Oxidation of Stainless Steel Tubings in High Temperature Steam*

By Kazuhisa KINOSHITA,** Tohru MIMINO** and Masanobu SHIBATA**

Synopsis

Austenitic stainless steels are likely to form oxide scales, which are easy to drop off to cause some troubles, by contacting with high temperature superheated steam in boilers. To solve this problem, it has been known that cold working applied on the surface of austenitic stainless steels is effective to prevent oxidation by high temperature steam. Then the authors trialed applied shot blasting to the inner surface of stainless steel tubing for cold working. After laboratory tests, stainless tubings shot blasted on the inner surface were set in boilers for practical use. After a year’s operation they were removed out and it was observed that there formed a lot of scale on non-worked surface, but that practically no scale was formed on the shot blasted surface. Shot blasting has no adverse effect on the sensitivity of stress corrosion cracking and on the cold bending, thus causing no difficulty in practical applications.

I. Introduction

Eighteen-eight series austenitic stainless steels are extensively used for high temperature service up to about 800°C without any problem as to oxidation in clean air environment. But the behavior is quite different in the high temperature steam; they can easily be oxidized even at about 650°C to form scales which tend to drop off in starting up or in shutting down.

This is sort of a problem for modern large scaled power boilers with stainless superheaters and/or re-heaters for having failures due to blocking by huge amount of such dropped off scales.

Though some people have reported[1-5] that cold working is very much effective to prevent such a type of oxidation, it never seem to have been applied to practical service.

The authors have found by chance that the stainless tubing which had been ground inside was almost perfectly resistant to steam oxidation at high temperature even after about 24,000 hr. These things made the authors to come to a conclusion that shot blasting inside the tubings would be much more effective and practical for preventing steam-oxidation (oxidation in steam), then its application to practical service has been investigated.

II. Oxidation of Stainless Steels by High Temperature Steam

1. Structure of Oxide Scales

It is known that the scale formed by steam-oxidation is consisted of roughly two layers; alloying elements such as Cr and Ni are concentrated to the inner layer and the outer layer is consisted of almost pure iron oxide.

Figures 1 and 2 show the distribution of each element along the thickness of the scales obtained by the X-ray microanalyser, Fig. 1 showing the inside scale for SUS 304 HTB (corresponds to ASTM A-213 TP 304H) re heater tubing of a 156 MW power boiler after service for about 10,000 hr and Fig. 2 showing that for SUS 321 HTB (corresponds to ASTM A-213 TP 321 H) superheater tubing of the same boiler. Table 1 shows chemical compositions of the samples used. The elements analysed were Fe, Cr and Ni as well as Mn, Si, Cu and Ti (only for SUS 321). It is obvious that Fe being 60% is only a metal constituent for the outer layer and the other elements are concentrated to the inner layer. It has been confirmed by X-ray diffraction that the outer layer is mainly consisted of magnetite (Fe₃O₄) with small amount of Fe₂O₃.

The loose structure is a typical feature of the outer layer of the scale as shown in Photo. 1 through microscopic examination. This has been taken from SUS 316 HTB (corresponds to ASTM A-213 TP 316 H) superheater tubing for a 175 MW power boiler and had been in service for about 6,500 hr and it is shown that almost continuous cavities exist adjacent to the boundary between outer and inner layers. The photograph shows particularly the grain boundaries being preserved as they were in the inner layer, that would show that the inner layer is an in-situ oxidation product of the matrix.

This particular type of scale seems to drop off easily due to the difference in thermal expansion between itself and matrix for its loose structure and brittleness. The detailed study has been reported[6] on the time of dropping off that the scale drops off mainly during lowering the temperature and some during rising the temperature but never during the operation.

2. Change of Scaling Rate Due to the Difference in Surface Conditions

In general, metal corrosion is affected by its surface conditions and the smoother the surface, the less the corrosion rate for wet corruptions in ambient temperature range.

However, the oxidation of stainless steels in the high temperature steam is quite different, being influenced not by surface roughness, by whether it has been cold worked or not and also by the grain size.7) Following references are to be shown to clarify these things.

Ruther, et al.[1] reported that the oxidation characteristics for 18-8 series stainless steels and Ni alloys


(Inconel 600, Incoloy 800) in the steam at the temperature of 630°C are influenced by the surface conditions; those having been cold worked showing superior resistance to oxidation than those as heat treated.

The effects of surface treatments are the more remarkable, the less the oxygen content is (comparison of 0.03 to 0.2 ppm O₂ and 30 ppm O₂) in the static test. In the dynamic test, however, the oxygen content (0.05 to 30 ppm) and steam velocity (30 to 90 m/ sec) have no apparent effect on the oxidation rate.

The same authors also reported that the addition of Al or Si to type 304 stainless steel is effective in improving oxidation resistance for the steam of the same conditions as shown above. But the amounts of those alloying elements should be considerably high (2% or over of Al and 3% of Si) for getting satisfactory effects.

The problem of utilizing these alloying elements is not so simple because these elements, especially their considerable amounts of alloying might deteriorate their high temperature strength and might have some effects on other characteristics. Ruther, et al. also pointed out that the effect of cold working on improvement of the resistance to the steam-oxidation might be due to the increase of diffusion rate of Cr in the matrix to form protective scale films.

M. Warzee, et al. reported that the oxidation of types 304 and 410 (15% Cr) stainless steels in the superheated steam in the temperature range from 400°C to 600°C might be depressed considerably by cold working the surface. And they also pointed out that the oxidation characteristics would not be changed by the surface roughness alone, and by the difference of the surface conditions such as pickled, electrolytically polished or with mill scale.

They also ran the experiment in water at the temperatures less than 350°C getting results difficult to explain as to the cold working for their complex features.

D. Caplan made experiments on 10 to 26% Cr ferritic stainless steels in 600°C and 1 kg/cm² steam, and found a large effect of cold working on preventing oxidation for high Cr (24 to 26%) steels but no effect for low Cr (10 to 15%) steels.

S. Jansson, et al. ran a series of experiments on Cr–Ni steels (18Cr–11Ni and 15Cr–15Ni) in 500°C to 800°C and 50 kg/cm² steam and found a large effect of surface cold working (grinding) on oxidation characteris-
tics. (Fig. 3). They reported that the effect became ineffective at the temperature above 700°C and cold worked samples showed very high oxidation rate after 500 hr at 800°C.

It could be concluded from the experimental works shown above that the oxidation by superheated steam on high Cr stainless steels including both austenitic and ferritic can be prevented effectively by applying cold working on the surface but the effective service temperature would be less than 700°C. As some of the workers pointed out, the mechanism of preventing oxidation by cold working is considered to be due to acceleration of Cr diffusion in the matrix by introducing vacancies by cold working into matrix.

This is considered to be the case on the grain boundaries being coincident to the fact that the finer grain size is favorable for better oxidation resistance in the steams and its critical temperature of losing oxidation resistance is assumed to be the temperature at which recrystallization begins.

3. Observations on Boilers in the Plants

The investigations mentioned above were of the experimental works in the laboratories for relatively short times. The authors have observed a stainless steel tubing (SUS 304 HTB) which exhibited quite a different type of oxidation inside—there was practically no scale on a part of the tubing, which had been ground inside, but on the other part was a usual type of oxidation layer of thickness of about 0.10 mm. The 75 MW power boiler uses reheated steam of 541°C and 25.6 kg/cm² (at the exit of reheater) and has been in service for about 24 000 hr from the start of the operation.

The sample tube was taken from the exit leg which had the hottest steam inside and the wall temperature was estimated to be about 600°C.

The tube was a combination of two tubes by welding, lower one having usual thick scale inside and the upper one having very thin scale showing the surface as if it was completely new that have been just ground.

Photograph 2 shows the microphotographs with high magnification (×800) of the cross section of the scale. While the scale shown in Fig. 2 (b) is about 110 μ thick, the scale of those having been ground (Fig. 2 (a)) is not measurable even at this high magnification except those at the local points where the scale penetrates.

This observation apparently indicates that the effect of cold working (grinding) is much effective for so long time, about 24 000 hr, for preventing oxidation by steam.

III. Cold Working of Inner Surface of the Stainless Steel Tubing

1. Preliminary Experiment

It was considered to be practical to study the opti-
Six different grades of stainless steels, i.e. types 304 H, 321, 321 H, 316 H and 304 H and Tempaloy A-1, which is an 18-8 Ti Nb steel developed by our company for superheater tubing material, were taken as samples for this work. (Types 321 and 321H are different each other for their grain sizes, finer grain size for the former.) The chemical compositions of the samples used are shown in Table 2. Different surface conditions for each grade, respectively, were as follows: pickled, with mill scale, expanded I, with ground scale, expanded II, expanded III and almost zero for expanded ones.

This work showed that the cold work is effective to increase the resistance to steam oxidation, especially shot blasting is very much effective. Though the grinding seems to be effective, there are some differences in thicknesses of the scales between grades and also in the same samples. This seems to be due to the difference in the degree of grinding effect itself between each sample.

Table 3. Thicknesses of scales obtained from an experiment with superheated steam at 680°C for 200 hr (\(\rho\))

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>Surface treatment</th>
<th>Pickled</th>
<th>With mill scale</th>
<th>Expanded</th>
<th>Ground</th>
<th>Shot blasted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tempaloy A-1</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>SUS 321 H</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>SUS 347 H</td>
<td>15</td>
<td>10</td>
<td>10</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>SUS 304 H</td>
<td>30</td>
<td>10</td>
<td>15</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>SUS 316 H</td>
<td>20</td>
<td>15</td>
<td>20</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>SUS 321</td>
<td>20</td>
<td>10</td>
<td>8</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

As easily available tubings were taken, their size varied form 19 to 50 mm O.D. (outer diameter). The inner surface of the tubings was uniformly ground by a hand grinder for the ground samples, and shot blasting was applied on the outer surface, which was the testing surface, because of difficulties to get uniform and strong blasting effect inside.

Small pieces of 15 \(\times\) 10 \(\times\) wall thickness (mm) were cut from the sample tubes mentioned above and heated to 680°C in the steam at atmospheric pressure for 200 hr. The steam was obtained by boiling city water without deaeration, the flow rate being 0.6 m/hr. The thicknesses of the scales obtained from this experiment are tabulated in Table 3.

The thickness was measured through an optical microscope for several fields and the average values thus obtained are shown in the table. The thicknesses of the scales for those shot blasted are less than that measurable by 400 times magnification and were determined to be zero. Also the depth of the cold worked zone was measured by heating those samples at 650°C for 2 hr getting precipitation of carbides on the slip bands, and the results showed that the depth was about 0.20 mm for shot blasted samples while about 0.02 mm for ground and almost zero for expanded ones.

Though it is not a special way to shot blast or sand blast inner surface of a large diameter pipe for polishing or peening, it would be very special to get full effect of shot peening on inner surface of small diameter tubing such as boiler tubings.

In the preliminary works, the shot blasting from one end of the tubing by inserting a straight nozzle was tried but no effect of peening was obtained although some cleaning effect was seen.

Then the co-operative work was started with Nippon Blasting Machine K.K. to develop a special nozzle for shot blasting inner surface of tubings 25 to 50 mm I.D. and the proper nozzle for practical use has been obtained for getting sufficient effect of peening. The nozzle is made of a special material with an 8 to 9 mm I.D. hole which has an angle of 45° to the center axis and goes back at constant speed, while the tubing being shot blasted is revolving at a proper speed. Therefore this method of blasting must be done on straight tubings and is difficult to be applied to bent tubes or those which have been fabricated into pannels.

### 2. Cold Working Inner Surface by Shot Blasting

Though it is not a special way to shot blast or sand blast inner surface of a large diameter pipe for polishing or peening, it would be very special to get full effect of shot peening on inner surface of small diameter tubing such as boiler tubings.

In the preliminary works, the shot blasting from one end of the tubing by inserting a straight nozzle was tried but no effect of peening was obtained although some cleaning effect was seen.

Then the co-operative work was started with Nippon Blasting Machine K.K. to develop a special nozzle for shot blasting inner surface of tubings 25 to 50 mm I.D. and the proper nozzle for practical use has been obtained for getting sufficient effect of peening. The nozzle is made of a special material with an 8 to 9 mm I.D. hole which has an angle of 45° to the center axis and goes back at constant speed, while the tubing being shot blasted is revolving at a proper speed. Therefore this method of blasting must be done on straight tubings and is difficult to be applied to bent tubes or those which have been fabricated into pannels.

### 3. Plant Tests

Two plant tests were run in the power stations for about one year each in order to verify the effect of inner surface cold working by shot blasting to the stainless steel tubings on the steam-oxidation in the actual service conditions. The results are shown below:
1. Plant Test in The Power Station A

Three pieces of test tubes SUS 321 HTB (38.1 mm O.D. \times 6.7 mm wall thickness \times 1000 mm), which inner surface had been shot blasted through a half length of the piece (500 mm), were inserted to the superheater of a power boiler for generating 156 MW electricity with the steam of evaporation rate 540 t/hr, temperature of superheated/reheated steam 569°/541 °C, and pressure 174 kg/cm².

The test tubes were inserted in February, 1972, one of which were taken out for the investigation after nine months during the regular official inspection period. Other two pieces will be taken out after two or more years for further investigation.

Two longitudinal blasting speeds, i.e. 30 mm/min (No. 1) and 60 mm/min (No. 3), were applied for the test tubes for determining the effect of the processing speed.

On the test tubes taken out, it was observed that the scale on the shot blasted surface was very tight and thin and never dropped off even at the point close to the machine-cut surface, and there was no effect of the difference in both of the blasting speeds. But non-worked surface had rather thick scale being easy to drop off.

The cross sections of the scales are shown in Photo. 3. (Original magnification \times 800). Photographs 3 (a) and (b), which are those for blasted surfaces No. 1 and No. 3, respectively, show that there are practically no oxide scale on the surface. In Photo. 3 (c) is shown thick layers of scale for No. 1 tube being 50 to 100 \mu in total thickness. The photograph shows that it is consisted of two or partially three layers of different types of scale. The photos for No. 3, which were omitted to show, showed only inner layer for dropping off the outer layer.

Photograph 4 shows etched samples (\times 400) of those shown above; (a), (b) and (c) in Photo. 4 correspond to (a), (b) and (c) in Photo. 3, respectively. The cold worked zones are apparent in Photos. 4 (a) and (b) as a pattern of carbides precipitated on the slip bands. The depth of the zones, being about 100 \mu for both samples, shows that the difference of blasting speed (30 mm/min and 60 mm/min) in this degree does not affect its effect.

It is apparently shown in Photo. 4(c) for the microstructure of non-worked sample that scaling proceeds into the grains leaving the grain boundaries behind.

The results mentioned above indicate that the shot blasting is quite effective to preventing the steam oxidation.

Considerable amount of dropping-off scale was

---

Photo. 3. Sections of scale on a test tube (Power plant A) \times 800 (\times 1/2)

(a) No. 1 tube, shot blasted at 30 mm/min
(b) No. 3 tube, shot blasted at 60 mm/min
(c) No. 1 tube, non-worked

Photo. 4. Microstructures of shot blasted and non-worked surfaces \times 400 (\times 3/4)

(a) No. 1 tube, shot blasted at 30 mm/min
(b) No. 3 tube, shot blasted at 60 mm/min
(c) No. 1 tube, non-worked
found in the test tubes, which tube Nos. 1 and 3 had been welded together before a test run and were taken off for the investigation. The thickness of the scale was determined to be about 50 \( \mu \) by using a micrometer, corresponding to the thickness of outer layer of the scale shown in Photo. 3(c). Therefore, the outer layer of oxidation scale in the stainless tubings after a year's service seems to be very easy to drop off in shutdown period.

2. Plant Test in the Power Station B

In the power station B, also three pieces of SUS 316 HTB (63.5 mm O.D. \( \times \) 8.5 mm wall \( t \times 400 \) mm/l) test tubes were inserted near the exit of the suspension-type superheater of a power boiler, out put 175 MW, evaporation rate 590 t/hr, temperature 569°/541°C and pressure 174 kg/cm\(^2\). One of the test tubes were taken out after a service for about 8000 hr.

The inner surface of the test tubes had been shot blasted through a half length of each piece. The method of blasting was the same as described before, the longitudinal blasting speed being 60 mm/min.

The appearance of a split test tube is shown in Photo. 5, the right half of the tube having been shot blasted and the left half having been as pickled, and the direction of upstream for combustion gas flow being shown up of the picture.

Especially the oxidation scale on combustion gas side of the tube surface without blasting (upper left hand side of the photo.) had grown thicker and large amount of the scale had dropped off when the test tubes were cut. The thickness of the dropped off scale was determined to be about 0.10 mm.

The scale on the exhaust gas side had also grown considerably thick and some amount seemed to have dropped off. In contrast with these, the tight scale had formed on the shot blasted surface having no indication of growth.

The microphotographs of sections of scale are shown in Photo. 6 (a) being combustion gas side of non-worked surface (\( \times 400 \)) and the thickness of the scale has grown to 150 to 200 \( \mu \) thick in two layers. It is not certain whether a portion between outer and inner layers be caused by rising the outer layer or by forming continuous cavities.

Exhaust gas side of non-worked surface has been shown in Photo. 1 showing characteristic shape of cavities in the outer layer. The thickness of the inner layer is somewhat thinner for exhaust gas side being 60 to 70 \( \mu \) than combustion gas side being 90 to 100 \( \mu \).

A cross section of blasted surface is shown in Photo. 6 (b) (\( \times 800 \)) showing practically no scale on the surface.

4. Examination of Application to Actual Service

It has been shown that shot blasting is a very effective method of preventing steam oxidation for stainless steel tubings, although there still remain some points to be checked before applying this method to the actual service. These shall be discussed referring to the experimental data.

1. Stress Corrosion Cracking

Though the stress corrosion cracking is a little problem for superheaters or reheaters of boilers because of their dry environment during usual service, there are some possibilities of getting cracking in the case not in operation because of concentrated corrosive solutes. Therefore this kind of problem is not a serious one but still cannot be overlooked.

Considerably high stress is retained on the surface after being shot blasted for its strong impinging effect. Such stress is considered to be compressive and therefore to be safe for stress corrosion cracking.

In order to ascertain its effect on the stress corrosion behavior, testpieces were prepared from SUS 321 HTB and 316 HTB tubings with shot blasted inner surface and tested in boiling 42% MgCl\(_2\) aqueous solution for 200 hr.

Chemical analyses of the testpieces are shown in Table 4. Sample tubings for this test were as heat treated condition that had not been rotary straightened for avoiding to get residual stresses caused by the straightening process.

Testpieces were color checked after boiling in MgCl\(_2\) solution, showing only some little cracks on one end of SUS 316 tube due to the effect of saw cutting. This could be a proof of there being no dangerous effect of increasing possibilities of getting any stress corrosion cracking by applying shot blast on the surface.

2. Bending Work

Usually 20 to 30% maximum of tensile deformation is applied locally to outer wall when a tube is cold-
Table 4. Chemical analyses (wt%) and processing history of testpieces for a stress corrosion cracking test

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUS 321</td>
<td>0.05</td>
<td>0.53</td>
<td>1.82</td>
<td>0.027</td>
<td>0.007</td>
<td>0.14</td>
<td>12.10</td>
<td>17.33</td>
<td>0.23</td>
<td>0.49</td>
</tr>
<tr>
<td>SUS 316</td>
<td>0.06</td>
<td>0.39</td>
<td>1.56</td>
<td>0.018</td>
<td>0.008</td>
<td>0.12</td>
<td>13.30</td>
<td>17.08</td>
<td>2.60</td>
<td>—</td>
</tr>
</tbody>
</table>

Processing history: Billet → Hot extrusion → Cold rolling (Cold pilger) → Heat treatment → Cold drawing → Heat treatment → Shot blasting → Stress corrosion cracking test in 42%MgCl₂

bent. This means that the deformation by bending is superimposed to that by shot blasting. The question whether this can be any problem of getting micro-cracks were checked by running an experiment shown below.

An SUS 304 HTB tube, which inner surface had been shot blasted, were deformed by tension until coming to a rupture with thin carved lines in 5 mm intervals on the outer surface for determining the amount of local deformation.

The result was that the carved lines were rather deep giving a rupture point at the line, consequently the amount of deformation was not as much as that expected, but it reached as high as about 50%.

Longitudinal cross section of the ruptured specimen is shown in Photo. 7, that has been given maximum deformation of about 50%. No crack is observed on the upper surface in the photo, which is the shot blasted inner surface of the tube.

Therefore it could be concluded that there is no fear of getting any cracks on the shot blasted surface due to accumulated deformation when the tubing is cold bent in usual manners.

IV. Discussions

It has been shown by various types of experiment that the cold working on the surface of stainless steels is quite effective for preventing oxidation by high temperature superheated steam.

The next subject to be checked is how long it will be effective; the plant tests mentioned above are to be continued for several years for checking its effects. Then only a time will make sure the results.

This method of preventing steam oxidation seems to be quite a unique one because of its effect coming from the cold worked zone which is different from the surface treatments such as plating and others that are easy to fall off by physical or chemical actions.

Since some problems arising from the application have been solved already, this method could easily be applied to the boilers for new construction and if so, their excellent effects would be quite a lot.

V. Conclusions

Effects of shot blasting inner surface of stainless steel tubings on steam-oxidation have been shown as one of the methods of preventing troubles caused by dropped-off scales produced by steam-oxidation.

Unconceivable effects were obtained from plant tests that the oxidation had been depressed completely for about one year. It is not confirmed how long this will be effective, but the result that the effect of grinding was still active after 24 000 hr must be a proof of it being effective for a considerably long period of time.

Also it has been shown there are no fear of getting any cracks by stress corrosion or bending work.

Acknowledgements

The authors express their hearty thanks to boiler makers and power generating companies for their co-operation to the plant tests and Nippon Blasting Machine K.K. for its co-operation to the blasting work.

REFERENCES