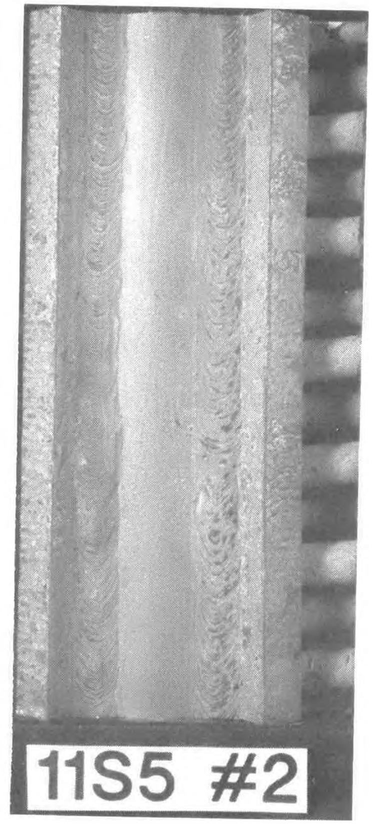
0 Degree Position



90 Degree Position



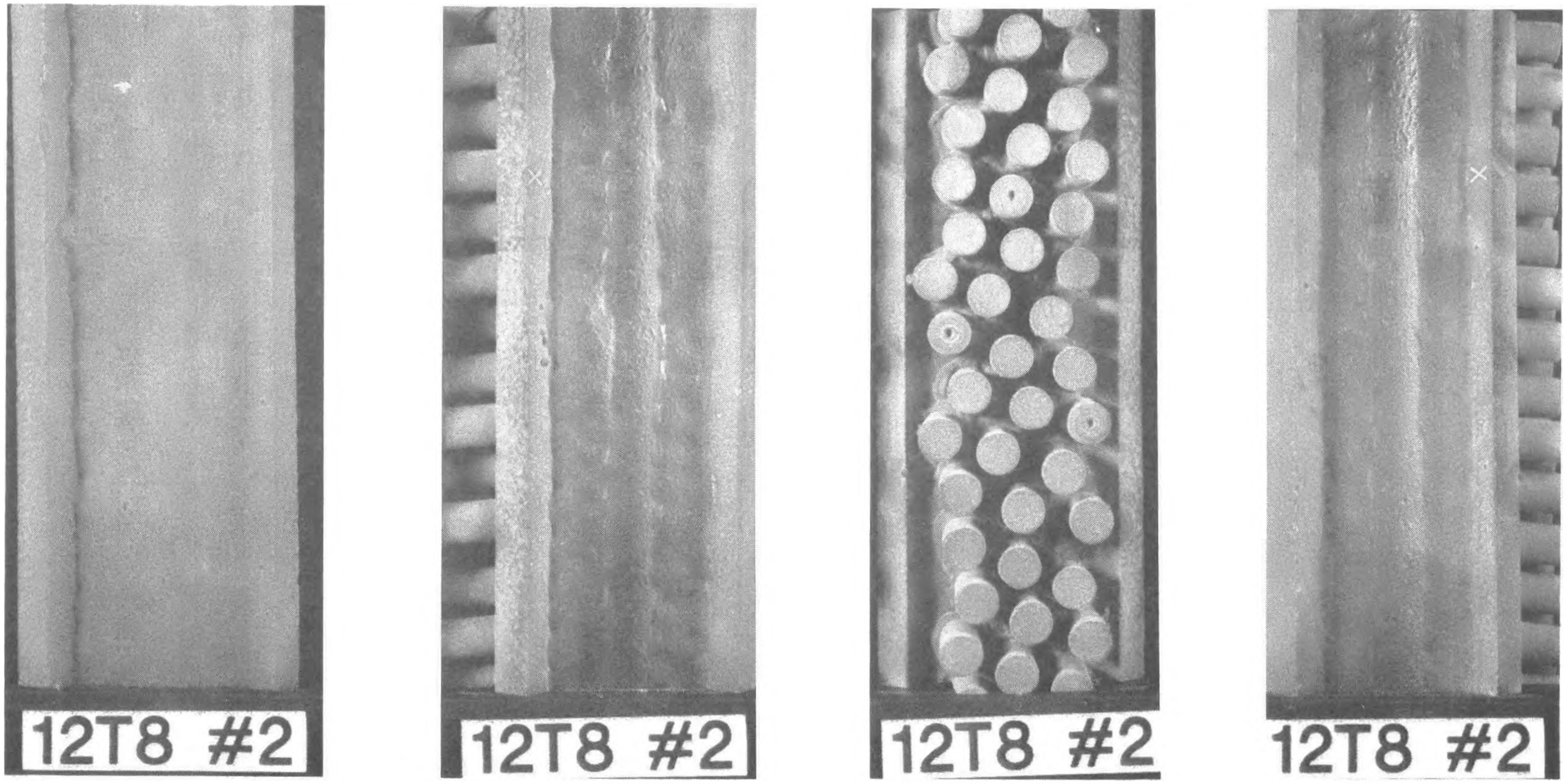
180 Degree Position



270 Degree Position

FIGURE 5

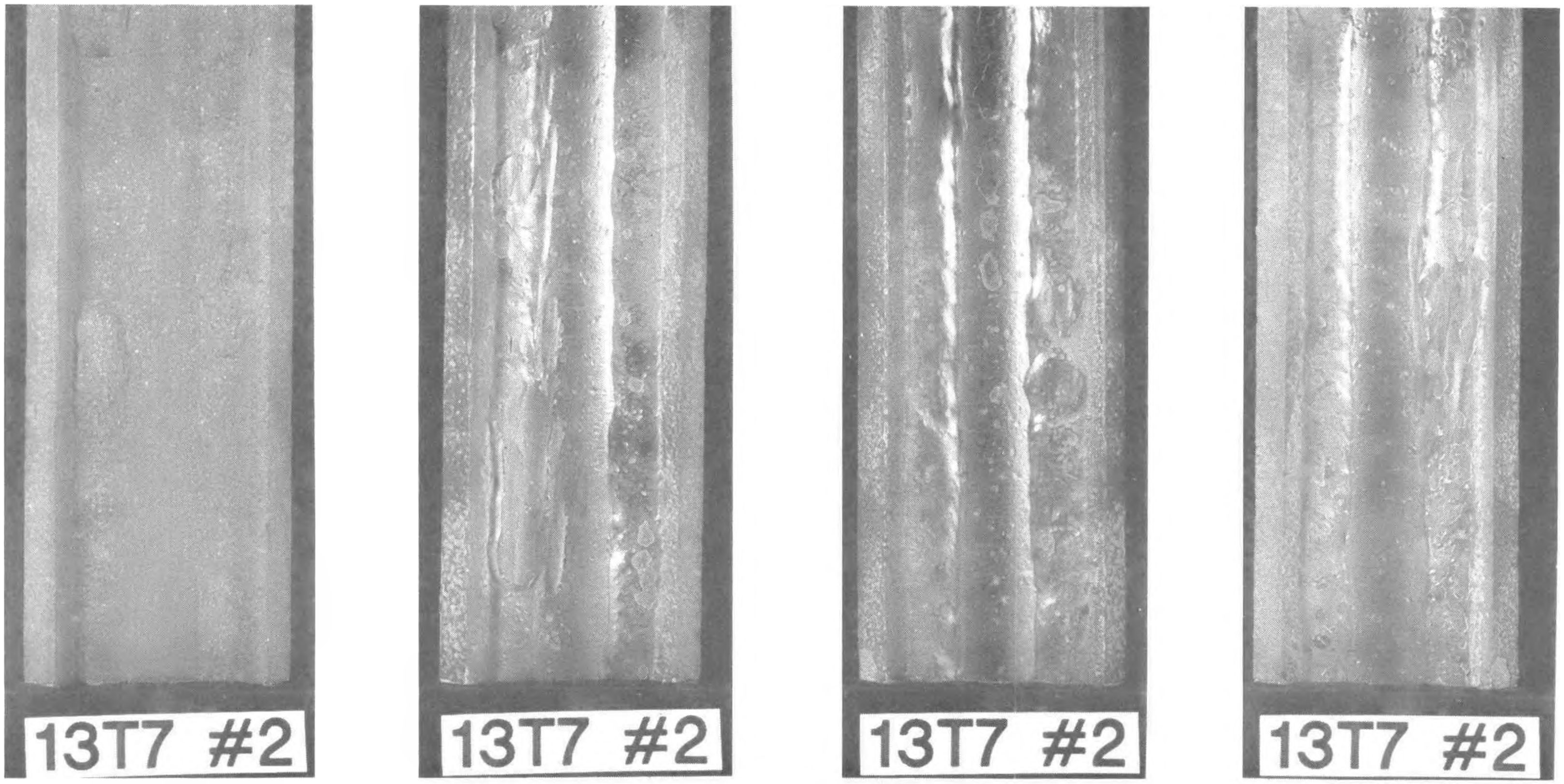
Appearance of As-Received Tubing Sample 11S5



0 Degree Position | 90 Degree Position | 180 Degree Position | 270 Degree Position

FIGURE 6

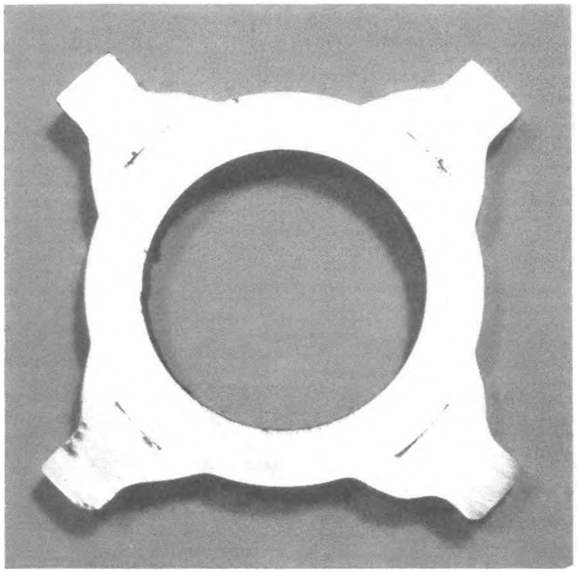
Appearance of As-Received Tubing Sample 12T8



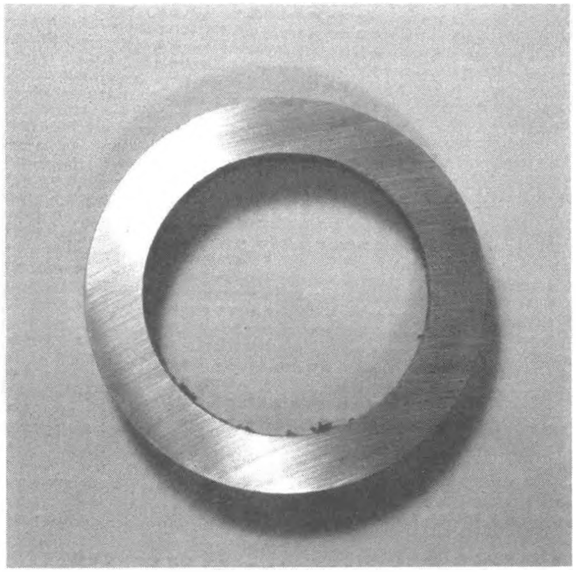
0 Degree Position　　90 Degree Position　　180 Degree Position　　270 Degree Position

FIGURE 7

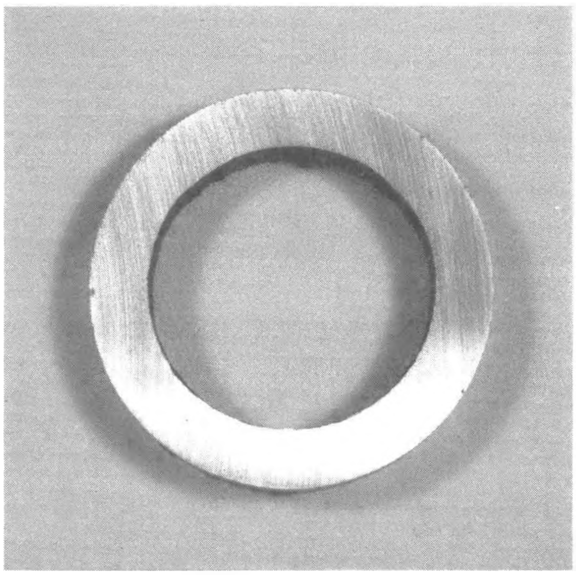
Appearance of As-Received Tubing Sample 13T7



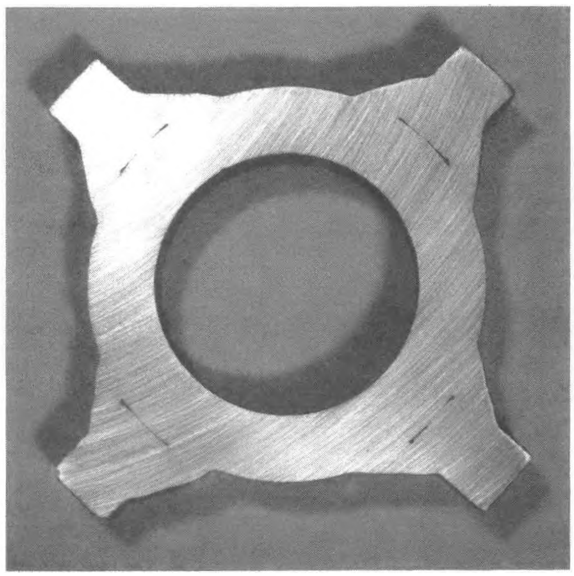
Tube Sample 2C7



Tube Sample 8C1



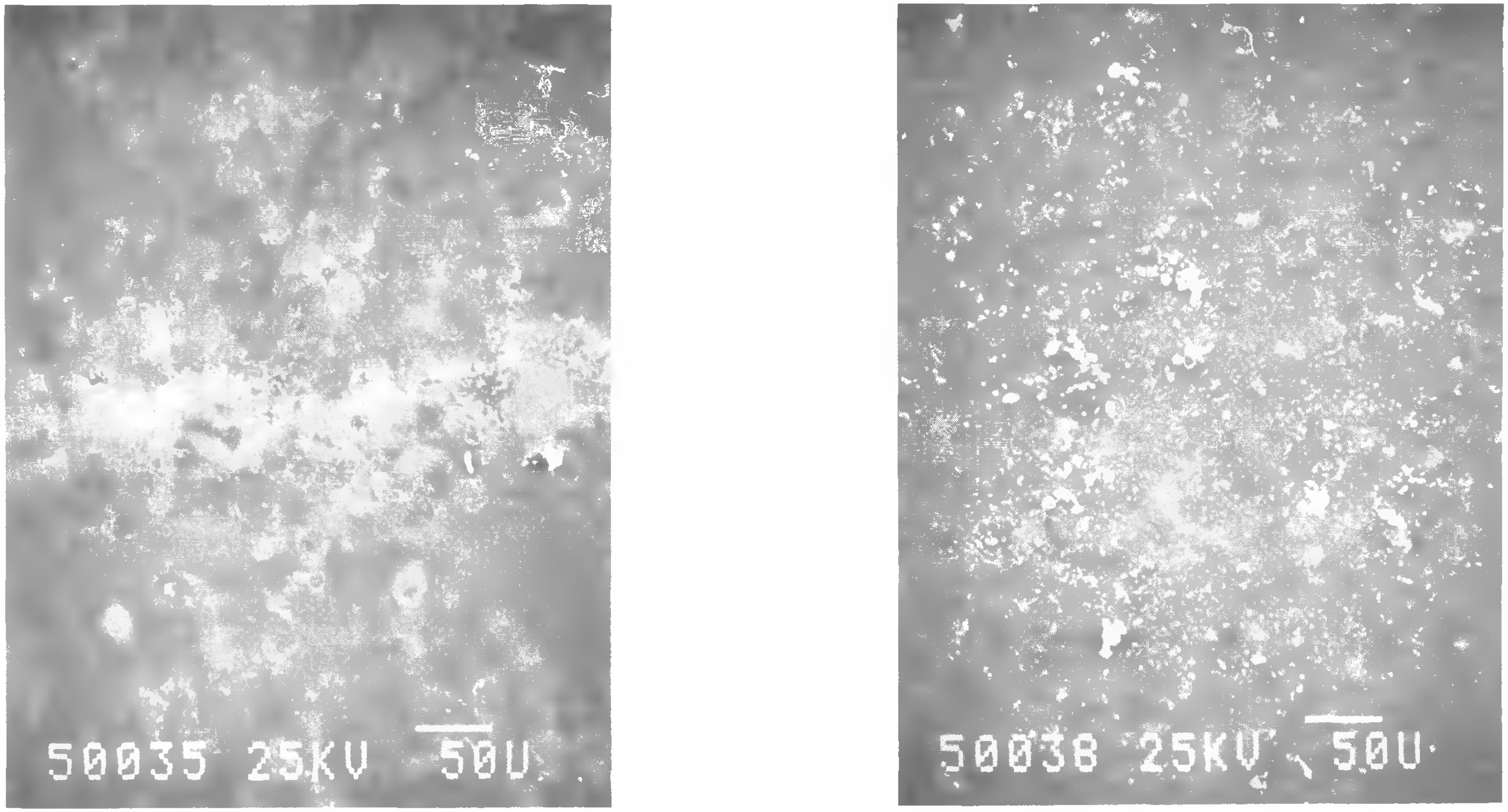
Tube Sample 9C5



Tube Sample 13T7

FIGURE 8

Cross-Sectional Profiles of Tubing Samples Examined



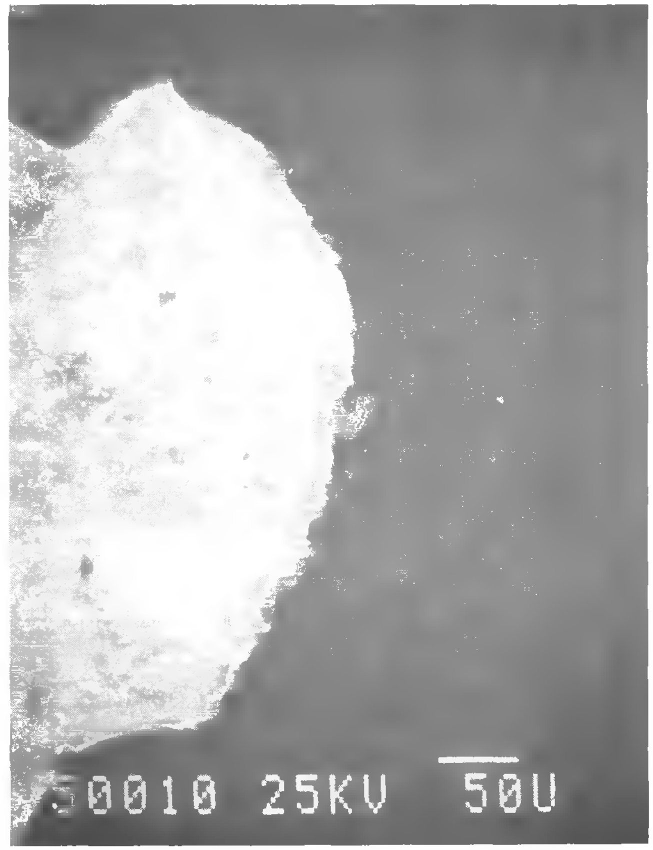
Non-Wastage-Susceptible Region

Wastage-Susceptible Region

FIGURE 9

Appearance of Fireside Surface of Tubing Sample 2C7
(SEM Photomicrographs)

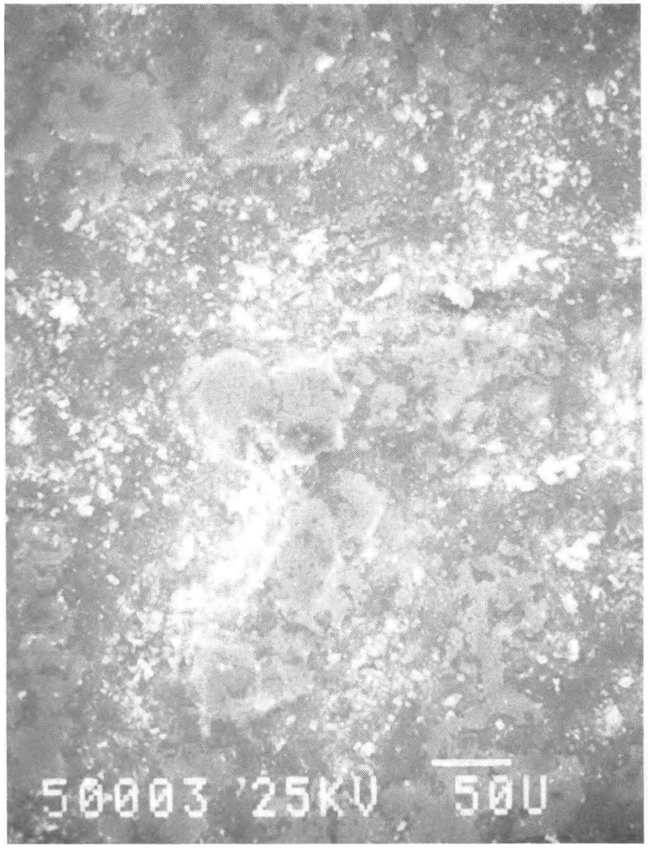
Non-Wastage-Susceptible Region



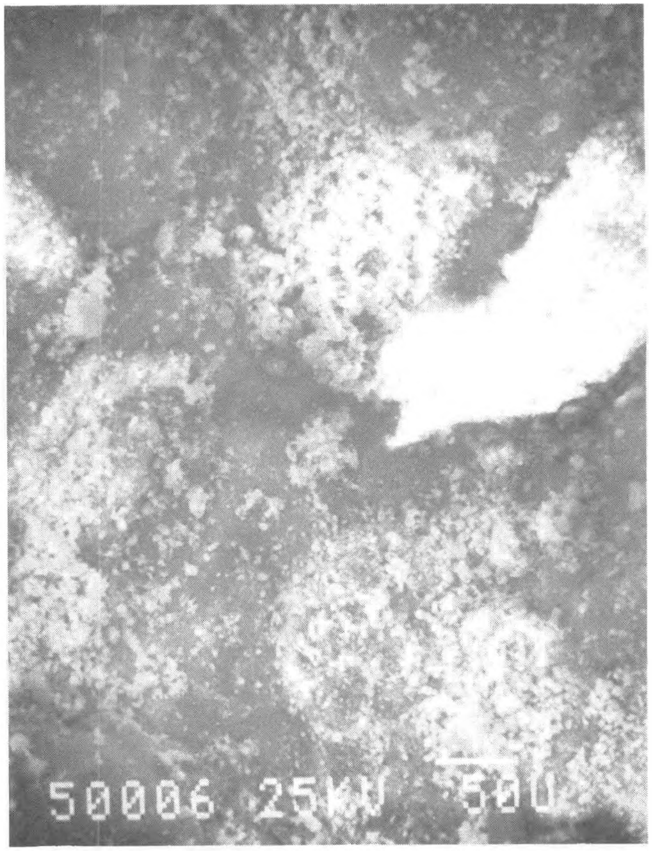
Wastage-Susceptible Region

FIGURE 10

Appearance of Fireside Surface of Tubing Sample 8C1
(SEM Photomicrographs)



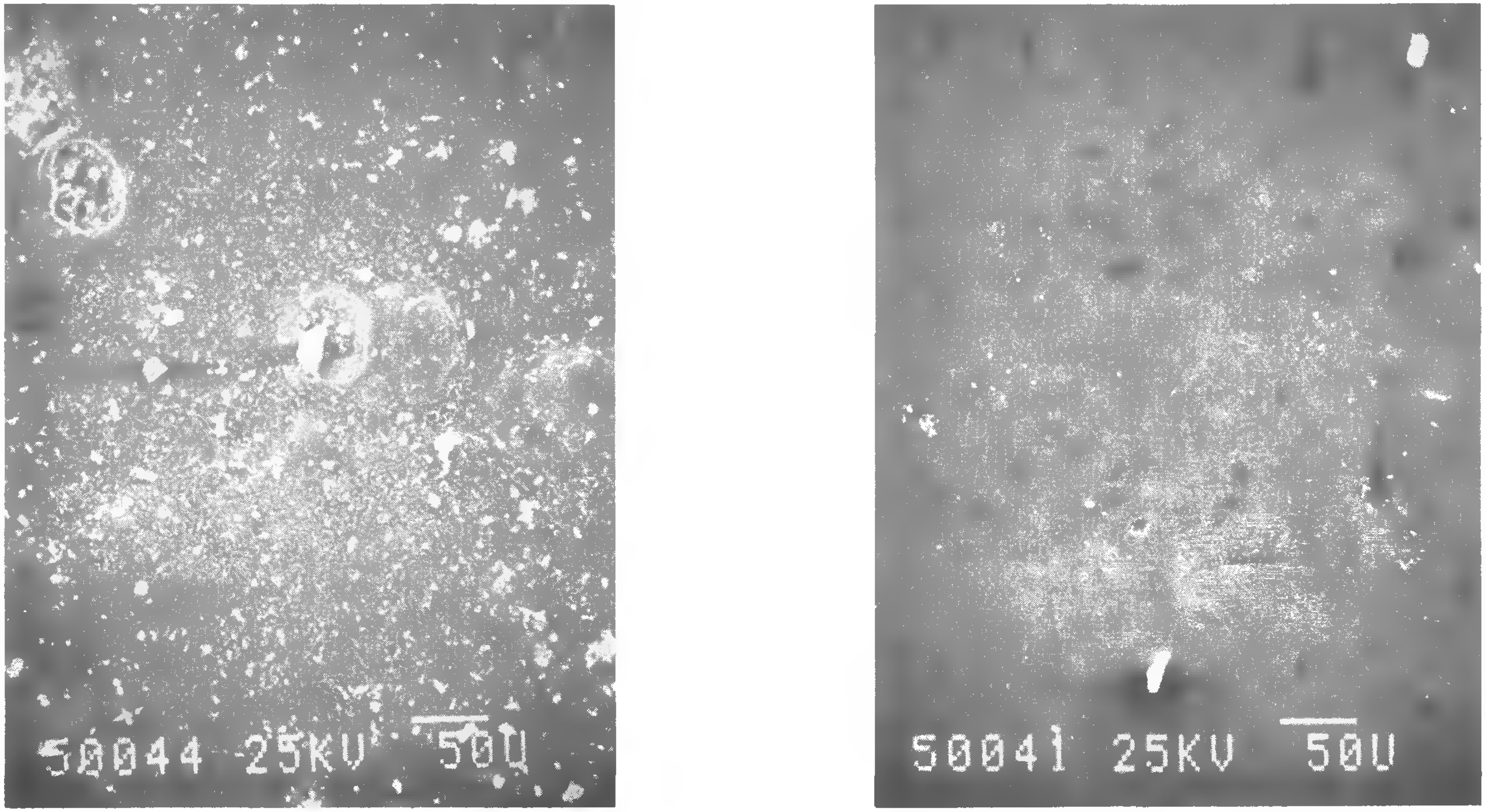
Non-Wastage-Susceptible Region



Wastage-Susceptible Region

FIGURE 11

Appearance of Fireside Surface of Tubing Sample 9C5
(SEM Photomicrographs)

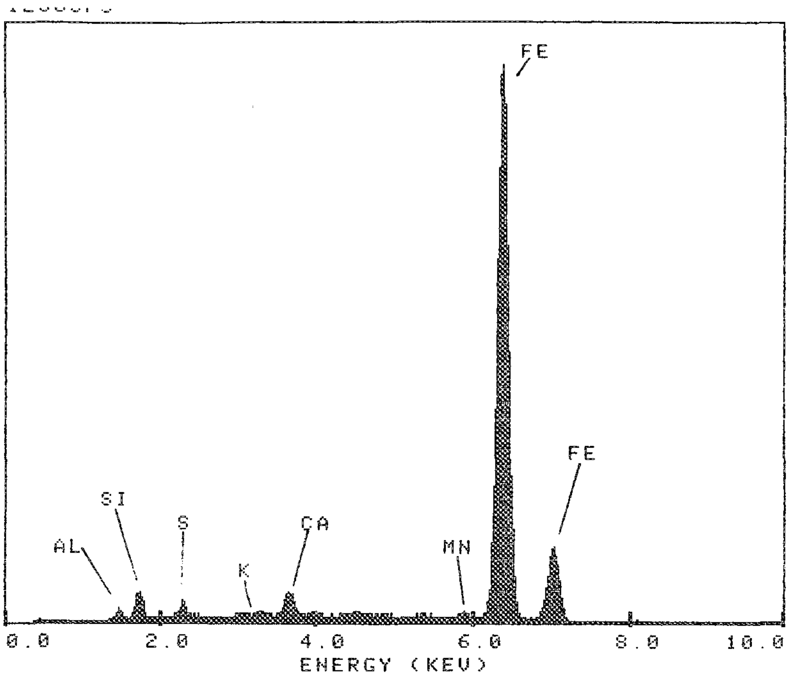


Non-Wastage-Susceptible Region

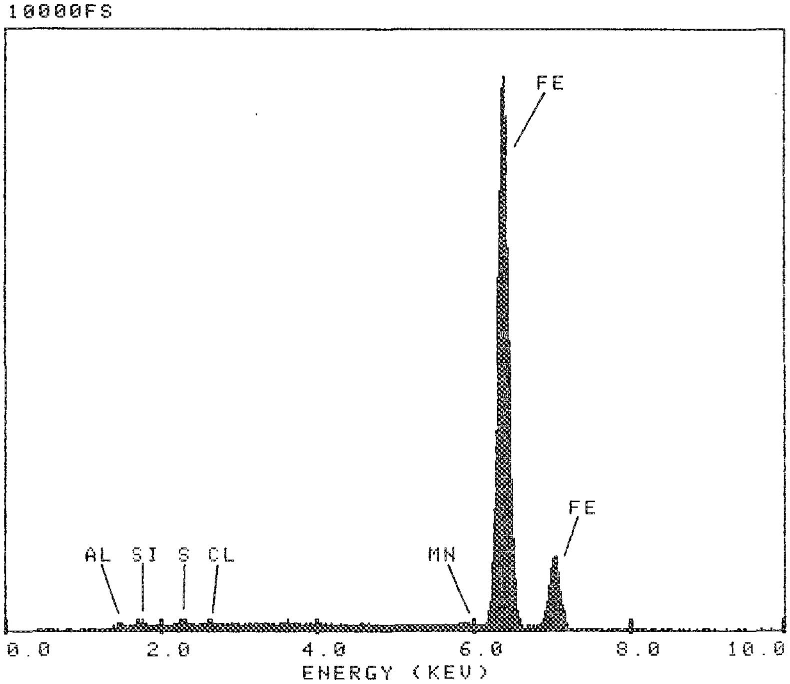
Wastage-Susceptible Region

FIGURE 12

Appearance of Fireside Surface of Tubing Sample 13T7
(SEM Photomicrographs)



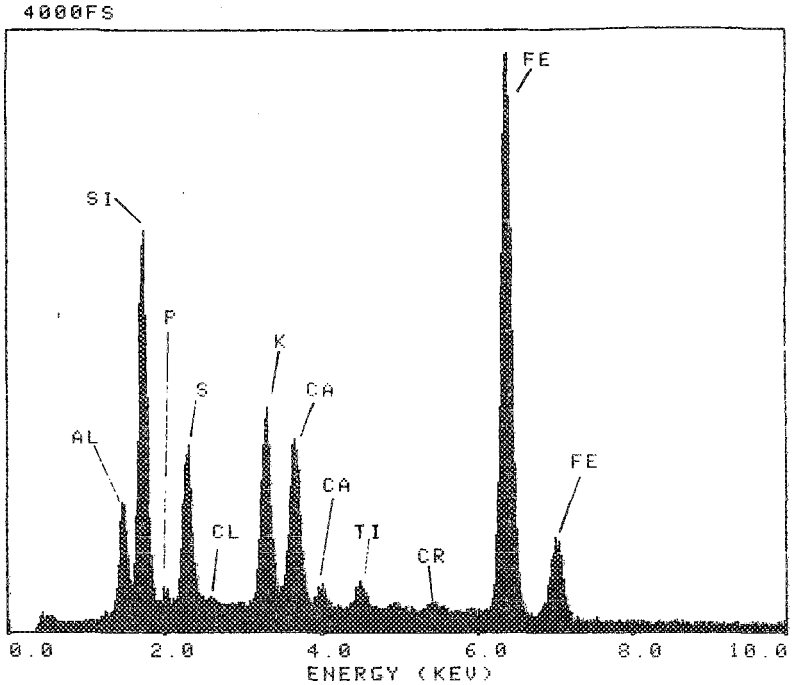
Non-Wastage-Susceptible Region



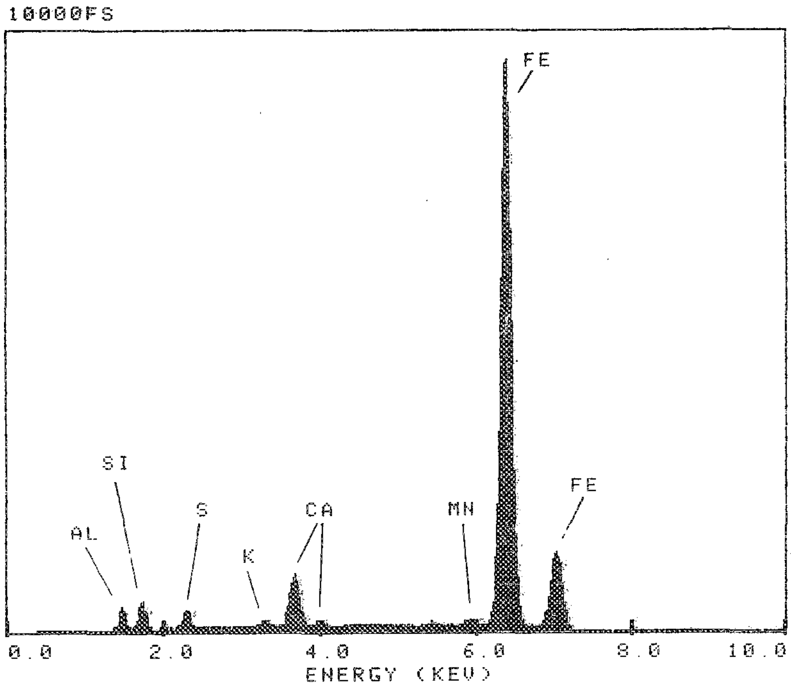
Wastage-Susceptible Region

FIGURE 13

EDS Spectra for Fireside Surfaces of Tubing Sample 2C7



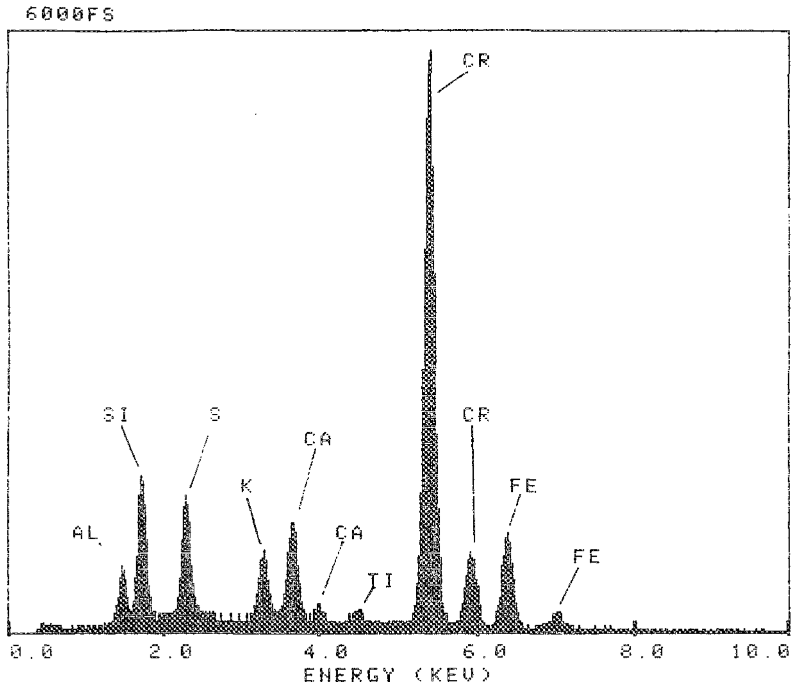
Non-Wastage-Susceptible Region



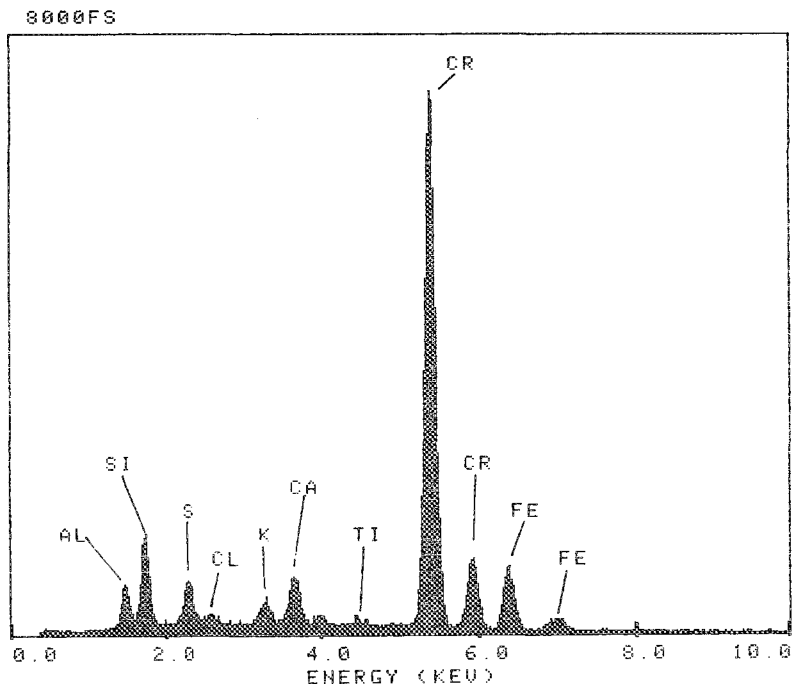
Wastage-Susceptible Region

FIGURE 14

EDS Spectra for Fireside Surfaces of Tubing Sample 8C1



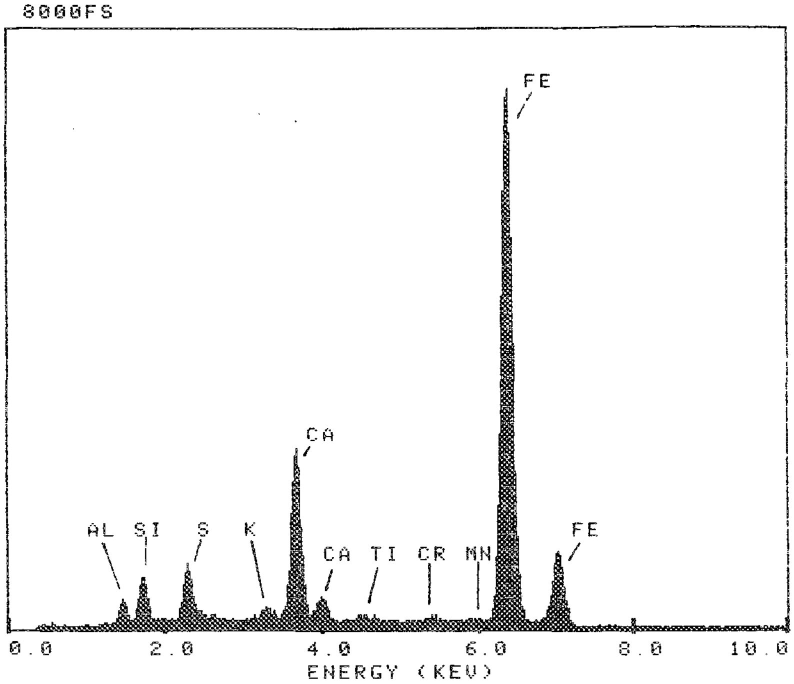
Non-Wastage-Susceptible Region



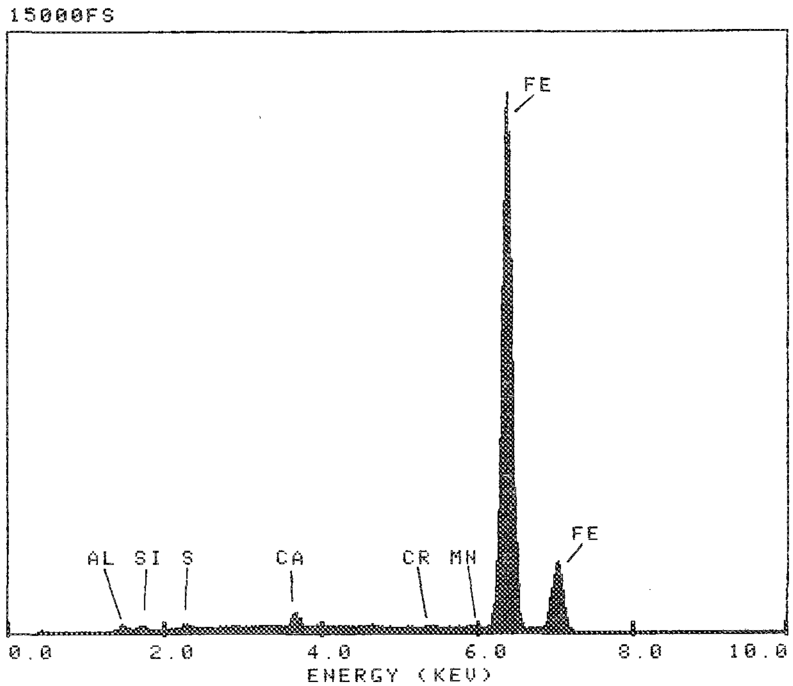
Wastage-Susceptible Region

FIGURE 15

EDS Spectra for Fireside Surfaces of Tubing Sample 9C5



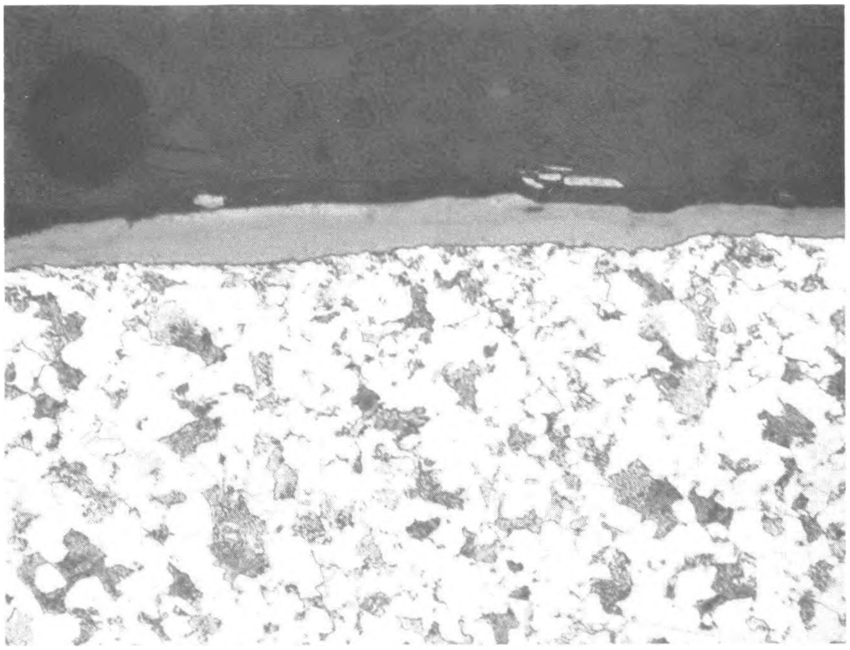
Non-Wastage-Susceptible Region



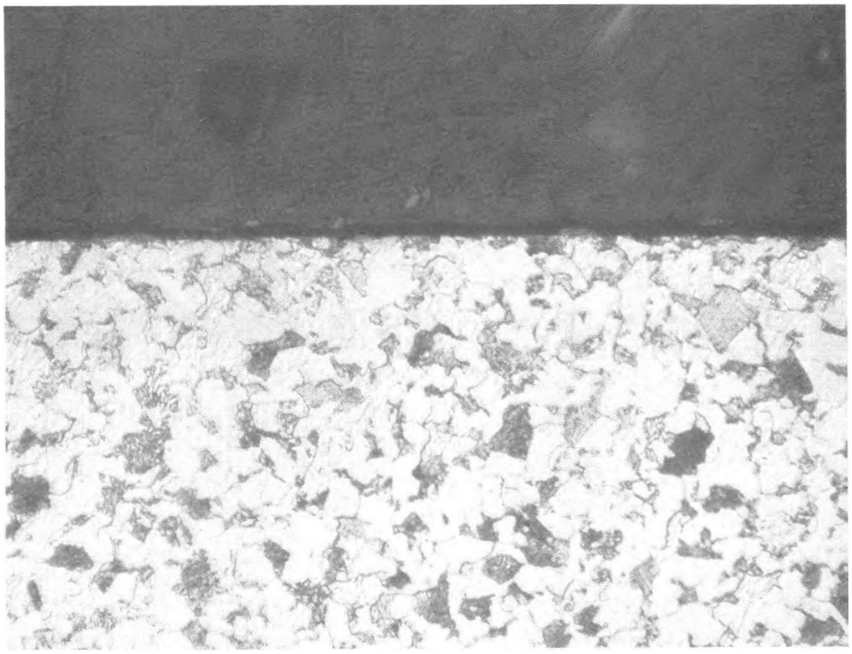
Wastage-Susceptible Region

FIGURE 16

EDS Spectra for Fireside Surfaces of Tubing Sample 13T7



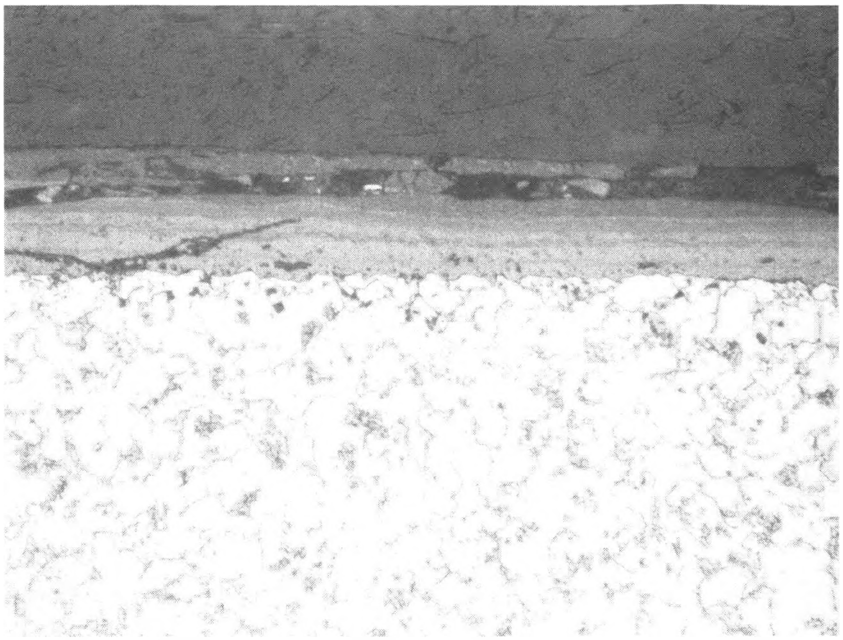
Non-Wastage-Susceptible Region (topside)



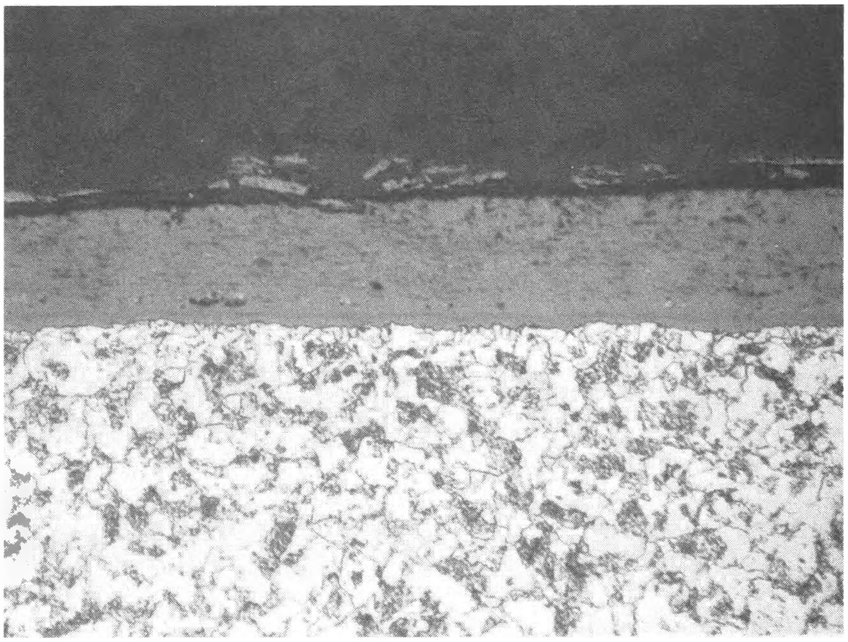
Wastage-Susceptible Region (underside)

FIGURE 17

Cross-Sections of Tubing Sample 2C7 at Fireside Surface
(Optical Photomicrographs, 2% Nital etchant, 400x)



Non-Wastage-Susceptible Region (topside)



Wastage-Susceptible Region (underside)

FIGURE 18

Cross-Sections of Tubing Sample 8C1 at Fireside Surface
(Optical Photomicrographs, 2% Nital etchant, 400x)

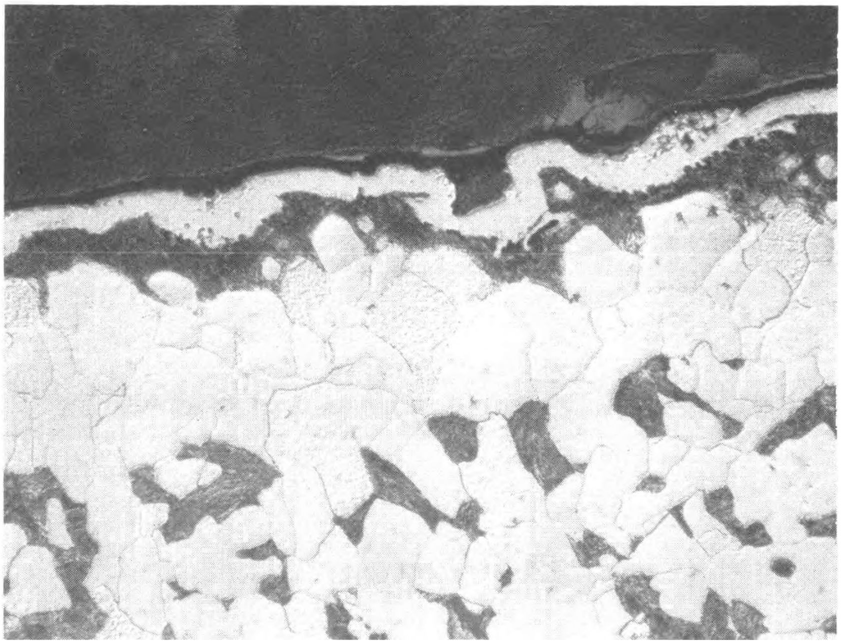
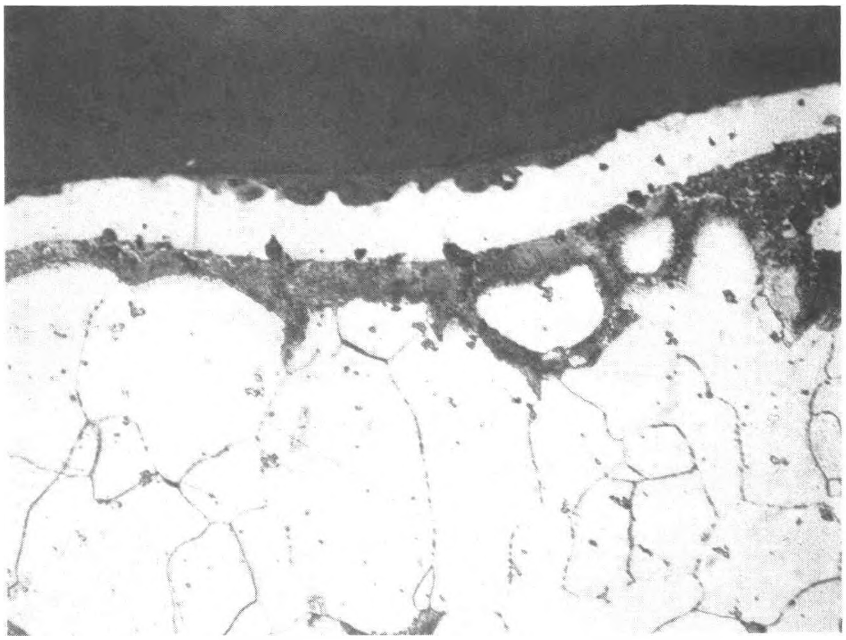


FIGURE 19-A

Cross-Section of Tubing Sample 9C5 at Fireside Surface
(Optical Photomicrograph, 2% Nital etchant, 200x)

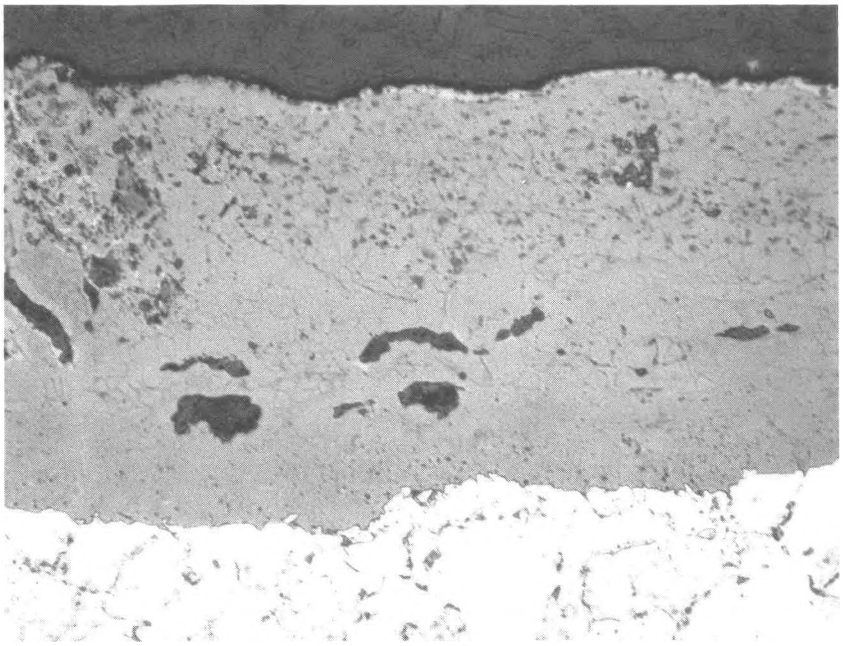


Non-Wastage-Susceptible Region (topside)

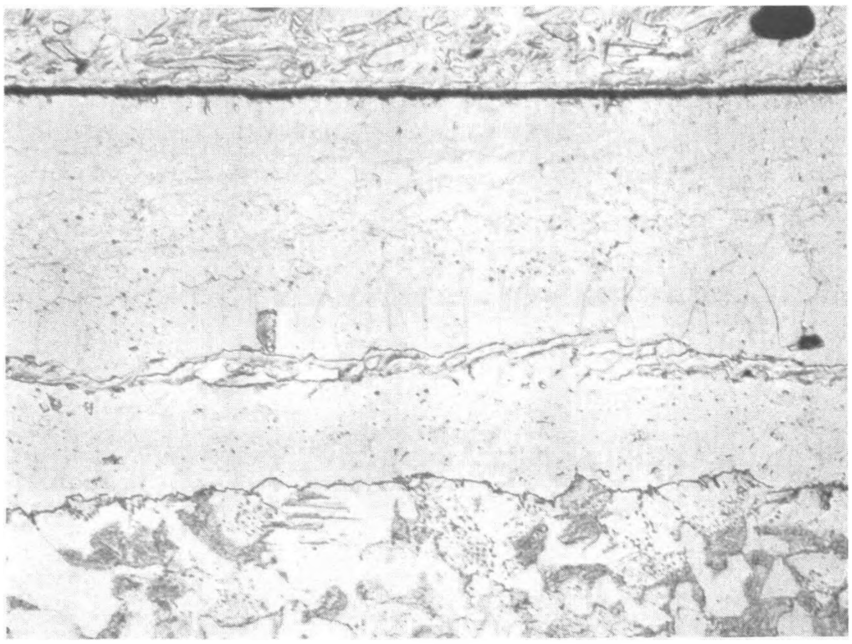
Wastage-Susceptible Region (underside)

FIGURE 19-B

Cross-Sections of Tubing Sample 9C5 at Fireside Surface
(Optical Photomicrographs, 2% Nital etchant, 400x)



Non-Wastage-Susceptible Region (topside)



Wastage-Susceptible Region (underside)

FIGURE 20

Cross-Sections of Tubing Sample 13T7 at Fireside Surface
(Optical Photomicrographs, 2% Nital etchant, 400x)

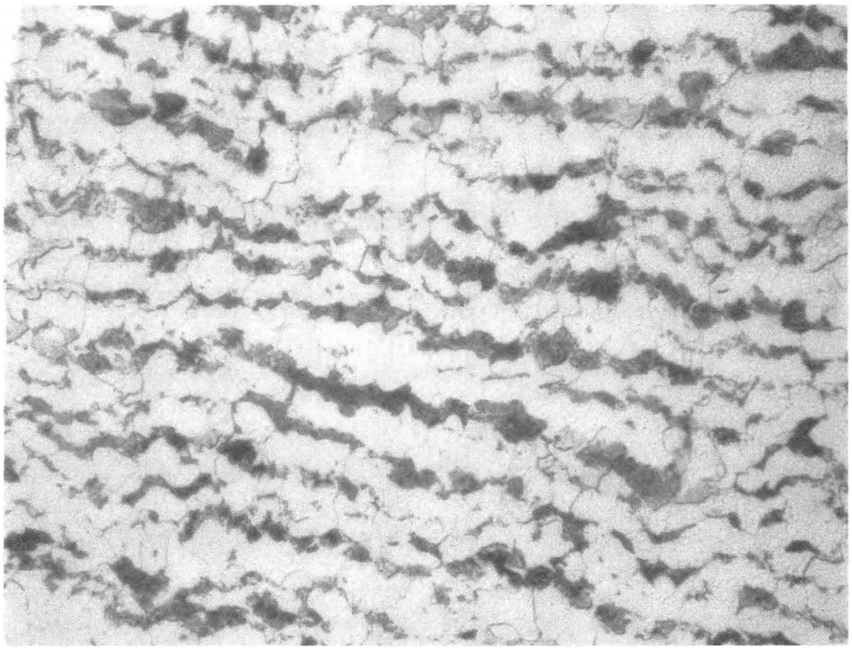


FIGURE 21

Microstructure of Tubing Steel from Sample 2C7
(Optical Photomicrograph 2% Nital etchant, 400x)

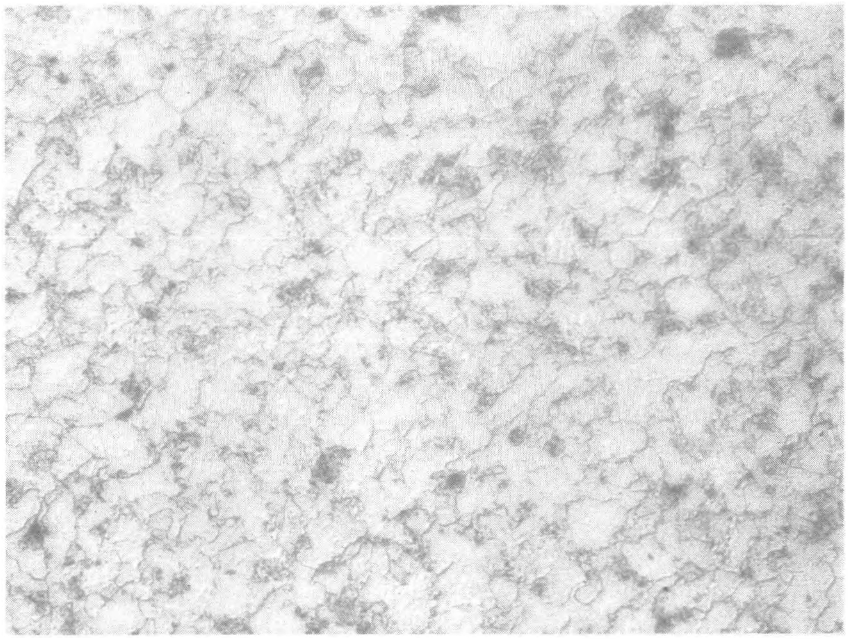


FIGURE 22

Microstructure of Tubing Steel from Sample 8C1
(Optical Photomicrograph 2% Nital etchant, 400x)

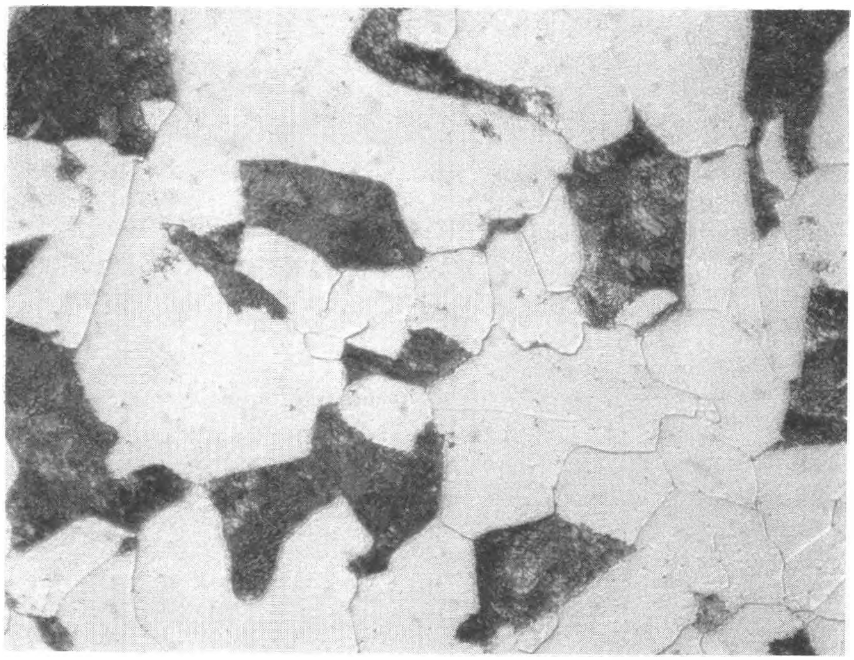


FIGURE 23

Microstructure of Tubing Steel from Sample 9C5
(Optical Photomicrograph 2% Nital etchant, 400x)

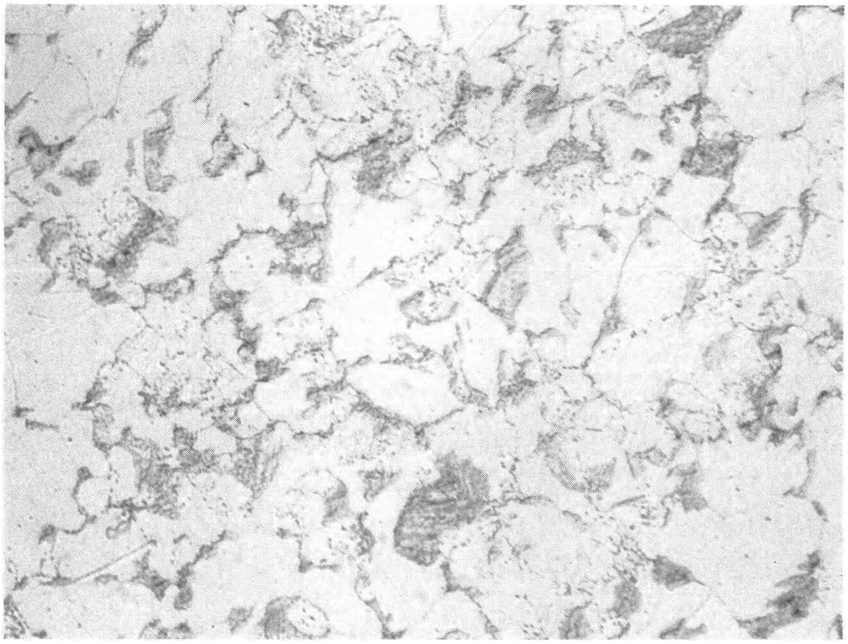


FIGURE 24

Microstructure of Tubing Steel from Sample 13T7
(Optical Photomicrograph 2% Nital etchant, 400x)

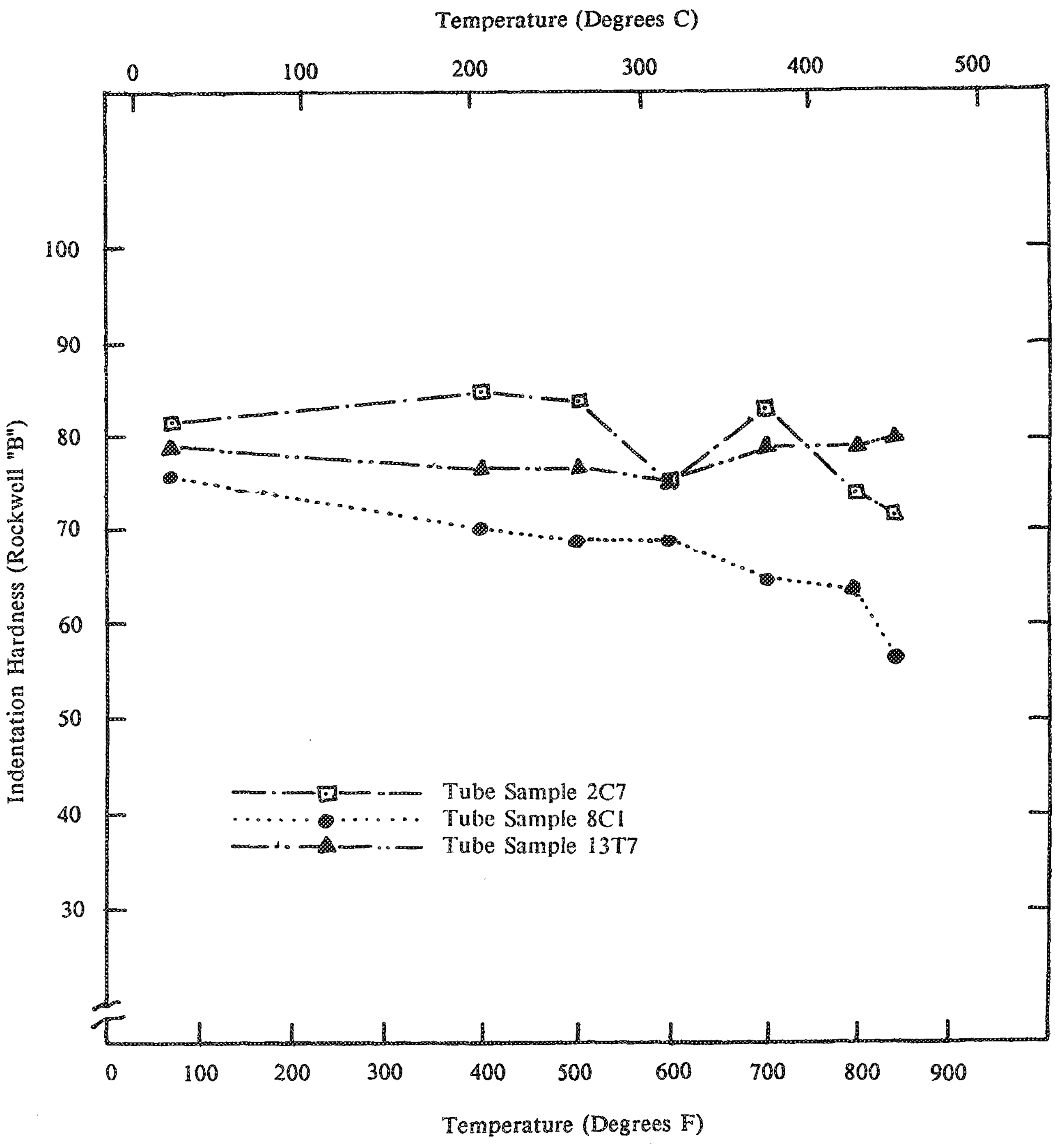


FIGURE 25

ELEVATED TEMPERATURE INDENTATION HARDNESS OF TUBING STEELS

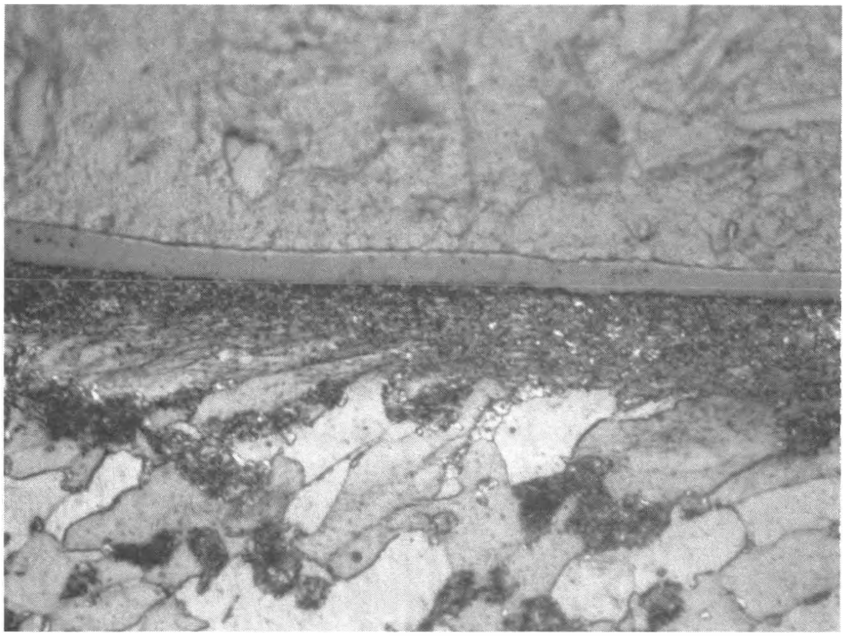


FIGURE 26

Cross-Section of Steel from Tubing Sample 2C7 Showing Scale/Substrate Interface after Laboratory Exposure to Still Air at 450C (Optical Photomicrograph, 2% Nital etchant, 1,000x)

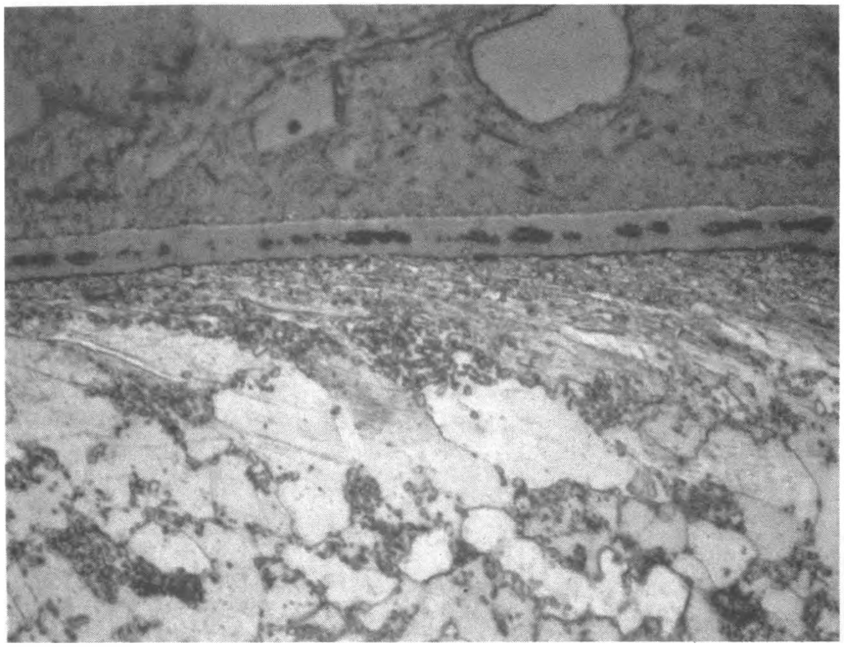


FIGURE 27

Cross-Section of Steel from Tubing Sample 8C1 Showing Scale/Substrate Interface after Laboratory Exposure to Still Air at 450C
(Optical Photomicrograph, 2% Nital etchant, 1,000x)

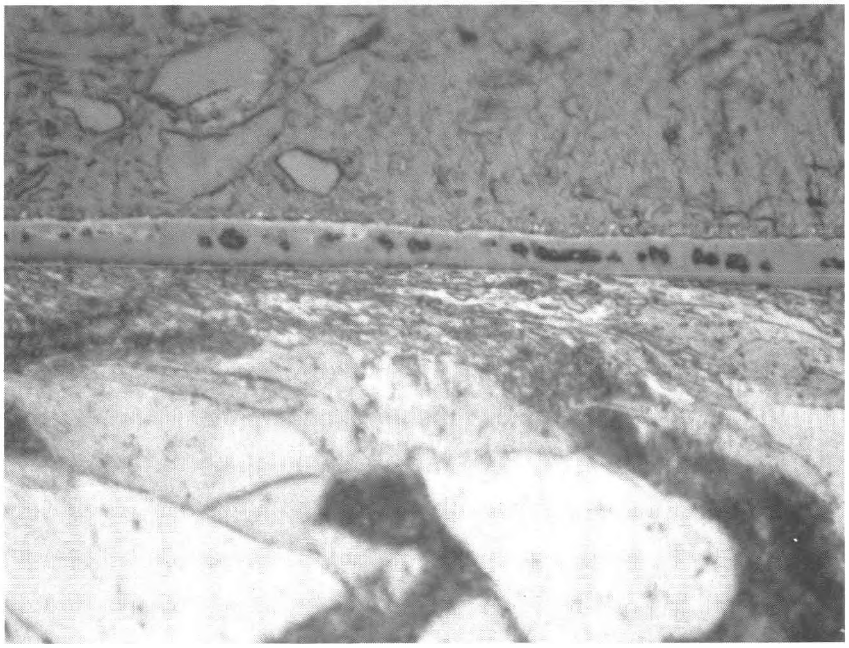


FIGURE 28

Cross-Section of Steel from Tubing Sample 9C5 Showing Scale/Substrate Interface
after Laboratory Exposure to Still Air at 450C
(Optical Photomicrograph, 2% Nital etchant, 1,000x)

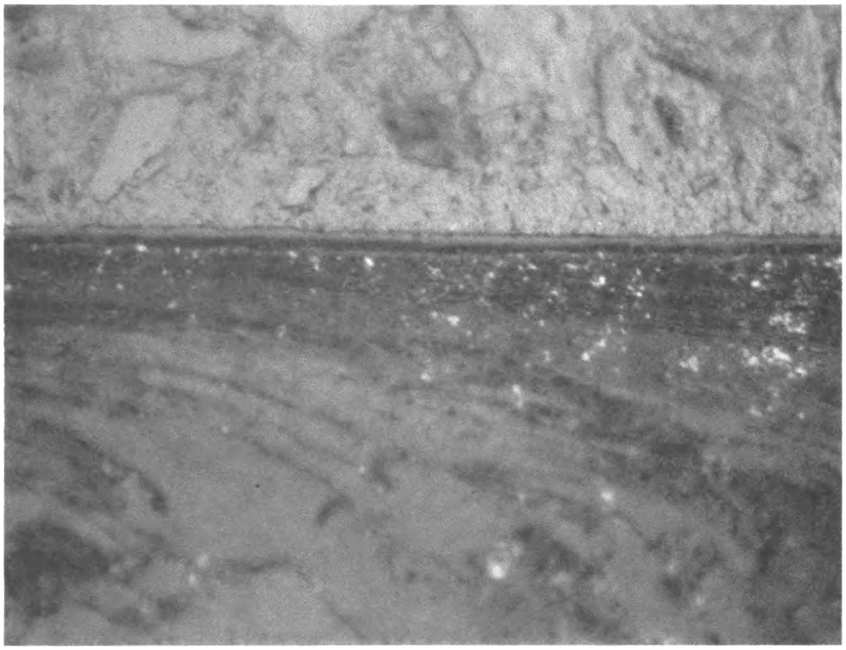


FIGURE 29

Cross-Section of Steel from Tubing Sample 13T7 Showing Scale/Substrate Interface after Laboratory Exposure to Still Air at 450C (Optical Photomicrograph, 2% Nital etchant, 1,000x)

11.0 LIST OF ACRONYMS AND ABBREVIATIONS

AFBC - Atmospheric Fluidized-Bed Combustor

CEGB - Central Electricity-Generating Board (UK)

DOE - U. S. Department of Energy

EDS - Energy-Dispersive Spectroscopy

FBC - Fluidized-Bed Combustor (or Combustion)

FWDC - Foster-Wheeler Development Corporation (USA)

LLNL - Lawrence Livermore National Laboratory

METC - Morgantown Energy Technology Center

PFBC - Pressurized Fluidized-Bed Combustor

SEM - Scanning Electron Microscopy

TVA - Tennessee Valley Authority

UK - United Kingdom

12.0 APPENDIX

Procedures Used in Removing Tube Samples from Tube Bank
and in Preparing Sample Tubes for Shipment

12.0 APPENDIX

Procedures Used in Removing Tube Samples from Tube Bank and in Preparing Sample Tubes for Shipment

FOSTER WHEELER DEVELOPMENT CORPORATION
JOHN BLIZARD RESEARCH CENTER
12 PEACH TREE HILL ROAD • LIVINGSTON, NEW JERSEY 07039 • PHONE 201-533-1100

March 9, 1988

Mr. Charles Witherell
Lawrence Livermore National Lab
P. O. Box 808
Mail Stop L 350
Livermore, California 94550

Subject: **Second Generation PFBC System**
R&D Contract DE-AC21-86MC21023
FWDC 9-41-3448 R210 Tube Samples

Dear Mr. Witherell:

The following tabulation describes the six tube samples, from Grimethorpe tube bundle "E," that were forwarded to you under separate cover per DOE's request.

Tube Ident. No.	Platen No.	Row No.	Protection/ Configuration	Material System	
2C7	2	7	Grooved & Finned	Tube: Fins:	SA-210 GrC AISI 1020
8C1	8	1	Grooved	Tube:	SA-210 GrC
9C5	9	5	Chromized	Tube:	SA-210 GrC
11S5	11	5	Finned & Studded	Tube: Fins: Studs:	SA-213 Tp347H 347SS 430SS
12T8	12	8	Finned & Studded	Tube: Fins: Studs:	SA-213 T22 AISI 1020 430SS
13T7	13	7	Grooved & Finned	Tube: Fins:	SA-213 T22 AISI 1020

The tube bundle consisted of 13 platens of nine rows each. Platens were consecutively numbered from the "north" end, and rows were consecutively numbered from bottom to top.

The samples represent tubes that were exposed to three consecutive runs of 500, 500 and 300 hours. The first and third runs utilized UK coal containing 0.2% Cl.

Mr. Charles Witherell
Lawrence Livermore National Lab

March 9, 1988
Page 2

All tubes were prepared for shipment (UK to USA) in accordance with the attached procedure. After receipt by FW, sample handling was as follows:

- The tubes were unpackaged from their sealed containers under heat lamps in an air conditioned office environment for examination and marking to designate sample removal locations.

- Each tube was placed into a polyethylene sleeve for protection during sample removal. The sleeve was purged with dry N_2/Ar and sealed.

- Two 6" long samples were removed from each tube while the tube was in the poly sleeve under dry N_2/Ar purge. Cuts were made 6" and 12" from the "west" end by dry band saw cutting in our machine shop.

- The cut face of the samples closest to the "east" end was marked by vibro-tool as follows:

  a) A numeral "1" for the extreme west end sample and a numeral "2" for the adjacent sample. (NOTE: All "2" samples were forwarded to you.)

  b) An arrow indicating the top of the tube while in the bundle.

  c) An "E" indicating that the marked face was closest to the "east" end.

  d) The tube identification number,(see prior tabulation).

- Each sample was placed into a protective PVC plastic pipe container which was marked with the tube identification number and sample number. A desiccant bag containing dried $CaSO_4$ granules was attached to the end of the container with scotch tape. The container was then double bagged in heat-sealed poly sleeving, each of which was purged with dry Ar prior to sealing.

Throughout these operations care was taken not to touch the samples with bare hands. Rubber and/or heavy cotton gloves were worn at all times while handling the sleeved tubes/samples, and contact with the sample surface was held to a minimum.

Please advise if any further information is desired and confirm satisfactory receipt of samples upon arrival. We look forward to the results of your analysis.

Very truly yours,

E. D. Montrone

E. D. Montrone
Chief Metallurgist

EDM:jb
Attachment

cc: A. S. Robertson

Removal and Transit Packing of Steel Tube Sections from the Grimethorpe Combustor for Metallographic Analysis with Special Consideration to the Surface Deposition of Chlorides

Procedure

(1) The combustor shut-down and subsequent cooling period must be carried out in such a manner that avoids condensation anywhere within the furnace. The section of tubing is then to be removed from the combustor as rapidly as possible.

(2) Blow out all tubes with air to remove water and to dry them sufficiently to prevent water leaking from cut ends onto fireside surfaces.

(3) The platen containing the tube section is to be the first one lifted up into the freeboard. The surface of the section is not to be disturbed, touched or marked in any way. This means that no diameter or wall thickness measurements, or any other form of inspection involving any form of contact, are to be made. As soon as the tube section is accessible, it is to be covered by a suitable protective cover (e.g., plastic or other impermeable material that will not be contaminated). It is imperative that this cover does not contain any chlorides. If tape of any kind is to be used, this too must be free of chlorides and in any case, should not be applied directly to the metal surface. All tubes should be protected immediately so that lower tube rows are not contaminated by debris from the cutting of higher rows.

(4) The tube section is then to be cut from the platen ensuring that any residual moisture present in the platen is not allowed to contaminate the external surface of the tube section. If moist, the bore of the tube is to be dried thoroughly by means of a pull through. The cutting process must be carried out dry by means of saw (portable power or hand) without lubrication to avoid contamination. Abrasive wheel or flame cutting should be avoided.

(5) If the tube sections are to be stored before packing for dispatch (this should be avoided), the plastic wrapping should be left intact and the sections stored in a safe, dry (indoors) heated location.

(6) The section is then to be placed in a suitable container ready for dispatch. Sufficient packing, thoroughly dry and chloride free, is to be used to keep the tube secure and help prevent any surface damage occurring through rolling or rubbing against other tubes. Prior to placing the tube in the container, measures will have been taken to ensure that it contains no moisture. Once the section is placed in the container, along with a suitable non-chloride containing desiccant, it is to be purged through with nitrogen. The container is to then be sealed such that the inert atmosphere is preserved and water cannot ingress. Any sealant used is to be free of chlorides. For maximum effectiveness, this seal should not be broken until received by the laboratory.