STATUS REPORT ON STUDIES OF RECOVERY BOILER COMPOSITE FLOOR TUBE CRACKING

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ABSTRACT

Cracking of the stainless steel layer of co-extruded 304L stainless steel/SA2 10 Gd A 1 carbon steel black liquor recovery boiler floor tubes has been identified as one of the most serious material problems in the pulp and paper industry. A DOE-funded study was initiated in 1995 with the goal of determining the cause of and possible solutions to this cracking problem. These studies have characterized tube cracking as well as the chemical and thermal environment and stress state of floor tubes. Investigations of possible cracking mechanisms indicate that stress corrosion cracking rather than thermal fatigue is a more likely cause of crack initiation. The cracking mechanism appears to require the presence of hydrated sodium sulfide and is most likely active during shut-downs and/or start-ups. Based on these results and operating experience, certain alloys appear to be more resistant than others to cracking in the floor environment, and certain operating practices appear to significantly lessen the likelihood of cracking. This report is the latest in a series of progress reports presented on this project.

INTRODUCTION

Co-extruded (composite) tubes made with an outer layer of 304L stainless steel (304L) on a SA210 Gd Al carbon steel (CS) core were first introduced in Scandinavia to provide improved corrosion resistance for black liquor recovery boilers that were designed to operate at higher than conventional pressures and temperatures. These tubes were first used in place of carbon steel for complete wall panels in 1972 and for floors in 1978. Introduction in North America was more than five years behind application of these tubes in Scandinavia [1].

Use of the composite tubes solved the corrosion problems experienced by carbon steel tubes, but the stainless steel layer of these tubes was found to be susceptible to cracking around air ports, in smelt spout openings, and in floor tubes covered by molten smelt during operation. A serious concern developed because of the possibility that cracks in the floor tubes could result in leakage of water into the smelt bed with the possibility of a subsequent explosion. A number of studies were conducted to determine the cause of the cracking, and the cracking was attributed to mechanisms ranging from thermal fatigue to corrosion fatigue to stress corrosion cracking [2-5].

Because this cracking was considered a very serious problem for the paper industry, the U. S. Department of Energy provided funding for a multi-disciplinary program to investigate the cause of cracking in composite tubes and to

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identify improved materials or alternate operating procedures. The status of the studies on this project is the topic of this paper.

BACKGROUND

This project was divided into a number of tasks, and work on these tasks was distributed among the three participating research organizations, Oak Ridge National Laboratory, the Pulp and Paper Research Institute of Canada and the Institute of Paper Science and Technology. The tasks include:

- summarizing the existing information on composite floor tube cracking;
- characterizing the cracking by examining exposed tubes;
- characterizing the thermal, chemical and mechanical environment of tubes;
- measuring the residual stresses in as-fabricated and exposed tubes;
- using finite element modeling to predict the stresses at operating conditions;
- conducting laboratory studies of thermal fatigue, corrosion fatigue and stress corrosion cracking to evaluate various cracking mechanisms and
- evaluating alternate materials and changes in operating procedure to minimize the likelihood of cracking.

The balance of this paper will be used to summarize the progress on each of these tasks.

RESULTS

Summary of Existing Informatios

A report has been prepared and published [I] summarizing the information available in the published literature as well as in many unpublished inspection reports and failure analyses. Reports and analyses were provided by paper companies, boiler manufacturers, inspection companies and tube fabricators. It was noted in this publication that composite floor tubes in all boiler designs are expected to be vulnerable to this kind of attack. Furthermore, no failure mechanism could be identified although some cracks appeared to be due to thermal fatigue while others seemed to be caused by an environmentally assisted mechanism.

Characterization of Cracking

A large number of cracked tubes have been examined to identify the common characteristics of the cracks. Cracking in these tubes ranges from widely opened cracks in tubes that were probably operated in the cracked state for an extended period to the more typical transgranular cracks more often seen in tubes in North America to relatively short, narrow cracks; these three types are shown in Fig. 1. The widely opened cracks shown in Fig. la can usually be seen without any magnification or highlighting technique. During a dye penetrant inspection, these cracks “bleed” so much penetrant that they produce an indication that rapidly spreads over a fairly large area. The more typical cracks can almost always be seen during a dye penetrant check provided the surface of the sample has been appropriately cleaned and prepared. The fine cracks that are shown in Fig. lc are so small that they are not expected to give an indication during a dye penetrant check.

Features of the more typical cracks, which are shown in Fig. 1 b and have been described in numerous reports [6-8], include the following characteristics:

- transgranular cracking,
- relatively little crack branching,
- cracks that penetrate as far as the interface turn and proceed in the stainless steel parallel to the interface,
- cracks that reach the interface sometimes end with a corrosion pit that extends into the carbon steel, and
- opposite sides of a crack often have matching surfaces suggesting the sides have been pulled apart.

It is possible that cracks like those shown in Fig. lc are relatively new cracks while the cracks in Fig. 1 b have been subjected to thermal cycles that resulted in tensile stresses that tended to pull open the cracks.

Environment Characterization

A good knowledge of the environment of floor tubes is essential if the cracking mechanism is to be identified. Toward this end, samples of smelt and wash water have been collected and analyzed. One smelt sample was collected before water washing from the lower wall of a boiler with a decanting floor. Other samples were collected from the floor of slope-floored boilers after water washing. Analysis of these samples did not reveal the enrichment of sulfur, potassium and chlorine in the smelt taken from very near the tube surface that has been reported in Scandinavian studies of smelt compositions [1]. Efforts to collect additional samples will continue, possibly in collaboration with Finnish researchers [9].

Wash water samples have been collected from several boilers and analyzed to determine elemental concentrations and the pH. These results show concentrations of dissolved materials decrease with time into the water wash while the pH remains fairly constant and in the range of 11.5 to 13.0 depending on the boiler.

A significant effort has been directed toward defining the thermal conditions of floor tubes, and it has been learned that the temperature as measured on the crown of tubes can vary considerably. In a boiler in central Canada, the floor tubes near the spout wall experienced temperature spikes of at least 50 C° no more than once a week while tubes about 2 meters from the spout wall averaged as many as 6 thermal spikes per day. Unexpectedly, the areas on the floor where cracking was most severe were the areas where the thermal spike frequency was lowest. More information on the floor tube temperature measurements has been provided in two recent reports [10-11].

Residual Stress Measurement

Because of the significant difference in thermal expansion coefficients between carbon steel and 304L stainless steel (12.1×10^{-6}/°C vs 17.3×10^{-6}/°C), large stresses might be expected to develop during thermal cycling of composite tubes made of these materials. By using a combination of neutron diffraction and X-ray diffraction, the strain, and subsequently the stress, has been measured across the walls of composite tubes. These measurements have shown that axial and circumferential surface stresses are compressive in as-fabricated 304L/CS composite tubes from both of the major suppliers. Measurements have also been made on as-fabricated composite tubes made of modified Alloy 825/CS and modified Alloy 625/CS. Results of these room temperature measurements on the modified Alloy 825/CS tube show that the axial stress at the surface is close to zero and the hoop stress is tensile and no more than half the yield strength. Stresses in the modified Alloy 625/CS are similar in direction but smaller in magnitude. These results on room temperature stresses in individual tubes are used in the modeling studies to predict stresses in welded panels.

As will be described in the next section, the axial and circumferential surface stresses in composite 304L/CS tubes that are part of a tube panel are expected to be tensile after being cooled from operating temperature to room temperature. Stress measurements have been made on tube panels removed from recovery boiler floors, and the results show that, as predicted by the modeling, the surface stresses are tensile at room temperature.

To provide experimental results on the stresses in tubes at operating conditions and higher, neutron diffraction has been used to measure the stresses in the stainless steel layer of a composite tube while the tube is being heated. As the tube was heated from room temperature to a nominal operating temperature of about 300°C, the stresses at mid-thickness of the stainless layer changed from tensile to compressive, as predicted by the finite element model. As shown in Fig. 2, on further heating to about 400°C, some yielding occurred during the first temperature cycle, but on subsequent cycles from room temperature to 400°C, the deformation was elastic. This indicated that the yield stress of the 304L stainless steel was higher than predicted in published data, so subsequent modeling studies used the measured rather than the published values for the yield strength.

Finite Element Modeling of Stresses

The finite element modeling has utilized ABAQUS software to predict the stresses that will develop when composite tubes with the previously measured fabrication residual stresses are welded to a clad membrane to produce the tube panels [12]. The model was then extended to account for the effects of tube pressurization and the application of heat on one side to produce a temperature gradient across the tube wall on the fireside of the boiler.

The modeling predicted that before being heated the first time, the axial stresses were compressive and the circumferential or hoop stresses were tensile in the tube panel. All these surface stresses became compressive as the panel was heated from room temperature to operating temperature, but when the panel was cooled to room temperature the axial and hoop stresses became tensile. As noted in the previous section, room temperature strew measurements confirmed these room temperature stress results.

A potentially important issue with regard to stresses is the stress state of tubes during and after the thermal spikes that have been confirmed to occur on recovery boiler floor tubes. Modeling studies show that stresses remain compressive during the thermal spike but on cooling to operating temperature, stresses can become tensile. Whether or not tensile stresses develop depends on the magnitude of the spike and the material properties that are used in the modeling calculations. Previous modeling work showed that a thermal spike of 50 C° or more above operating temperature was sufficient to cause the hoop stress at the tube crown to become tensile. Even with the increase in yield strength of 304L stainless indicated by the thermal cycling experiments, this limiting temperature is expected to increase to about 60 C°. Consequently, it appears that thermal spikes result in tensile stresses being developed over essentially all the floor during any sustained operating period. However, it should be recalled that, at least on the Canadian boiler that has been studied extensively, the areas of greatest cracking are the areas with the lowest thermal spike frequency. Thus it does not appear that the surface stresses at operating temperature are the primary factor in whether or not cracking will occur in a particular area.

Examination of stresses in the carbon steel layer near the interface on the fireside showed that axial stresses are compressive, thereby preventing cracks from propagating into the carbon steel layer. However, axial stresses are tensile in both 304L and carbon steel layers near the interface in the membrane, so that transverse cracks can extend into the carbon steel layer as has been observed in some membranes.

In an effort to evaluate alternate materials to replace 304L stainless as the clad layer, the modeling studies described above were repeated for Alloy 625/CS and Alloy 825/CS composite tubes. Manufacturing stresses in the composite tubes were assumed to be the same as those measured in the 304L/CS tubes. Modeling of welding to make the tube panels showed development of tensile hoop stress and compressive axial stress at the tube crown. Upon heating to operating temperature, stresses change in magnitude but not in sign. The stresses then return to their original values upon cooling to room temperature, indicating that they remain elastic through the cycle. An important aspect of these results is that axial stresses for both Alloy 825 and Alloy 625 remain compressive throughout the cycle as shown in Fig. 3. Observations of floor tubes taken after service show that most cracks are circumferential and hence their growth is aided by axial tensile stresses. In this regard, Alloys 625 and 825 are better choices than 304L SS for the outer material of composite tubes.

Thermal Fatigue Studies

Thermal fatigue has been studied fairly extensively because it was frequently suggested as the cause of much of the cracking in composite tubes. These studies have included a thorough review of existing fatigue data for 304L stainless steel, optical and transmission electron microscopy examination ofsamples from laboratory tests and mill exposed tubes, and laboratory fatigue studies [13].

The thermal fatigue data collected during this study is compared to the ASME Sect. III, Subsect. NH design curve for 427°C isothermal fatigue of 300 series stainless steels in Fig. 4. This figure shows that all thermal fatigue data fall near or above the design curve regardless of the peak temperature used for the thermal cycle. If thermal cycles to 450°C are considered, the cyclic strains would be about 0.25% and the cladding would be expected to be able to tolerate 100,000 cycles or more. As noted in the section on environmental characterization, there is no evidence that a tube experiences anywhere close to that number of thermal cycles.

The optical microscopy reveals that the characteristics of cracks seen in floor tubes have some features more typical of stress corrosion cracks than fatigue cracks. Furthermore, transmission microscopy of cracked tubes and tubes from the laboratory studies revealed that the cracked tubes have definitely been exposed to thermal cycles but far fewer in number than seen in the uncracked fatigue test samples. As a result of these observations and studies, it is

clear that thermal fatigue alone is not the cause of the floor tube cracking. However, exposure of the tubes to a limited amount of thermal cycling is definitely occurring and should not be overlooked in considering various cracking mechanisms.

Stress Corrosion Cracking Studies

For the reasons just presented, thermal fatigue has been eliminated as the primary mechanism for formation of cracks in 304L/CS composite floor tubes. Given the characteristics of the cracking and the environment, this leaves stress corrosion cracking (SCC) as the most likely cause. For this to be the case, two conditions must be met: the tube surface must be stressed in tension, and a suitable (liquid) corrosive environment must be present. Although the stresses on the surface of a 304L/CS composite tube become compressive as the floor is heated to operating temperatures, new modeling data suggests that the surface may not remain in compression throughout an entire operating cycle. A change to tensile surface stresses will always occur on cooling below about 220°C (428°F), but it also appears possible for high temperature transients to stress the tube locally in a way that subsequently leaves the surface in tension. [11]. It now seems that the first condition for SCC may be satisfied at nearly any time through the operating cycle of the boiler. However, it still remains to be established whether crack initiation begins during periods of normal operation, or during some other, non-steady-state, or shutdown condition.

Hydrated sodium sulfide

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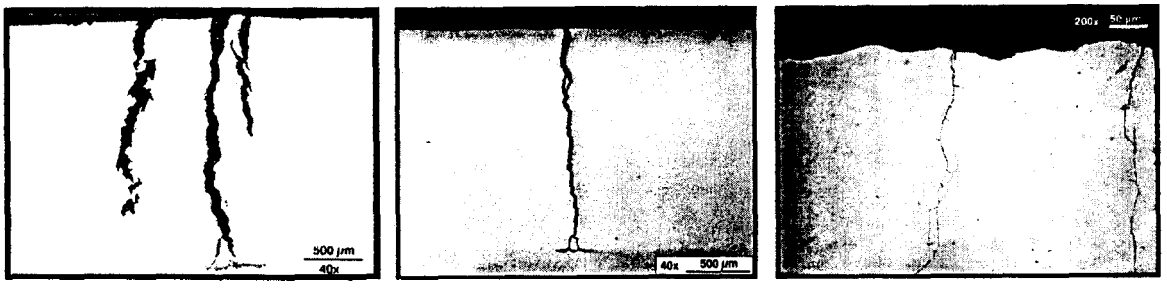


a) b) c)

Figure 1. Micrographs of cracks in the stainless steel layer of 304L/SA210 carbon steel; a) widely opened cracks, b) typical cracks, and c) short, narrow cracks.

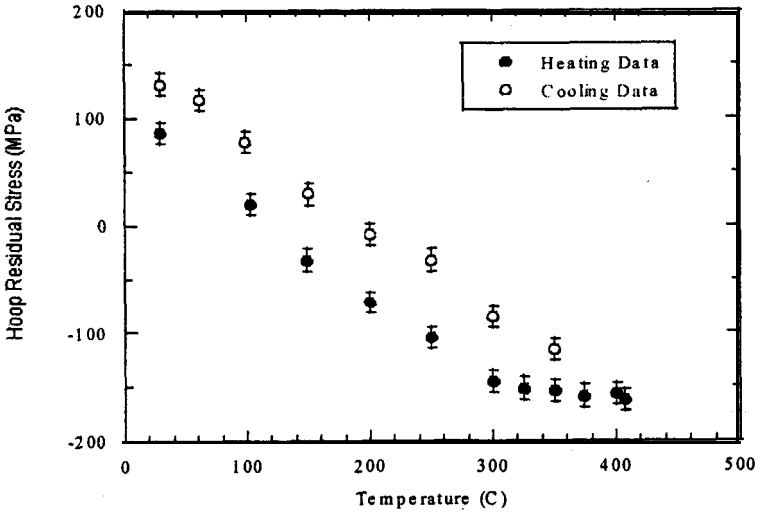
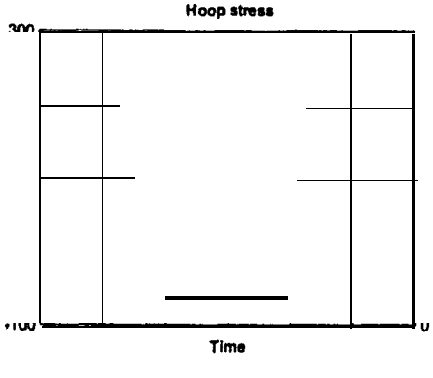
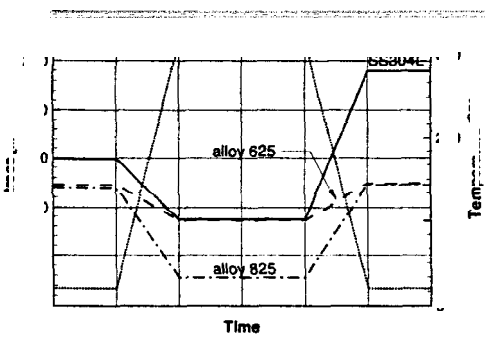
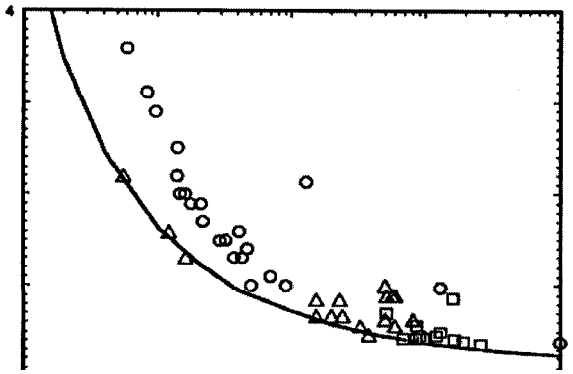


Figure 2. Stress in a 304L/CS composite tube's stainless layer as measured using neutron diffraction vs. the temperature during thermal cycling between room temperature and 400°C. The stainless layer exhibits elastic



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