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OTTAWA June 7th, 1943.

REPORT

of the

ORE DRESSING AND METALLURGICAL LABORATORIES.

Investigation No. 1423.

Examination of Defective Boiler Tubing.

(Copy No. 8.)

Bureau of Mines
Division of Metallic
Minerals
-
Ore Dressing
and Metallurgical
Laboratories

CANADA
DEPARTMENT
OF
MINES AND RESOURCES
Mines and Geology Branch

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Origin of Request and Object of Investigation:

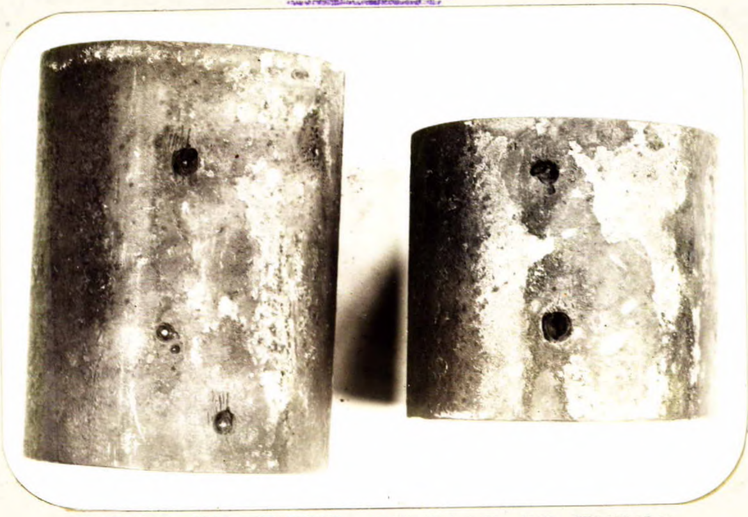
On May 26th, 1943, Engineer Rear-Admiral H. A. Sheridan, British Admiralty Technical Mission, 58 Lyon St., Ottawa, Ontario, sent in two samples, taken from defective boiler tubes, for examination.

It was stated (letter of May 26th, File No. 21-16-8-3) that these tubes had pitted after a relatively short period of service in a cylindrical boiler of H.M.S. "Anticosti". It was also stated that best quality seamless steel tubes were specified and it was desired to establish whether these samples were seamless or whether they were butt-welded. A full report on this examination was requested.

Macro-Examination:

The samples submitted were oxidized on both the inside and outside of one half of the tube. The oxidized areas exhibited a number of large pit-holes. Figures 1, 2 and 3 are photographs illustrating the nature of these defects. The unoxidized surface was not attacked, as may be seen by reference to Figure 3 which shows the inner surface of one side of the tube.

Figure 1.



SCALE ON OUTER SURFACE OF TUBES.

(Approximately ½ size).

Figure 2.

SHOWING SCALE ON INNER SURFACE OF TUBE.

Figure 3.

SHOWING INNER SURFACE OF TUBE FREE FROM SCALE.

(Approximately to size).

(Macro-Examination, cont'd) -

A full section of the tube was polished and given an etch at 180° F. in a solution of 12 per cent H_2SO_4, 38 per cent HCl and 50 per cent H_2O. Figure 4 is a photograph showing the duplex nature of the etched surface, the outer half of the material being quite sound with the remaining inner material apparently being of lower density.

Figure 4.

PHOTOGRAPH SHOWING RIMMED STRUCTURE.

(Approximately to size).

Chemical Analysis:

The steel tube was found to have the following composition:

		Per cent
Carbon	-	0.07
Manganese	-	0.33
Silicon	-	0.008
Phosphorus	-	0.006
Sulphur	-	0.036

Hardness Tests:

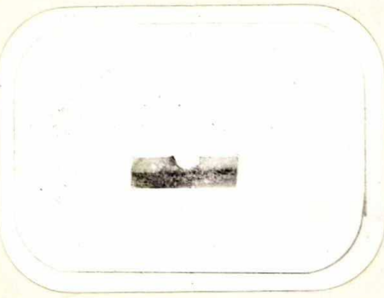
A hardness survey showed the tube to be somewhat softer on the outer surface than on the inner portion.

		Vickers Hardness Numbers (10-kg. load)			
Outer Portion	-	100,	110,	110,	111,
Inner "	-	117,	119,	119,	120.

Sulphur Print:

A sulphur print was taken at one point of pitting. This is illustrated in Figure 5.

Figure 5.



SULPHUR PRINT.

(Approximately to size).

Microscopic Examination:

Specimens cut from the tubing were mounted in bakelite, polished, and then examined in the unetched condition under the microscope. The steel contained a large number of oxide and some sulphide inclusions. The specimens were next etched in a solution of 4 per cent picric acid in alcohol and re-examined. Figure 6 is a photomicrograph, at X100 magnification, showing the fine-grained structure of the steel. Figure 7 is a photomicrograph, at X100 magnification, showing scale (the grey constituent) on the outer surface of the tube. Figure 8 is a photomicrograph, at X100 magnification, showing the

(Microscopic Examination, cont'd) -

start of pitting on the outer face of the tube.

Figure 6.

X100, picral etch.

GRAIN STRUCTURE OF STEEL.

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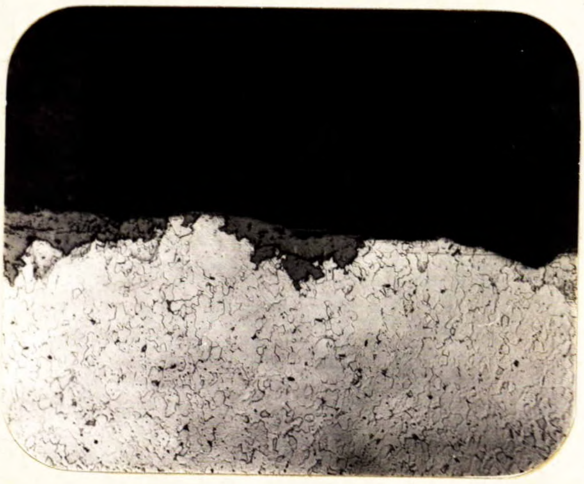
Figure 7.

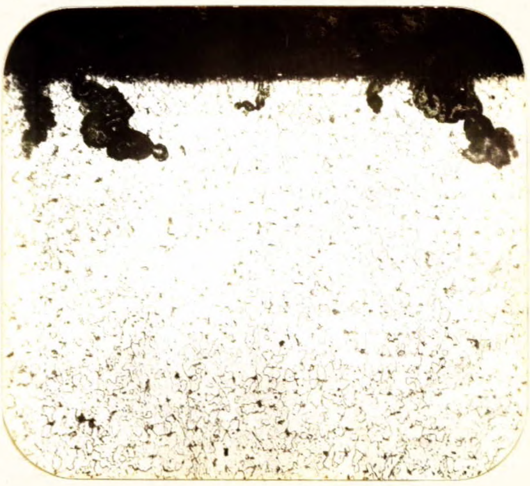


X100, picral etch.

SHOWING SCALE ON
SURFACE OF TUBE.

-

Figure 8.



X100, picral etch.

START OF PITTING ON
SURFACE OF TUBE.

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Remarks in Literature on Causes of Pitting in Boiler Tubes:

(1) "Pitting is a more dangerous type of attack on iron and steel than that of slow and uniform wasting away of the surface. Pitting is not usually the result of the chemical composition of the steel. In some cases it may be due to porosity or other physical imperfections in the metal itself, but it is more commonly due to external causes, such as the breaking of a protective film, the presence of mill scale, or contact of two pieces in such fashion as to form a capillary space between them, leading to localized 'crevice corrosion' from an oxygen-concentration cell."

"Localized attack may result from corrosion attributable to oxygen-concentration cells such as occur in 'water-line' corrosion due to immersion at various depths in a solution where oxygen diffusion is hindered and the electrolyte in contact with the iron has a different oxygen content at different places."

"An analogous cause of corrosion is the presence of discontinuous patches of mill scale on the surface of the iron or steel, which localizes corrosion at the edges of the scale."

Stoughton states[2] that he has personally known severe corrosion and pitting in highly "oxygenated" steel and believes that such steel will corrode more severely than steel free from oxygen or oxides and that this is generally considered to be a fact. Stoughton includes oxygen in blowholes or some complex inclusions, as well as that present as ferrous or manganous oxide, in the term 'oxygenated'.

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(1) THE ALLOYS OF IRON & CARBON, Vol. II, pp. 537-8.

(2) ibid, p. 549.

(McGraw-Hill Book Co., Inc.)

Discussion of Results:

The macro-examination showed that the tubes were seamless and that the duplex nature of the etched surface proved them to have been made from rimming steel and not from a killed steel as specified. The low silicon content in the metal confirmed this latter conclusion. The sulphur print showed a concentration of sulphides in the central and inner portions of the tubing. This is characteristic of rimming steels. The sulphur content, however, is not considered excessive. It is thought that the scaled portion faced the bottom of the boiler, as the fact that all tubing in the boiler was attached removes the possibility that a low water level was responsible. The only alternative would appear to be an overheating of the bottom of the tubing as a result of steam insulation, which might take place in a rapid heating of a boiler.

The mechanism of this reaction is described by C. Benedicts (Trans. Amer. Min. Met. Eng. 1925, 71, 597). He states "that where steam bubbles do not detach themselves freely, the part covered with a large flattened bubble of steam may soon become badly overheated causing trouble both on waterside and fireside."

The microscopic examination showed that the pitting originated at a scaled portion of the tubing.

In a rimming steel ingot, the outer portions are much purer than the average, and the central portion is highly segregated.

According to Dr. Stoughton, highly oxidized steel is subject to pitting. In the present case, since the tubing pitted from the outside of the unsegregated portion of the tube, it is improbable that pitting was due to the use of

(Discussion of Results, cont'd) -

rimming steel in the tubing. Such steel, however, is definitely forbidden in the specification, as it is subject to other defects.

CONCLUSIONS:

It is concluded that the pitting of the tubing occurred as a result of highly localized corrosion in scaled areas which were present as a result of overheating in service, probably because of a too rapid heating of the boiler. The tubes are seamless but the tube steel is of the rimming type which definitely violates the specification.

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