

Materials issues in black liquor steam reforming/gasification

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ABSTRACT: Steam reforming/gasification of black liquor produced during wood pulping offers the potential for more efficient energy recovery, reduction of emissions, and improved safety. This technology is currently being implemented in two North American semichemical pulp mills. As might be expected in scaling up any process system, a number of problems have been encountered. Degradation of metallic and refractory components has been observed in several areas. This paper presents the results of the examinations of a number of these damaged metallic components. Carburization was observed in all cases, indicating the process environment was not as expected. Significant oxidation occurred, but the surface oxides formed appeared not to be protective. Studies currently in progress are directed toward identifying materials with resistance to the reformer/gasifier environments.

Application: This research will help improve the safety and reliability of black liquor steam reforming/gasification systems.

In a modern paper mill, the chemical recovery boiler serves a critical role in recycling pulping chemicals. It also produces steam that serves process needs and generates a significant portion of the mill's electrical power requirements. Recovery boiler manufacturers continue to work to improve the efficiency and safety of their products, but boilers do have some shortcomings. More specifically, recovery boilers are not particularly efficient at recovering energy from black liquor, their level of gaseous emissions can be a problem, and, in the event of failure of a wall or floor tube, there is a potential for an explosion caused by a smelt-water reaction. Improvements in design, operating conditions, and selection of structural materials have helped address these issues. Nevertheless, studies by Larsen, et al. [1,2] have shown that combined-cycle black liquor gasification offers some significant benefits over the combustion technology of recovery boilers.

Many organizations have worked on black liquor gasification technologies, and two of these have advanced to the stage of commercial application. The high-temperature technology developed by Chemrec AB operates at a high enough temperature ($\sim 950^{\circ}\text{C}$) that the inorganic components are present as a molten phase. This process is being used at a kraft mill in New Bern, North Carolina, USA [3,4]. The low-temperature technology developed by Manufacturing and Technology Conversion International and distributed in North America by ThermoChem Recovery International, operates below the melting point of the inorganic components ($\sim 605^{\circ}\text{C}$) [3,5]. The high-temperature process uses partial combustion of the organic components of the black liquor to produce heat and a product gas. The low-temperature process uses steam reforming to produce a higher Btu-content product gas. A demonstration-scale low-temperature reformer/gasifier operated in the mid-1990s at the New Bern kraft mill, and two North American semichemical pulp mills located in Big Island, Virginia, USA, and Trenton, Ontario, Canada, have recently installed reformer/gasifier systems. Two projects funded by the U.S. Department of Energy (DOE) are addressing materials issues in the low-temperature reformer/gasifier systems [6,7].

Both gasification processes have encountered a number of problems in the scale-up to the systems that are currently operating. The refractory problems encountered in the high-temperature system have been described in a number of reports and at several conferences [8,9], and some success is being reported in resolving this problem. However, other issues associated with this gasifier must still be resolved. The systems operating on the low-temperature process have been constructed more recently and consequently have less operating history, but materials issues have arisen that have required significant effort to address and resolve. The objective of this paper

is to describe some of the material failures in the two low-temperature reformer/gasifier systems and then to present either the solution being employed or the approach to finding a solution.

SYSTEM DESCRIPTION

The low-temperature reformer/gasifier, shown schematically in **Fig. 1**, includes a fluidized bed of sodium carbonate particles in which steam reforming of the organic components of the black liquor is carried out. Heat for the endothermic reforming reaction occurring in the fluidized bed is provided through a series of heat exchanger tubes, often referred to as *resonance* or *heater tubes*, which are immersed in the bed.

A pulsed combustion process is used to enhance heat transfer from these heat exchanger tubes. The pulsed process provides a number of advantages: high heat transfer rates, low levels of NO_x production, and more uniform distribution of heat in the tubes [5]. In the pulsed heating process, combustion occurs in the refractory-lined combustion chamber at a frequency of 50-100 Hz. As a result of the pulsating combustion, velocity fluctuations occur in the flue gas flow. These fluctuations promote heat transfer by disrupting the convective boundary layer that develops along the tube's inner surface. The pulsed combustion results in lower temperatures in the combustion chamber, but it also results in some unburned fuel leaving the combustion chamber and burning down the length of the tubes. The lower combustion chamber temperature results in less production of nitrogen oxides (NO_x), which is another benefit of this design. Combustion of a small portion of the fuel in the heater tubes helps distribute the heat more uniformly along the length of the tubes.

To temper the transfer of heat from the combustion gas to the pulse heater tubes, particularly in the first section of the tubes, 0.66-m (26-in.) long shield tubes are positioned inside the first portion of each of the heater tubes to provide some protection to this section of the tube and prevent the possibility of smelting on the tubes. **Figure 2** shows the major components of the heater tube modules, including the panel containing the aeroválves that control the pulsating combustion, the combustion chamber, the shield and heater tubes, and the exhaust plenum. **Figure 3** is a photograph of an actual heater tube module before installation in the reformer/gasifier.

One observation made by the authors during the previous experience with the New Bern low-temperature reformer/gasifier was that the stainless steel heater tubes were operating in a temperature range where precipitation of chromium carbide on grain boundaries (typically referred to as sensitization) was possible. Sensitization of a stainless steel alloy makes it susceptible to intergranular attack. In the New Bern case, sensitization of the stainless-type alloy, along with formation of polythionic acid during a shutdown when moist air contacted the sulfide scale present on the tubes, resulted in intergranular cracking characteristic of polythionic acid stress corrosion cracking. To avoid sensitization of the heater tubes in the Big Island and Trenton facilities, type 321 titanium-stabilized stainless steel was selected as the material for the heater tubes. Because of the anticipated service at considerably higher temperatures, type 330 stainless steel and alloy 800H were selected for the shield tubes for the Trenton and the Big Island facilities, respectively. These choices were based on oxidation resistance to the anticipated conditions, but selections were also influenced by material availability.

A DOE project, "Performance of materials in black liquor and biomass gasifiers," provided funds for several tasks. One of those tasks was for laboratory studies in simulated environments to identify alternate materials for shield tubes and heater tubes in a reformer/gasifier processing kraft black liquor. Another task in the project provided for examination of degraded components and determination of the degradation mechanism(s).

LABORATORY CORROSION STUDIES

As one task of the DOE-funded project, laboratory tests have been conducted to expose selected materials to environments that simulate those anticipated for the steam reformer/gasifier. More specifically, oxidation tests have been conducted in air at temperatures of 1000°C and 1100°C to simulate the conditions the shield tubes are expected to encounter. As part of these tests, the samples are cooled and weighed on a regular schedule. For the 1000°C test, the samples are weighed every 500 h; the samples exposed at 1100°C are removed and weighed every 100 h. **Figure 4** shows weight change results for selected alloys at the two test temperatures. The results of these tests show the alloys tested can be roughly divided into three groups: conventional stainless type chromia-forming alloys, superaustenitic chromia-forming alloys, and alloys that form an alumina surface layer. Although the alloys

that form an alumina scale showed the least weight gain, issues such as fabricability, weldability, and availability would have to be addressed before these alloys could be selected as a replacement for the shield tubes.

Other laboratory tests conducted include exposure of possible heater tube materials at 675°C to the simulated fluidized bed environment of a reformer/gasifier processing kraft black liquor. Because the observation of carbide formation in the heater tubes had not been made at the time the test was designed, no carbon-containing component was included in the test gas. Consequently, this test only provided information about the relative behavior of selected alloys in an environment containing steam, hydrogen, hydrogen sulfide, and argon. The gas composition was selected to give the oxygen and sulfur partial pressures originally expected for the fluidized bed environment.

Unlike the heater tube alloys, the shield tube alloys are expected to encounter temperatures of 1100°C or higher. Because the alloys selected for the shield tubes, type 330 stainless steel and alloy 800H, did not perform well in the high temperature air oxidation tests, the operators of the reformer/gasifiers were encouraged to remove a shield tube for destructive examination. As will be described in the following section, serious degradation of this tube was found, so additional shield and heater tube samples were provided by the reformer/gasifier operators.

COMPONENT EXAMINATIONS

During the past year, various components—primarily heater tubes—were provided by the two facilities for examination. The first component examined (a shield tube) was selected because of concerns raised by laboratory oxidation studies [6-8] that thinning rates might be excessive. When this component was found to be degraded, a request was made for additional samples. During initial efforts to begin operation, both facilities encountered problems with overheating of the pulse heater tubes. First, samples of severely damaged heater tubes were examined and evidence of degradation by several modes was observed. Subsequently, additional type 321 stainless steel heater tube samples that had experienced less apparent degradation were examined. As problems continued to be observed, samples of other alloys were examined, as were other structural components that had been exposed to the reformer/gasifier environment. Brief summaries of some of these examinations are provided.

One of the analysis techniques used extensively in the examination of these tubes was an oxalic acid etch. According to the test specification (ASTM A262), the sample should be immersed in a 10% oxalic acid solution for electrolytic etching with a current of 1 A/cm² for 90 s [10,11]. If chromium carbide precipitates are present on the grain boundaries, this region will be preferentially attacked leaving what appear to be ditches on the grain boundaries when examined at 400-500 X magnification, thus the common name of “ditch test.” If there are no carbide precipitates on the grain boundaries, the oxalic acid etch will preferentially attack some grains, leaving a surface that appears to have many steps.

Trenton shield tube examination

To address the question of whether the high temperature laboratory oxidation studies provided a reliable prediction of shield tube alloy performance, the shield tube (actually 1 in. schedule 40 pipe) shown in **Fig. 5** was provided for examination; this consisted of wall thickness measurements and metallographic analysis. Wall thickness measurements were made at eleven equally spaced locations along the length of the tube and at eight equally spaced points around the circumference of the tube at these eleven locations. The results (**Fig. 6**) indicate significant thinning along one side of the tube. The orientation of this tube was not marked when the tube was removed, so there is no way to determine whether the thinning was primarily on the top, bottom or some other position. Nevertheless, the extent of thinning was greater than the normal variation expected in tube wall thickness indicating significant degradation, almost certainly oxidation, along a portion of the tube.

Samples were taken from this shield tube at five approximately equally spaced locations along the tube, and these were prepared for standard metallographic, scanning electron microscope (SEM) and electron microprobe examinations. **Figure 7** shows a micrograph of a typical cross-section of the tube wall along with higher magnification views of the inner and outer surfaces. These micrographs show unexpected and extensive precipitation on grain boundaries and in the matrix. To better characterize these precipitates, a scanning electron

microscope (SEM) was used to produce a micrograph (**Fig. 8**), which shows distinct grain boundary and matrix precipitates. Further refinement in the analysis was accomplished by using the electron microprobe to produce the elemental maps shown in **Fig. 9**. These maps show the distribution of selected elements within an area covering a few grains. From these data and a separate elemental analysis, the precipitates in the grain boundaries appear to be primarily chromium carbides, probably an $M_{23}C_6$ carbide. The precipitates in the grains show a greater variability in composition than those on the grain boundaries. In all cases, chromium, silicon, and carbon are enriched, but the degree of enrichment varies considerably from one particle to another. Some precipitates are the $M_{23}C_6$ type chromium carbide, others are a silicon-enriched phase. The presence of these carbides would make the alloy susceptible to intergranular stress corrosion cracking, but a suitable corrosion agent and a tensile stress would have to be present for cracking to actually occur. The precipitates would also have a detrimental effect on the near room temperature ductility of the alloys.

Samples of this and several other degraded components were submitted for chemical analysis. The results confirmed the composition of the alloys, but they also indicated that the carbon content of the various alloys was significantly greater than the nominal content specified for those alloys.

Despite the expectation of a low carbon activity in the gas passing through the shield tube, there must have been a higher than expected temperature, a higher carbon activity, or a non-protective scale for the tube to be extensively carburized after a relatively short exposure. The discovery of the significant thinning and the carbide precipitates in this shield tube indicated a need to examine additional shield and heater tubes.

Examination of degraded Big Island heater tube

The two type 321 stainless steel pulse heater tubes (actually 1½ in. schedule 40 pipe) shown in **Fig. 10** were removed from the heater tube bundle of a reformer/gasifier (**Fig. 11**) after very short service because of overheating of the tubes caused by bed fluidization problems. As shown in the inset picture in **Fig. 10**, one of these tubes had a through-wall crack, and that tube was selected for examination. Four longitudinal cross sections were cut from the region of the crack. Circumferential sections were cut at 3.8, 7.6, 11.4, and 73.7 cm (1½, 3, 4½, and 29 in.) from the apparent failure site. A short section from the end of the shield tube was included with the heater tube sample and circumferential sections were cut from each end of that shield tube.

The micrographs in **Fig. 12** show longitudinal cross sections through the crack; the micrograph on the left shows the outside diameter (OD), the micrograph on the right shows the inside diameter (ID). Some of the scale has spalled, but a massive reaction layer is apparent on both surfaces. The remaining metal is about 1 mm (0.040 in.) thick, which is only about 25% of the original thickness. Oxalic acid etching of the sample revealed the presence of grain boundary carbide precipitates on the OD and ID (**Fig. 13**), but the more extensive carburization on the OD strongly indicates the carbon entered from the bed side of this tube.

The cross section taken from this heater tube 3.8 cm from the crack suffered significant thinning and scale formation (**Fig. 14**), but the remaining metal was thicker than at the crack. After oxalic acid etching, severe grain boundary precipitation was evident, but, as in the previous sample, the precipitation was more extensive near the OD surface than the ID surface. In fact, examination of the other three cross sections showed the grain boundary precipitation extended through the full length of the tube section that was examined. The extent and distribution of carbide precipitates indicated there was a source of carbon on the fluidized bed side of the tubes. The fact that carbon had penetrated into the tube and formed an extensive carbide structure could be explained if the tube temperature had reached at least 850°C [12], well in excess of the intended bed temperature of 605°C.

Examination of “unaffected” tubes

Examinations have been conducted on about a dozen pulse heater tubes—sometimes with the companion shield tube—that were exposed in one of the two operational facilities or in the pilot scale facility operated at the New Bern mill in the mid-1990s. All of these tubes had operating times of at least a few weeks. None of them had an outward appearance that suggested they were degraded by the exposure. The examination of each tube consisted of, at least, measurement of wall thickness around the circumference of the tube at several locations along the length of the tube and preparation and examination of metallographic samples taken from several locations on

each tube. The results of examination of tubes, representing different sources and made of different materials, is described next.

Big Island tubes 17-12 and 18-9. To determine the extent of reaction of other heater tubes and to determine if there might be a variation in the extent of reaction with distance along the length of the tubes, six nearly full-length tubes were examined. Two of those tubes, identified as 17-12 and 18-9 by their location in a tube module, were provided in pre-cut sections. **Figure 15** shows these two tubes. Short sections of shield tubes were included with the two tubes. Two metallographic samples were cut from each of the alloy 800H shield tube sections and six samples were cut from each of the two 321 stainless steel heater tubes. After oxalic acid etching, all four shield tube samples showed continuous attack or “ditching” along the grain boundaries. **Figure 16** shows selected micrographs of the OD and ID surfaces from both shield tubes. For the shield tube from tube 17-12, planar defects such as twin boundaries and slip planes, as well as grain boundaries, appear to be preferentially etched, suggesting chromium carbides had formed in all these locations.

All of the samples from each of the two heater tubes were examined metallographically around the full circumference at each sample location. **Figure 17** shows the etched microstructures from each end of tube 17-12. **Figure 18** shows the equivalent microstructures for tube 18-9. Tube 17-12 shows continuous ditching of grain boundaries on both the OD and ID along the full length of the tube. For tube 18-9, although there might be a small reduction in the extent of the ditching toward the cooler end, essentially 100% of the grain boundaries still contained chromium carbide precipitates along the full length of the tube.

Big Island tube 10-17. After 43 days of service, the heater and shield tube (10-17) shown in **Fig. 19** were removed from one side of a heater module where it was thought to be well away from the area where any degradation had occurred. Wall thickness measurements did not indicate any significant loss of material from any area around the circumference of the heater tube or the shield tube. Metallographic samples were taken from each end and the center of the shield tube. Samples also were taken from each end and the $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ locations along the length of the heater tube. Oxalic acid etching of the shield tube samples showed that a continuous layer of chromium carbide had formed on the grain boundaries of all three samples. **Figure 20** shows a typical example. In addition to the formation of grain boundary carbides, a corrosion product resulting from intergranular attack was found on grain boundaries; this extended a short distance below both the OD and ID surfaces. **Figure 21** shows micrographs of an as-polished sample. The micrographs show the attack was more extensive on the ID than on the OD of this shield tube.

This 321 stainless steel heater tube was outside the region in the module where obvious tube damage had occurred. Consequently, we hoped carbon might not have entered this tube and that it had avoided the formation of chromium carbides on the grain boundaries. The sample taken from the end of the tube nearest the combustion chamber did not show carbide formation. In fact, the tube’s microstructure was that of an as-fabricated tube, with no evidence of sensitization (**Fig. 22**). However, we determined that this end of the heater tube had been inside the water-cooled tube sheet, so this section of the tube was not heated to or above bed temperature. Microstructural examination of the other four sections of this heater tube revealed the usual pattern of carbide formation on the grain boundaries (**Fig. 23**). Both sets of micrographs in this figure show the carbide structure is more continuous on the OD than the ID suggesting the source of the carbon was from the fluidized bed. The other point learned from these micrographs is that the extent of carbide formation does not vary significantly from the $\frac{1}{4}$ position to the end of the tube.

Trenton shield tube. The 330 stainless steel shield tube shown in **Fig. 24** is another component that was removed from a reformer/gasifier heater module. Wall thickness measurements did not show any significant pattern of wall thinning around or along the length of the tube. A few isolated measurements did average about 0.33 mm (0.013 in) less than the nominal wall thickness, but the remainder of the tube averaged approximately that amount above the nominal wall thickness.

Eight metallographic samples were prepared from this tube. The observations of carbide formation were consistent with what has been seen on previous shield tube examinations. **Figure 25** contains micrographs showing the results of the oxalic acid sensitization test on the second and seventh samples. Although it is fabricated of 330 stainless steel, a different material than the alloy 800H shield tube from Big Island tube 10-17,

this shield tube also shows some shallow intergranular attack, with accompanying corrosion product, on both the OD and ID of the tube. **Figure 26** shows an example of this attack.

Big Island heater tube sections. The two tubes shown in **Fig. 27** were removed from the hotter end of a heater tube after about 6 weeks of service. The type 321 stainless steel is the standard material used for the heater tubes, while alloy UNS N12160 is a nickel-cobalt-chromium (Ni-Co-Cr) alloy that was considered as a replacement for the 321 stainless. Wall thickness measurements did not show significant thinning on either tube. Metallographic samples were cut from the end of each tube, mounted, polished, and photographed after light etching, and then etching to determine whether the samples were sensitized. For the 321 stainless steel sample, **Fig. 28** shows micrographs of the OD and ID surfaces for the two etched states. The results of the sensitization test are consistent with the observations for other heater tubes examined; ditching indicates chromium carbides are present on both the OD and ID of this tube. **Figure 29** shows the microstructures on the OD and ID for the Ni-Co-Cr alloy in the two etched states. As with the stainless steel tube, the oxalic acid sensitization test shows chromium carbides are present on the grain boundaries.

DISCUSSION

The observation of extensive penetration of carbon into the shield and heater tubes in the two full-scale steam reformer/gasifier facilities was unanticipated. Many years ago, sensitization was observed in heater tubes removed from the New Bern demonstration-scale system, but switching to a stabilized stainless steel, such as type 321 or 347, was expected to resolve that problem. This was based on the assumption that the carbon involved in the formation of chromium carbide all came from the carbon originally present in the alloy. What was not anticipated was the penetration of carbon from the reformer/gasifier environments into the shield and heater tubes.

The rapid formation of extensive carbides in stabilized stainless alloys at temperatures expected to be less than 700°C indicates that there must be operating conditions that have not been properly defined. Possibilities include higher than expected temperatures, considerably higher than anticipated carbon activity, and systematic damage to make the chromium oxide surface layer nonprotective. Because of problems with fluidization of the bed, there is no question that the temperature of the tubes reached values much higher than intended. However, examination of tube 10-17 and the two short tube sections from Big Island showed that carburization occurred during recent operating periods when fluidization was better controlled and tube temperatures were assumed to be near the expected level.

Given the recent measurements of the reformer gas composition by the authors, there is no question that the carbon activity was higher than originally expected. However, even with the higher carbon activity, we would expect the 321 stainless steel heater tubes to be resistant to carburization at temperatures below 800°C [12]. Nevertheless, carburization is observed, so the question has to be raised as to whether sections of the heater tubes intermittently reached much higher than intended temperatures or if some other effect made the alloy susceptible to carburization.

Carburization of the 330 stainless steel and alloy 800H shield tubes was unexpected because the carbon activity was not predicted to be high enough for that to be a concern. Some carbonaceous material was expected to reach the shield tubes in the form of uncombusted fuel, but combustion was expected to continue as the gas passed through the shield tubes so that the carbon activity would not be high enough to cause any degradation of the tubes. Clearly, as with the heater tubes, something about the shield tube operating conditions was not as expected, so that carburization did occur.

Another possible explanation for the ease of carbon penetration is the possibility that the chromium oxide layer is not protective. The tubes are subjected to fluctuating stresses from several sources; the pulsed combustion results in a 50-60 Hz pressure cycling, the fluidization action of the bed imparts forces on the heater tubes that will flex the tubes, and the low frequency vibrations of the reformer vessel could cause some stress fluctuations in the heater tube bundle and consequently, the individual tubes. The question is whether any of these vibrations are sufficient to cause microcracks to form in the oxide layer on these tubes. If that were to be the case, then the microcracks could provide an easy path for carbon entry into the alloy. In every case, carburization occurs in the presence of oxide scales of varying thickness, thereby indicating that these surface products were not protective.

Therefore, work to identify alloys that can form protective scales under these conditions is being pursued and alloys with the potential for forming such a scale are being provided for field exposures.

Because of the carburization seen in the heater tubes, measurements of the fluidized bed gas composition were made at various facilities. These measurements determined that the concentration of methane and other carbon-bearing species was higher than originally anticipated. Consequently, a test system has been modified to permit exposure of selected metallic samples to an environment that contains mixed gases with an oxygen partial pressure and a carbon activity similar to that measured in the fluidized beds. Calculations have been made to determine the oxygen partial pressure and the carbon activity, and a gas mixture has been identified that will reproduce those conditions in laboratory corrosion tests.

CONCLUSIONS

The shield and heater tubes from two North American mills with operating steam reformer/gasifiers were examined to determine the extent of any degradation and to identify the mechanisms responsible for the degradation. Components that showed no apparent evidence of damage have been examined, and evidence of extensive carburization has been found. Shield tubes have shown carburization or oxidation, and heater tubes have shown extensive evidence of carburization.

The formation of chromium carbides on the grain boundaries sensitizes the tubes and leaves them susceptible to intergranular stress corrosion cracking particularly during downtime when acidic condensates can form. These carbides also reduce the room temperature ductility and make the tubes more prone to brittle failure at temperatures well below operating conditions. However, no brittle failures of heater or shield tubes have been reported.

The composition of the gas in the reformer vessel or in equivalent locations in pilot scale systems was determined, revealing the carbon activity was higher than expected.

Testing in a modified product gas is being conducted to address the effect of a carburizing component in the environment of the heater tubes.

Tubes of alternate shield and heater tube materials have been identified and installed and are being exposed in the reformer/gasifiers in an effort to find an alloy with increased resistance to carburization. However, short sections of two heater tube alloys, 321 stainless steel and a Ni-Co-Cr alternate material, showed roughly equivalent levels of carburization after about six weeks of exposure. **TJ**

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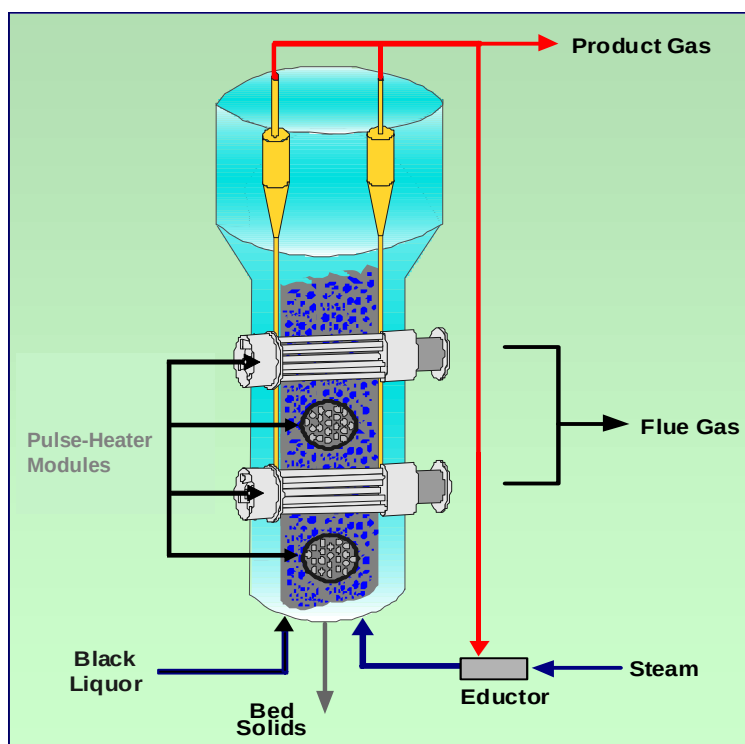


Figure 1. Schematic drawing of the low-temperature steam reformer/gasifier.

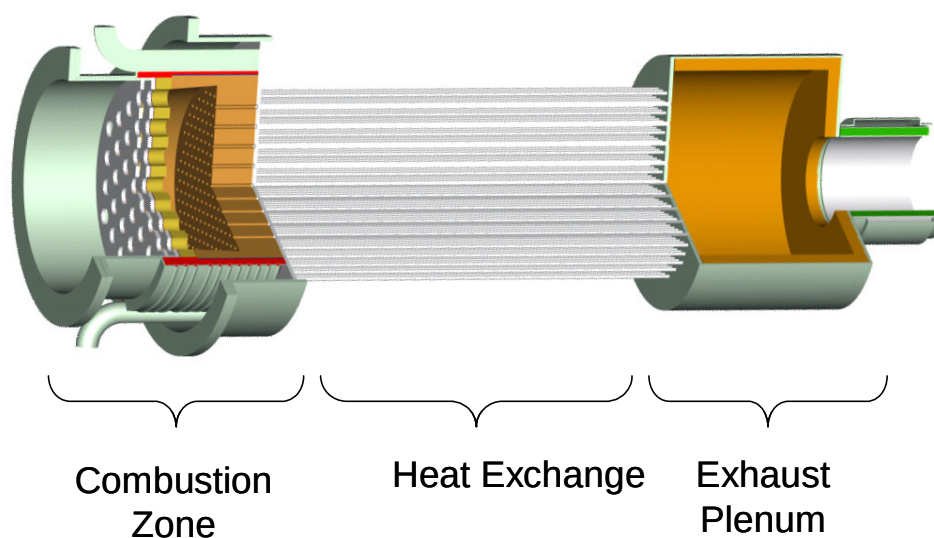


Figure 2. Schematic drawing of a pulse heater module. This drawing does not show the shield tubes, which are 66 cm (26 in.) long and are located in the portion of the heater tubes that are immediately downstream from the combustion chamber.



Figure 3. Pulse heater module showing the combustion chamber on the far left with the 253 heater tubes in the center and the exhaust plenum on the right.

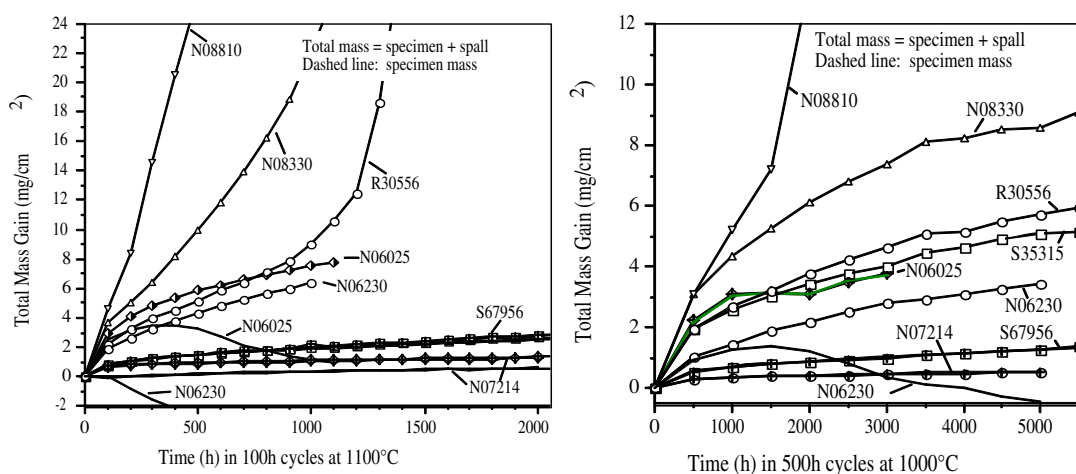


Figure 4. Weight change versus exposure time for selected alloys exposed at 1000°C and 1100°C in high temperature air.



Figure 5. Shield tube from the mill in Trenton, Ontario, Canada. Note the flared exhaust end on the right and the collar on the left end that provides for mounting in the tube sheet.

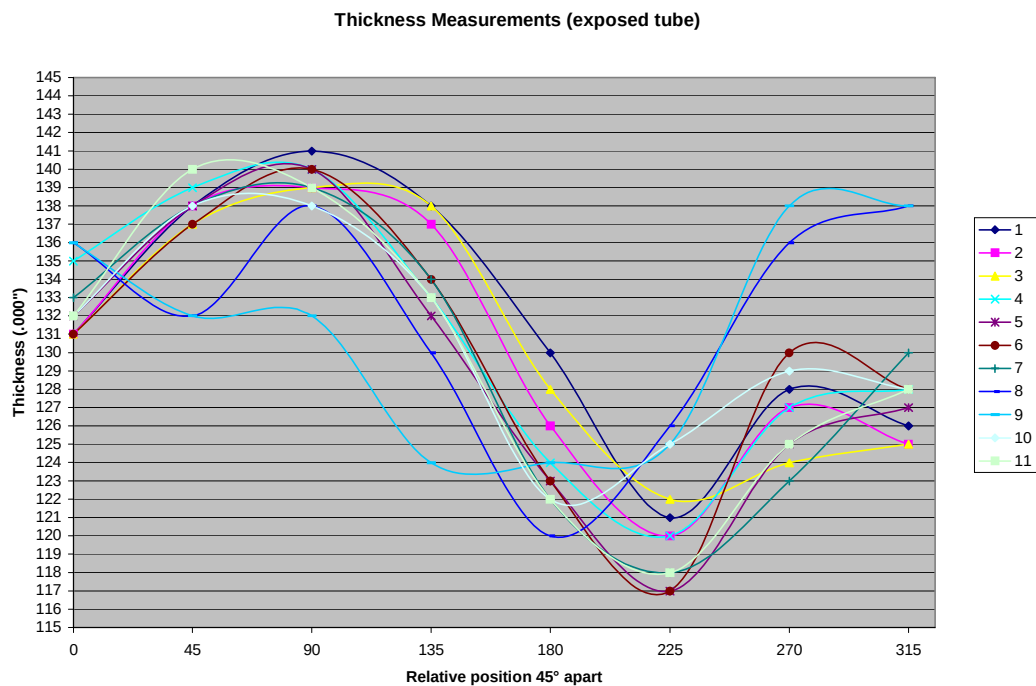


Figure 6. Wall thickness measurements as a function of position around the shield tube showing severe thinning on one side of the tube.

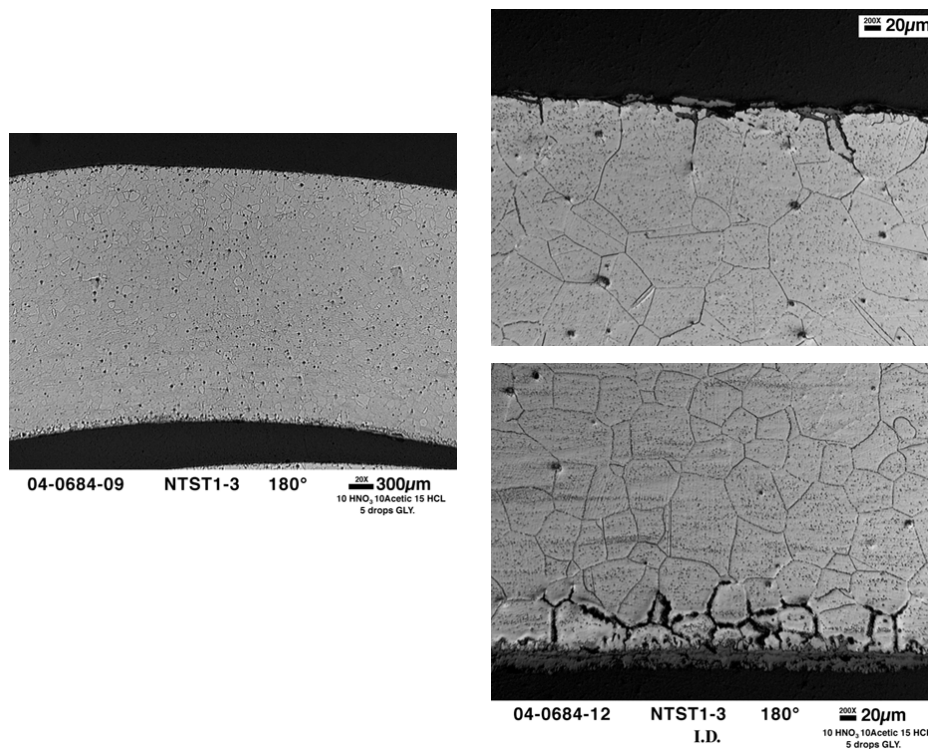


Figure 7. Micrographs showing the tube wall (left) and the outer (top right) and inner (lower right) surfaces of the shield tube. Note the outlined grain boundaries and the intergranular attack on both surfaces.

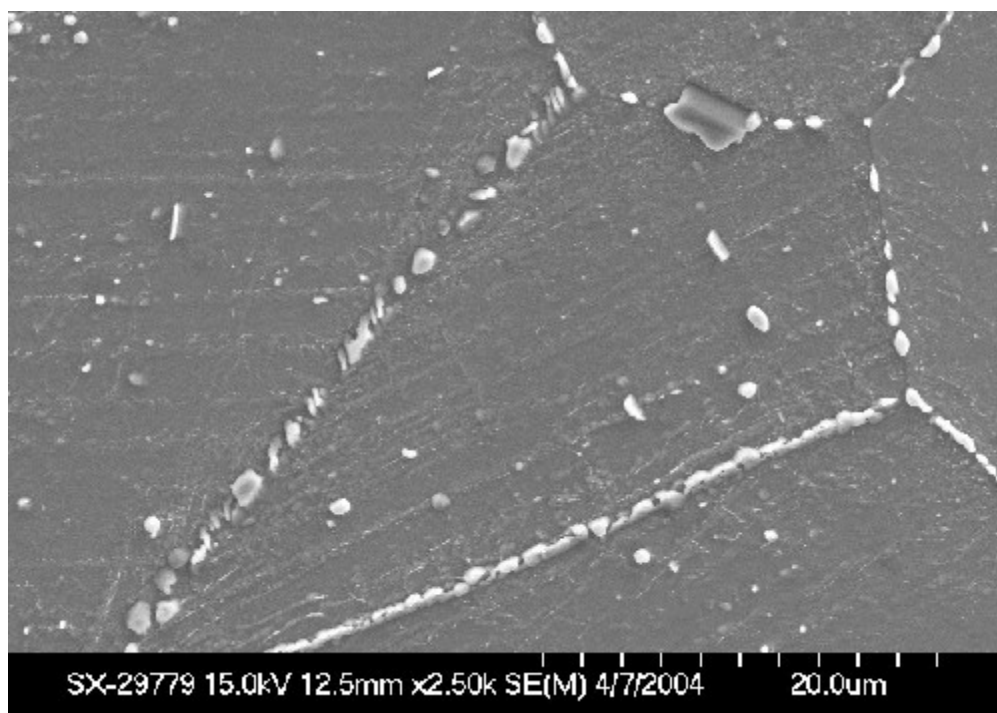


Figure 8. Scanning electron micrograph showing the grain boundary and matrix precipitates formed in the shield tube.

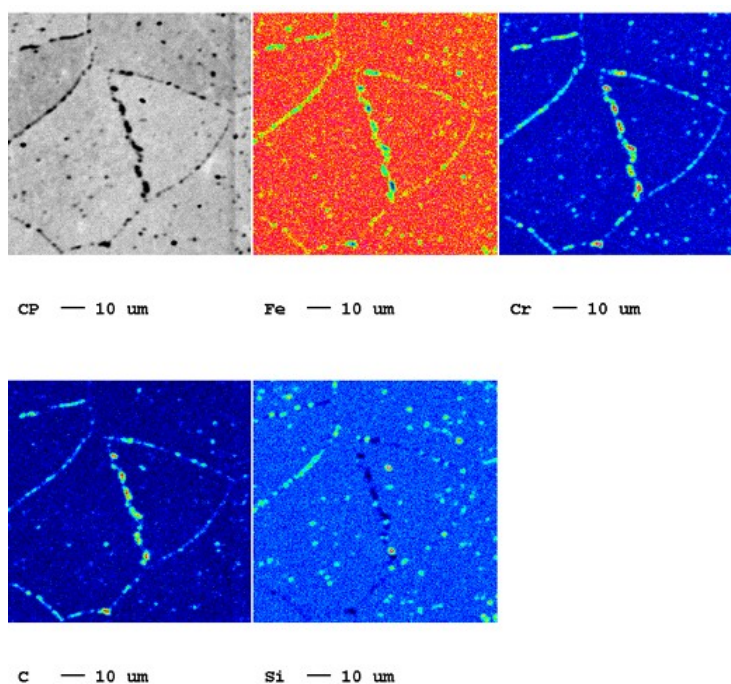


Figure 9. Electron microprobe elemental maps showing the concentration of chromium, carbon, and silicon in the grain boundary and matrix precipitates. The darker the color, the lower the concentration.

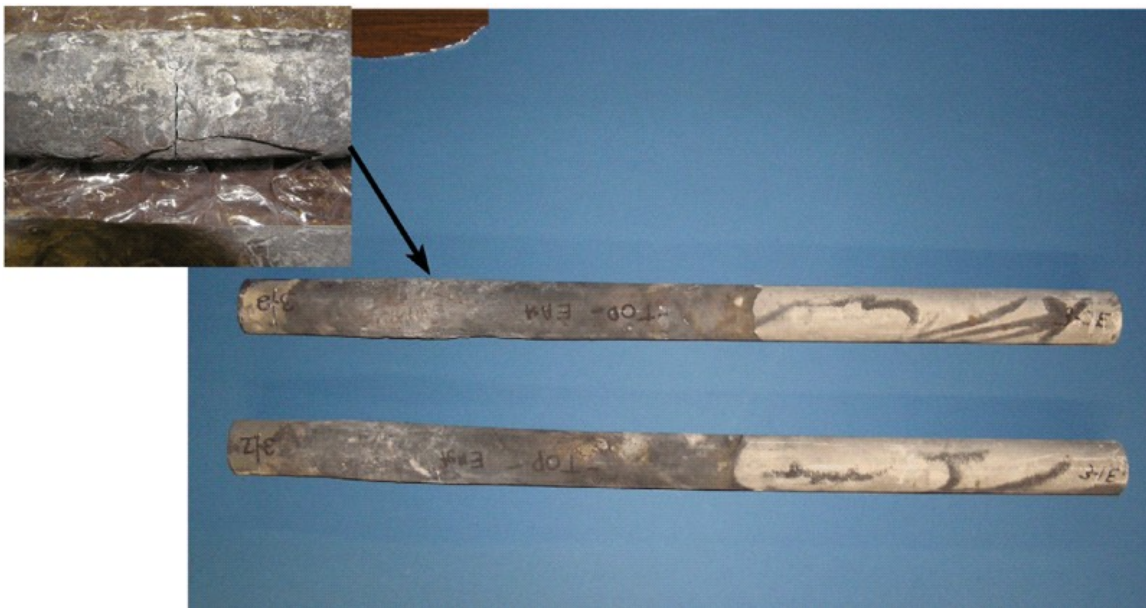


Figure 10. Pulsed heater tubes removed from the Big Island, Virginia, mill's reformer/gasifier. The inset photo shows a close up of the cracked area on one of the tubes.



Figure 11. Photo of the heater tube bundle from which the tubes in the previous figure were taken. The two damaged areas of the tubes are slightly above center in the picture.

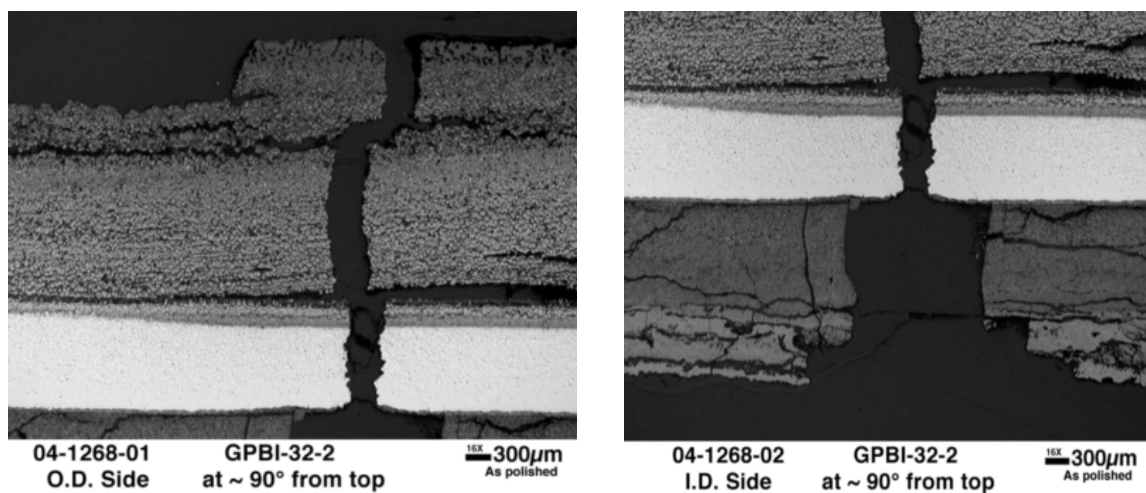


Figure 12. Micrographs showing the inner and outer surfaces of the pulse heater tube in the area where the through-wall crack occurred.

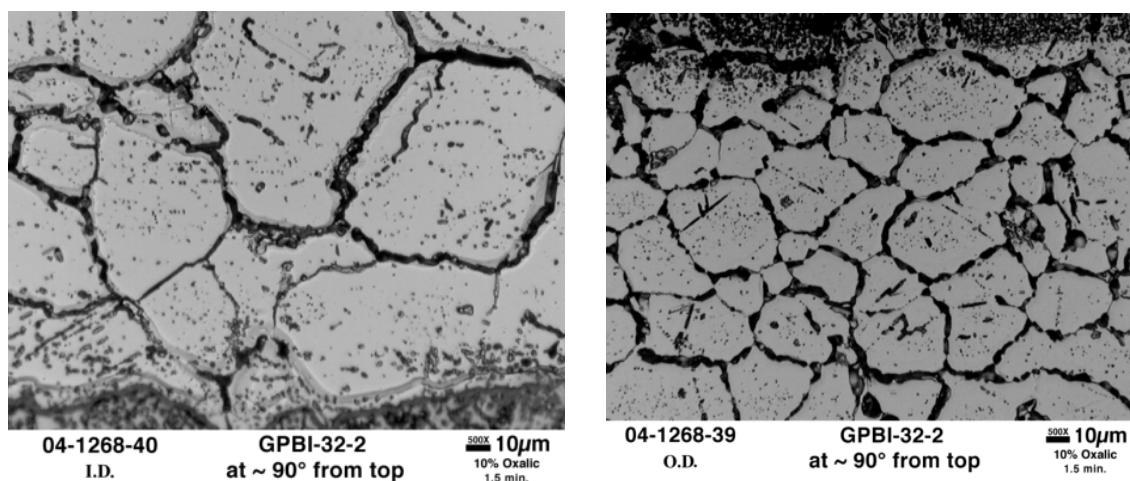


Figure 13. Micrographs showing the microstructure just below the inner and outer surfaces of the heater tube pictured in the three previous figures.

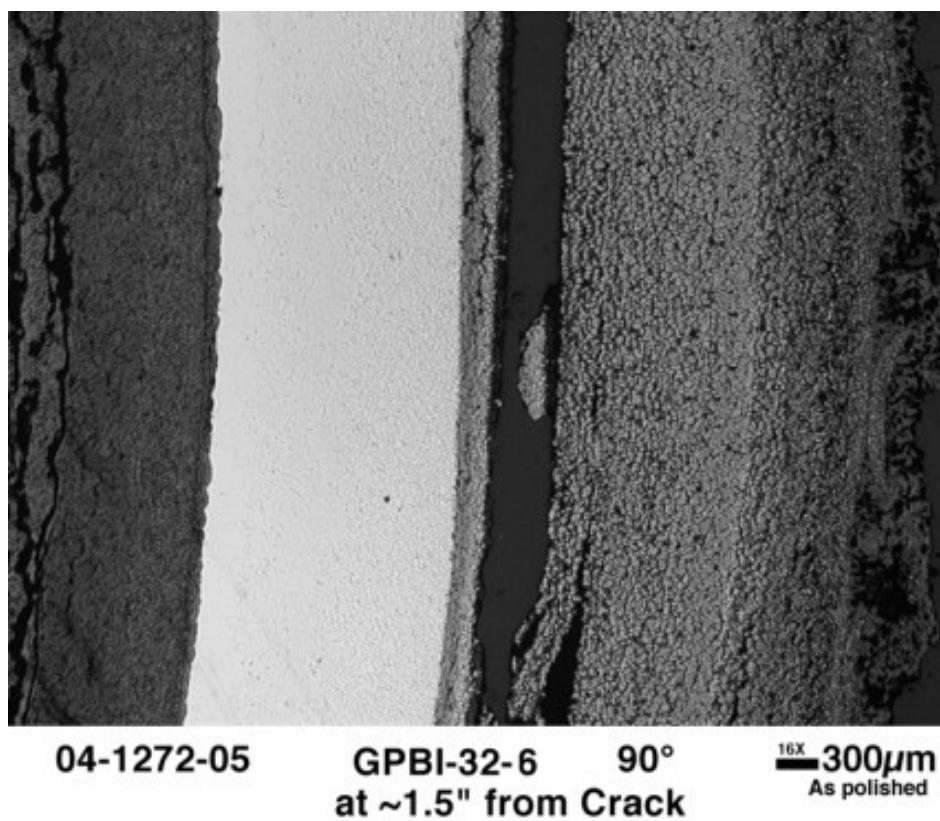


Figure 14. Cross section of the failed heater tube about 3.8 cm from the through-wall crack.



Figure 15. Heater tubes 17-12 and 18-9 that were taken from an area thought to be unaffected by overheating.

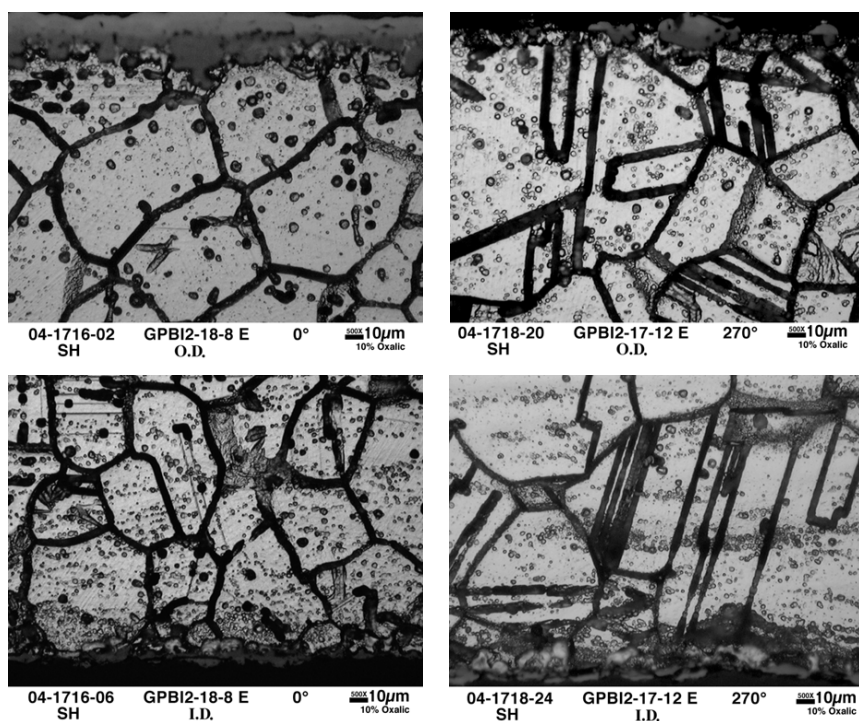


Figure 16. Micrographs showing the oxalic acid etched material just below the inner and outer surfaces of the shield tube from heater tubes 18-9 and 17-12.

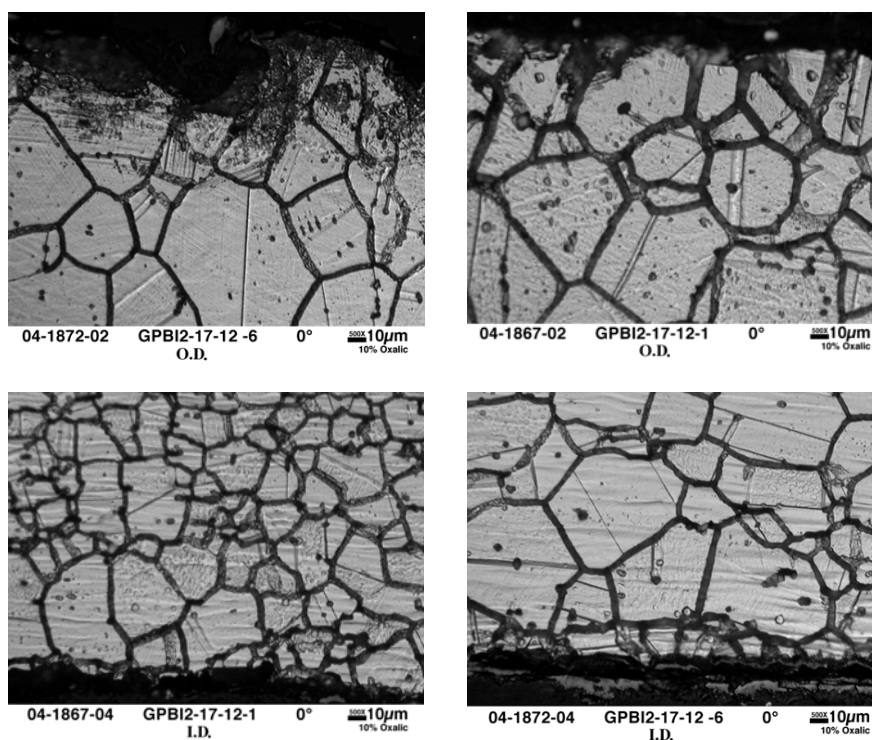


Figure 17. Micrographs showing the oxalic acid etched material just below the inner and outer surfaces from each end of heater tube 17-12.

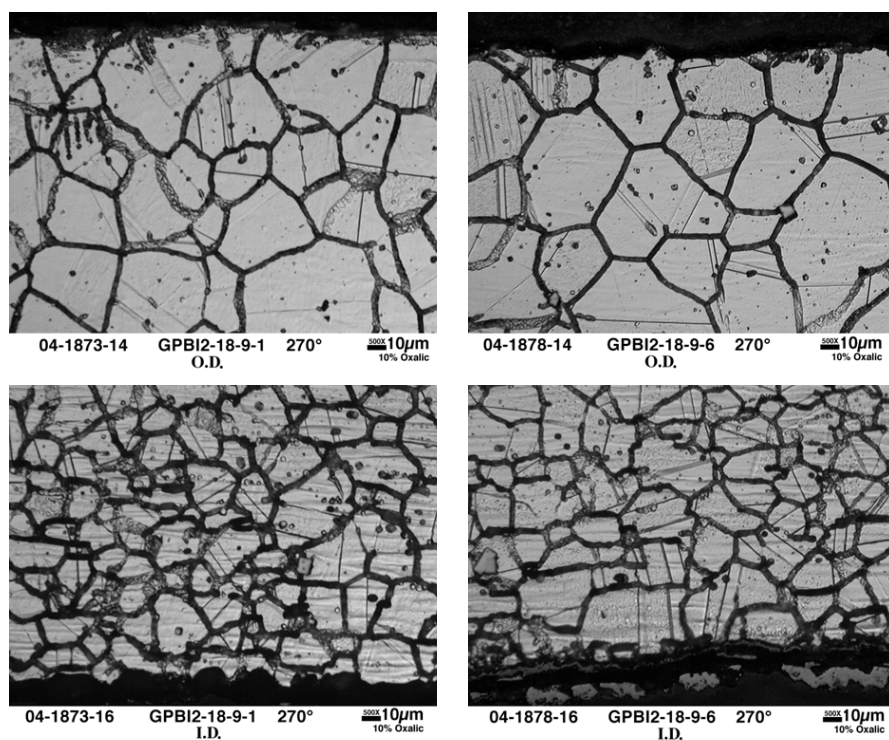


Figure 18. Micrographs showing the oxalic acid etched material just below the inner and outer surfaces from each end of heater tube 18-9.



Figure 19. Pulse heater tube 10-17 with shield tube. The shield (shorter) tube is 66 cm (26 in.) long.

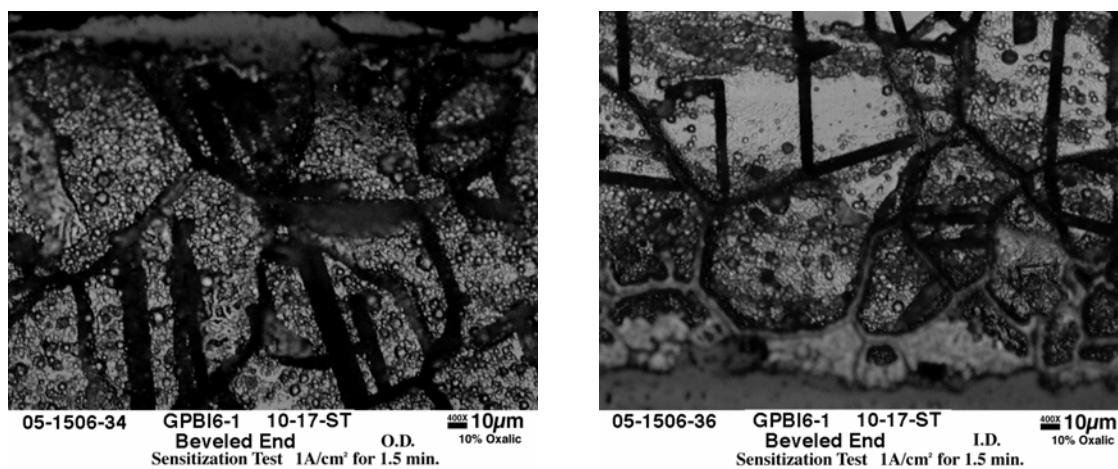


Figure 20. Micrographs of the oxalic acid etched surfaces of the flared end of the alloy 800H shield tube from heater tube 10-17.

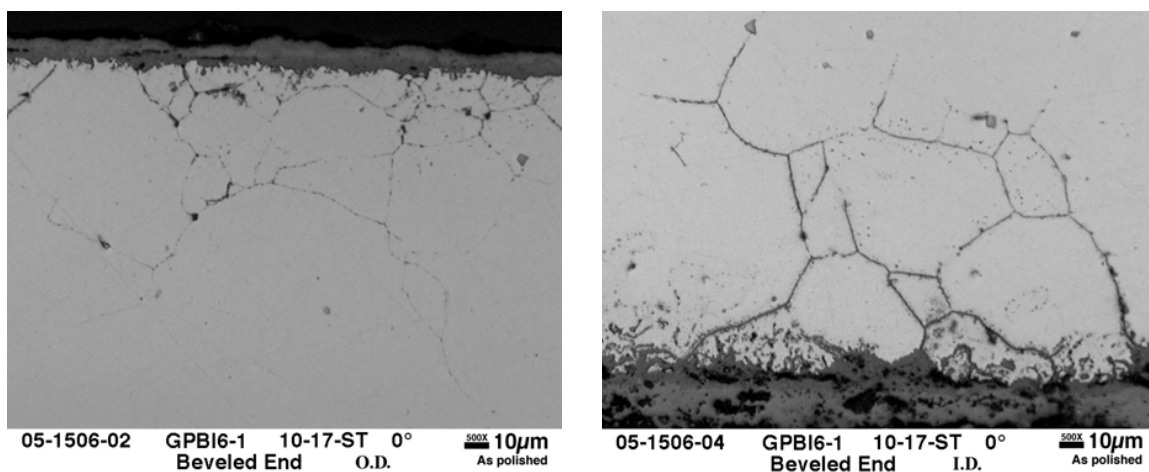


Figure 21. Micrographs of the as-polished surfaces of the flared end of the alloy 800H shield tube from heater tube 10-17 showing the presence of a corrosion product (dark color) on the grain boundaries near the surfaces.

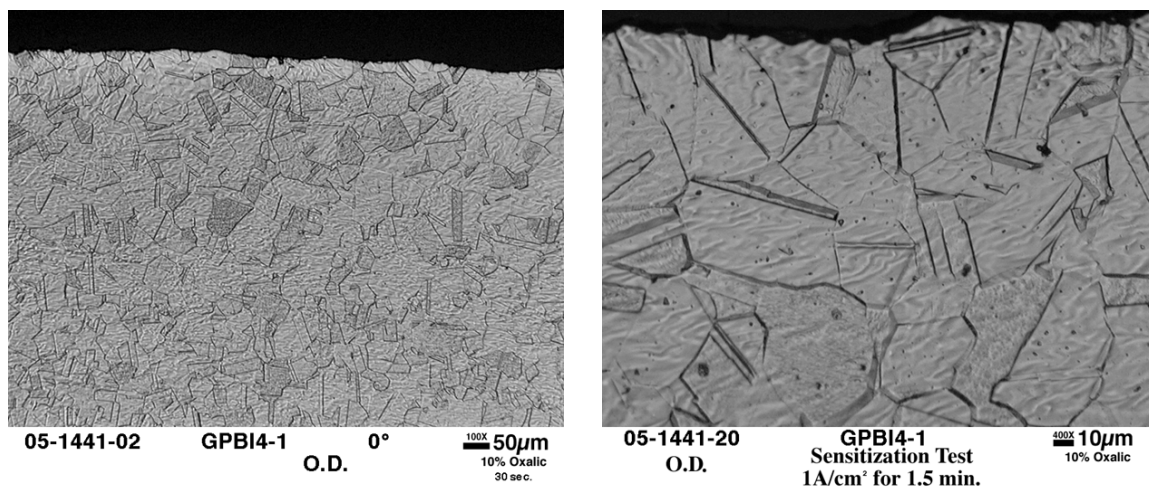


Figure 22. Micrographs of oxalic acid etched 321 stainless steel heater tube section that was inside the water cooled header of the pulsed heater module. The structure is that of an as-received stainless steel tube.

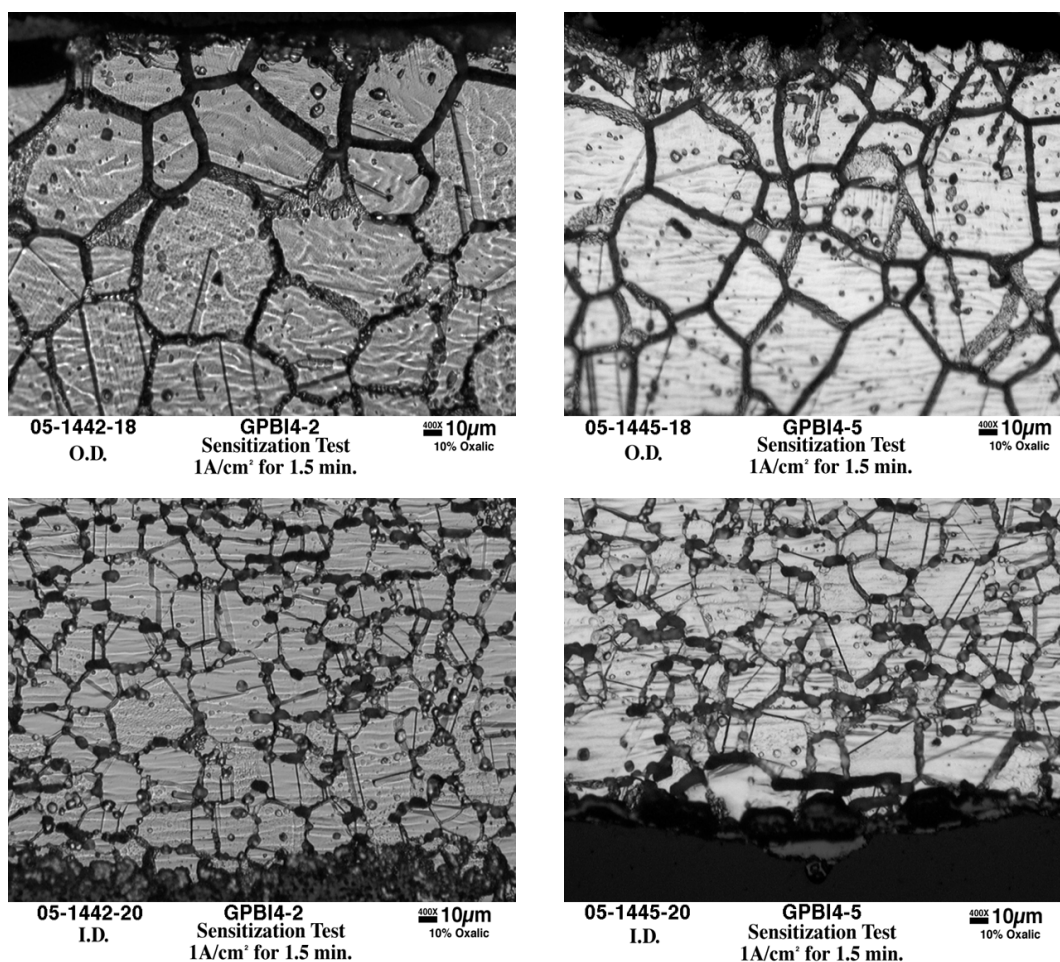


Figure 23. Micrographs of the oxalic acid etched material just below the inner and outer surfaces of sections taken from the end and the $\frac{1}{4}$ position along the length of tube 10-17.



Figure 24. Photos of the as-received 330 stainless steel shield tube from the Trenton, Ontario, mill and the tube as marked for wall thickness measurements and preparation of metallographic samples.

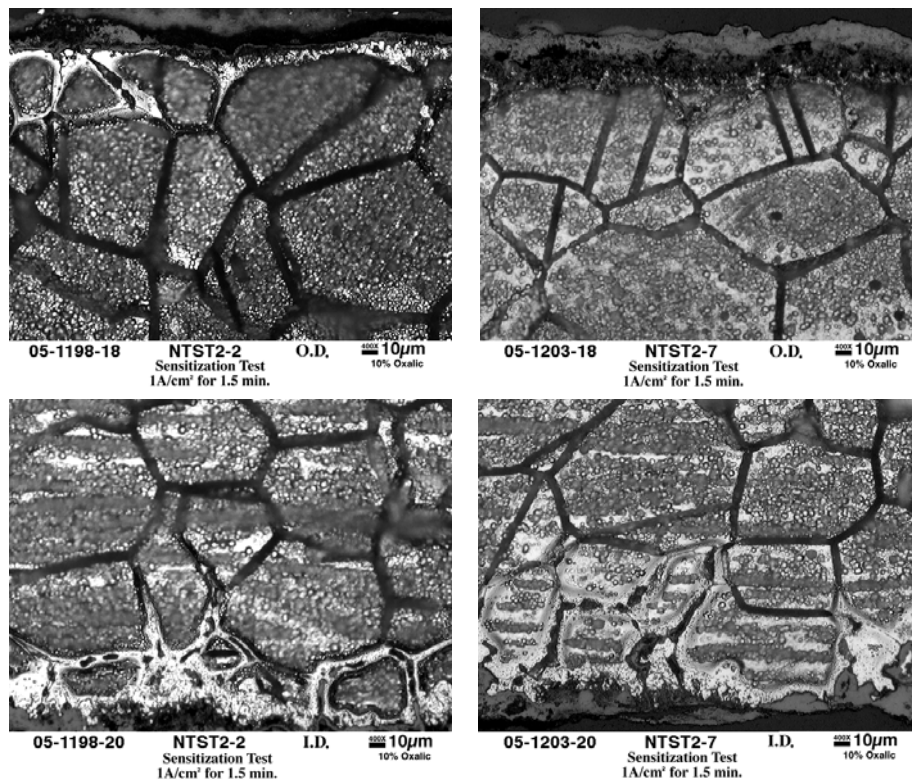


Figure 25. Micrographs of oxalic acid etched samples from the left and right ends of the Trenton, Ontario, mill's shield tube shown in the previous figure.

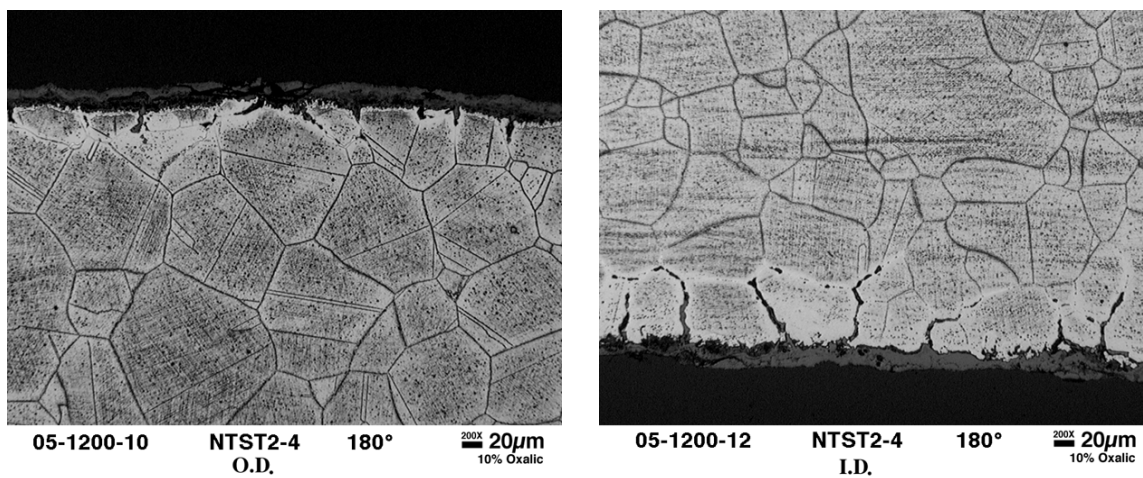


Figure 26. Micrographs of acid etched shield tube showing the intergranular attack originating on the inner and outer surfaces.



Figure 27. Photo of two sections of heater tube removed from the hotter end of the heater bundle.

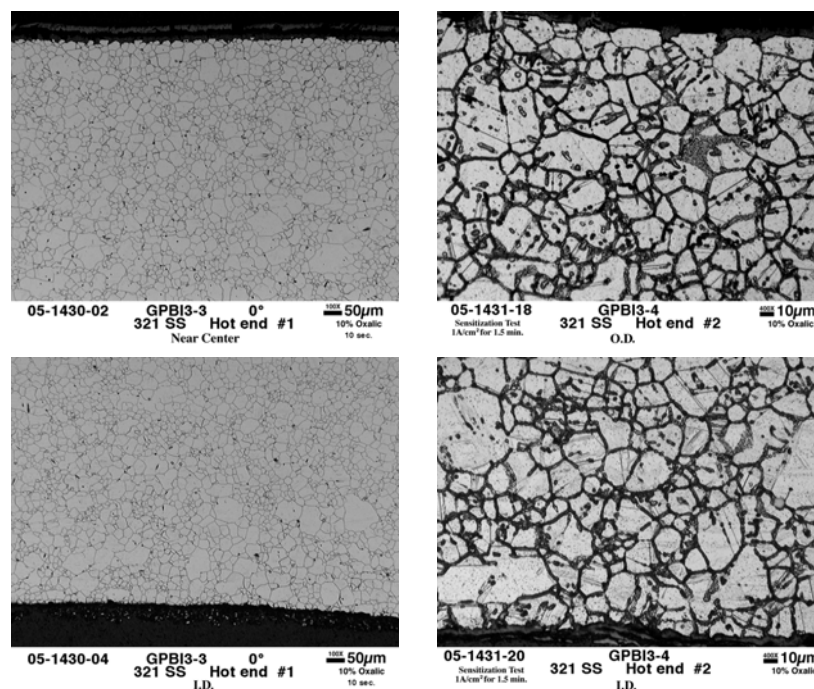


Figure 28. Low magnification micrographs (left) of the lightly etched inner and outer surfaces of the 321 stainless steel sample and higher magnification micrographs (right) of the more heavily etched inner and outer surfaces showing the ditching.

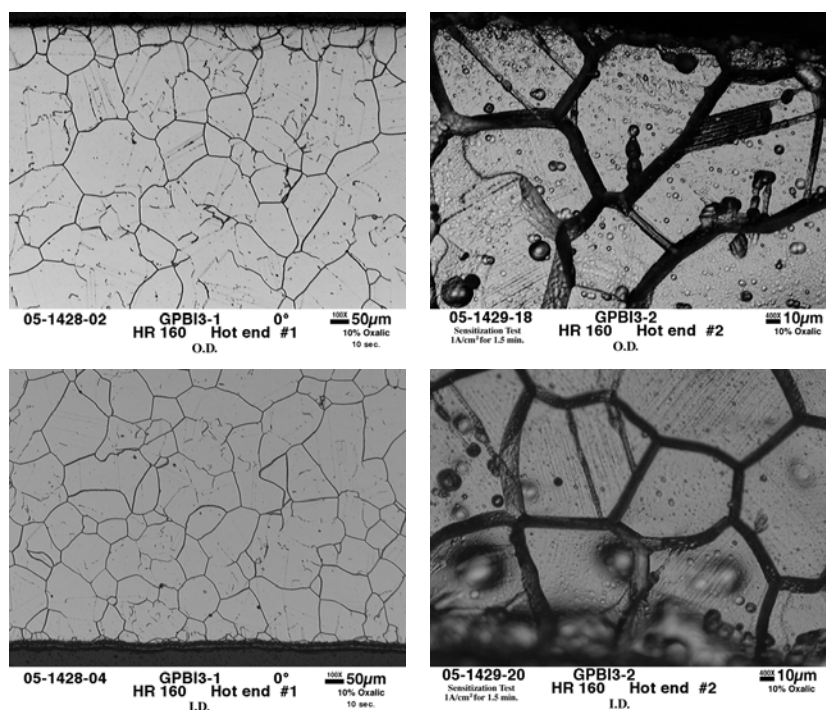


Figure 29. Low magnification micrographs (left) of the lightly etched inner and outer surfaces of the nickel-cobalt-chromium (Ni-Co-Cr) alloy sample and higher magnification micrographs (right) of the more heavily etched inner and outer surfaces showing the ditching.