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EXAMINATION OF TWO LENGTHS OF 4-6% CHROMIUM STEEL TUBING

by

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SUMMARY OF RESULTS

Metallurgical examination of a 5% chromium steel refinery-preheater tube showed that the service temperature in the affected region had been approximately 1400°F. The structure contained coalesced carbides, except that a shallow zone in contact with coke on the inside surface appeared to have been carburized, heated above the critical temperature, followed by reprecipitation during cooling.

Reduction of the metal section appeared to be due mainly to the service temperature and to erosion by siliceous slag from furnace refractory. This slag contained iron oxide and traces of vanadium from the oil ash.

It was recommended that the temperature be reduced by avoiding direct impingement of burner-flame on adjacent tubes. No discussion of alternate tube materials, of burner oxidation, or of oil-ash vanadium content was included as operating temperature of 5% chromium steel in refinery service is normally restricted to 1100°F, and data are readily available from tube manufacturers for specific operating temperatures and service conditions.

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INTRODUCTION

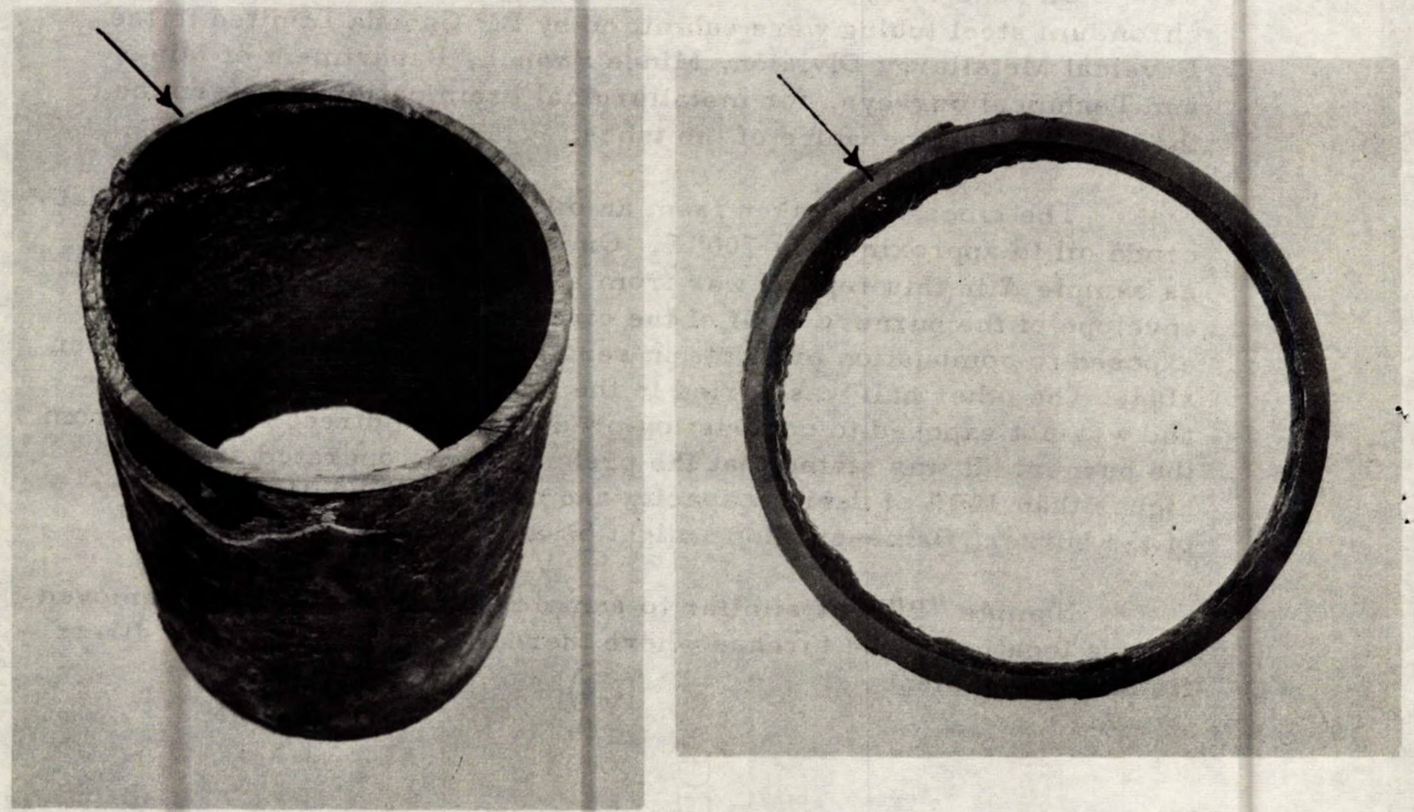
On June 19th, 1963, two 10 in. lengths of 5%, 6 in. diameter chromium steel tubing were submitted by BP Canada Limited to the Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, for metallurgical examination to determine the operating temperature of the tubes.

The tubes were taken from an oil-fired furnace used to preheat crude oil to approximately 700°F. One of the tube lengths (identified as sample A in this report) was from a location adjacent to the flame-envelope of the burner. Half of the circumference of this tube was exposed to combustion products in service, and was coated with frozen slag. The other half was buried in the refractory wall of the furnace and was not exposed to combustion products or to direct radiation from the burner. It was stated that the preheater was operated at rates higher than 100% of design capacity and that consequent enlargement of the burner, flame-envelope might be affecting adjacent tubes.

Sample "B" was similar to sample "A" in size but was removed from a location in the furnace where there was no possibility of direct flame impingement.

APPEARANCE OF SAMPLES

The appearance of sample A and of a transverse ring section, cut 3 in. from the end are illustrated in Figures 1a and 1b, respectively. Sample A is also shown in Figure 2. Sample B is shown in Figure 3.

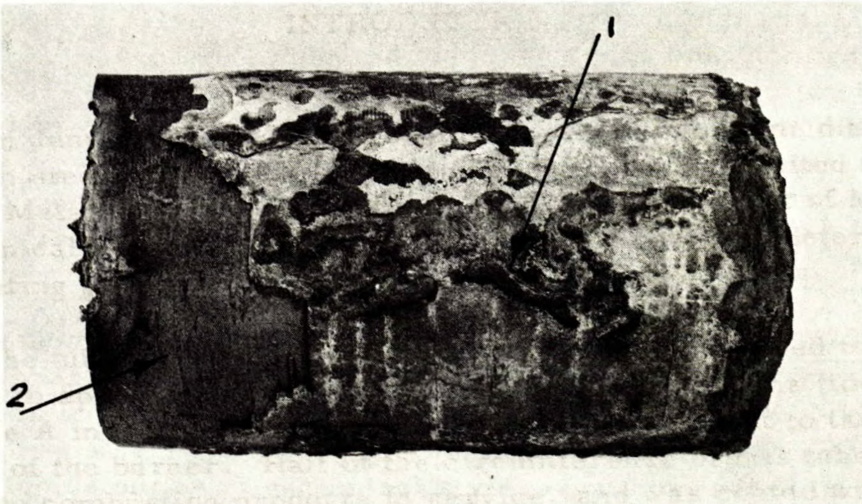


(a) X1/3

(b) X1/2

Figure 1. Sample A. Illustrates coke build-up on inside tube surface and presence of slag on outside surface. The exposed surface is shown at the left side of both pictures. Arrows (1) illustrate the reduction of wall thickness at the exposed surface.

Figure 2 illustrates the appearance of the exposed area of the outside surface of sample A. This surface was coated with frozen slag. Solidified droplets of slag are visible (arrow 1). The appearance of the thinned tube, after removal of the slag, is shown (arrow 2).



X1/3

Figure 2. Sample A. Illustrates exposed surface of tube and slag coating. Droplets of slag are shown, (arrow 1). The appearance of the tube surface after removal of the slag is shown, (arrow 2).

X1/3

Figure 3. Sample B. Reference sample from furnace area not affected by burner-flame.

METHOD OF EXAMINATION AND RESULTS

Metallurgical examination was made as follows:

(1) Visual examination
(2) Chemical and spectrographic analyses
(3) Metallographic examination
(4) Hardness tests and deep-etch examination of ring sections
(5) X-ray diffraction and X-ray fluorescence analysis of slag and coke deposits.

(1) Visual Examination

Sample A: The exposed half-surface of this tube was coated with frozen slag on the outside surface and contained a deposit of coke on the inside surface in the area corresponding to the flame-exposed area of the tube. Reduction of wall thickness from 1/4 in. to 1/8 in., approximately, had occurred in the most severely affected region of the sample.

Sample B: The wall thickness of this tube-length was approximately 1/4 in. and had not been reduced. Slag and coke deposits were not present. There was no apparent difference between the exposed and the protected surface of this sample. (Presumably, this tube was heated by radiation and convection but without direct impingement of the burner-flame).

(2) Chemical and Spectrographic Analyses

The results of chemical and spectrographic analyses carried out on samples A and B are shown in Table 1.

TABLE 1

Chemical Composition (Per Cent)

Element	"A"	"B"	ASTM A-200 (T-5)	Croloy** 5	Croloy** 5-Si	Croloy** 5-Ti
Carbon	0.07	0.07	0.15 max	0.15	0.15	0.10
Manganese	0.49	0.49	0.30-0.60	0.50	0.50	0.50
Silicon	0.30	0.31	0.50 max	0.50	1.00-2.00	0.50
Sulphur	0.022	0.021	0.030 max	0.030	0.030	0.030
Phosphorus	0.011	0.011	0.030 max	0.030	0.030	0.030
Chromium	4.86	4.86	4.00-6.00	4.00-6.00	4.00-6.00	4.00-6.00
Nickel	0.13	0.12	-	-	-	-
Molybdenum	0.54	0.54	0.45-0.65			
Titanium	N.D.	N.D.				
*Aluminum	0.02	0.02				

Samples A and B appear to be from same heat of steel.
* quantitative spectrographic analysis.

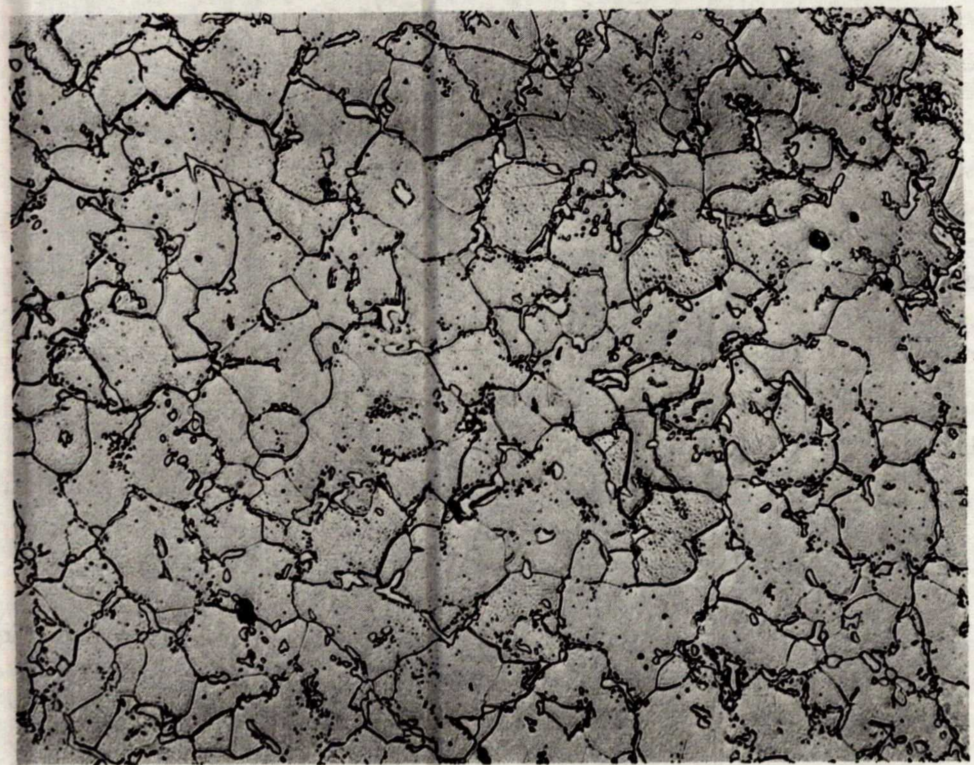
** typical composition limits for 5% Cr; 5% Cr-Si, and 5% Cr-Ti tubes — illustrative Babcock-Wilcox data for "Croloy" steel.

Samples A and B conform to the chemical composition requirements of ASTM Specification A-200; grade T-5. The similarity in composition indicates that both lengths of tube are from the same heat of steel.

(3) Metallographic Examination

Transverse and longitudinal sections were cut from the reduced section, and 180 degrees from the reduced section, sample A, and from sample B, for comparison of the metal with respect to microstructure, evidence of slag-attack at the outside surface and carburization at the inside surface. Spheroidization and coalescence of the carbide had occurred completely through the section in the affected area of sample A, indicating metal temperature throughout the section of 1300°-1400°F. The appearance of the coalesced-carbide microstructure is illustrated in Figure 4. The microstructure, observed 180 degrees from the area exposed to direct flame impingement in sample A is shown in Figure 5. The carbides are spheroidized but have not coalesced in this region. Figure 6 illustrates the microstructure observed in sample B. This microstructure purports to represent the condition of the tube in the "as-manufactured" condition although some spheroidization may have occurred since installation. The ferrite grain size is considerably finer in sample B than in sample A.

Figure 7 illustrates the appearance of the outside surface of tube A, in the area where maximum reduction of section was observed, and of a section through the surface slag deposit. Figure 8 illustrates the appearance of the coke deposit, of surface carburization and of the carbides observed at the inside tube surface.

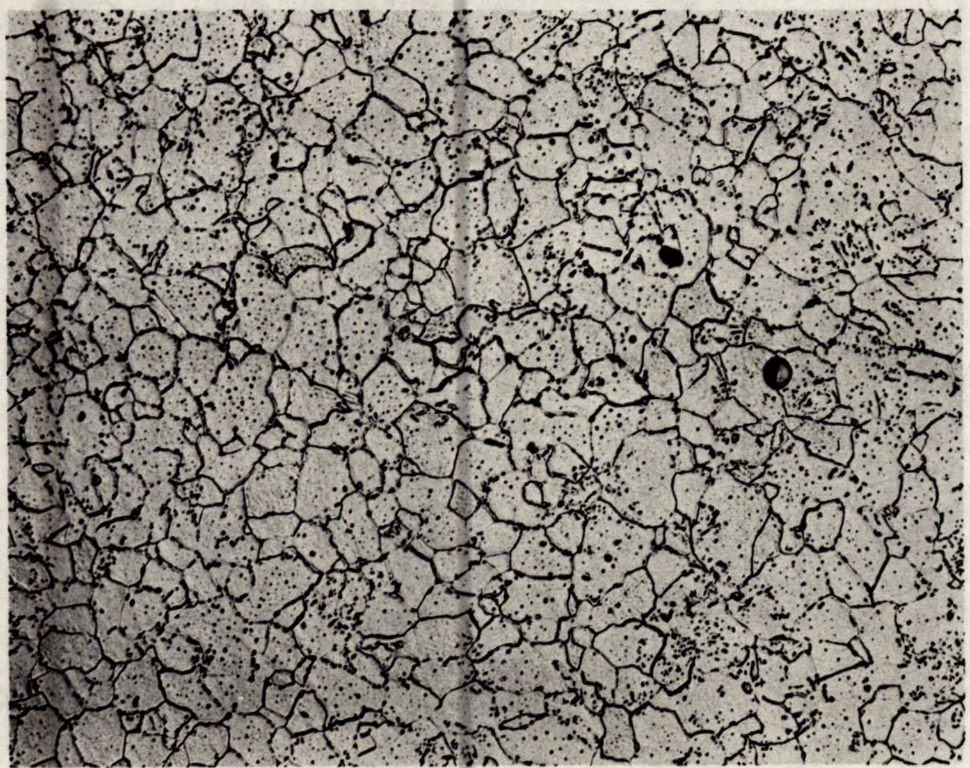


X500 etched 6% nital

Figure 4. Sample A. Area where section was reduced to 1/8 in. The microstructure consists of ferrite and coalesced, spheroidized carbide, indicating temperatures of 1300° - 1400°F in this location.

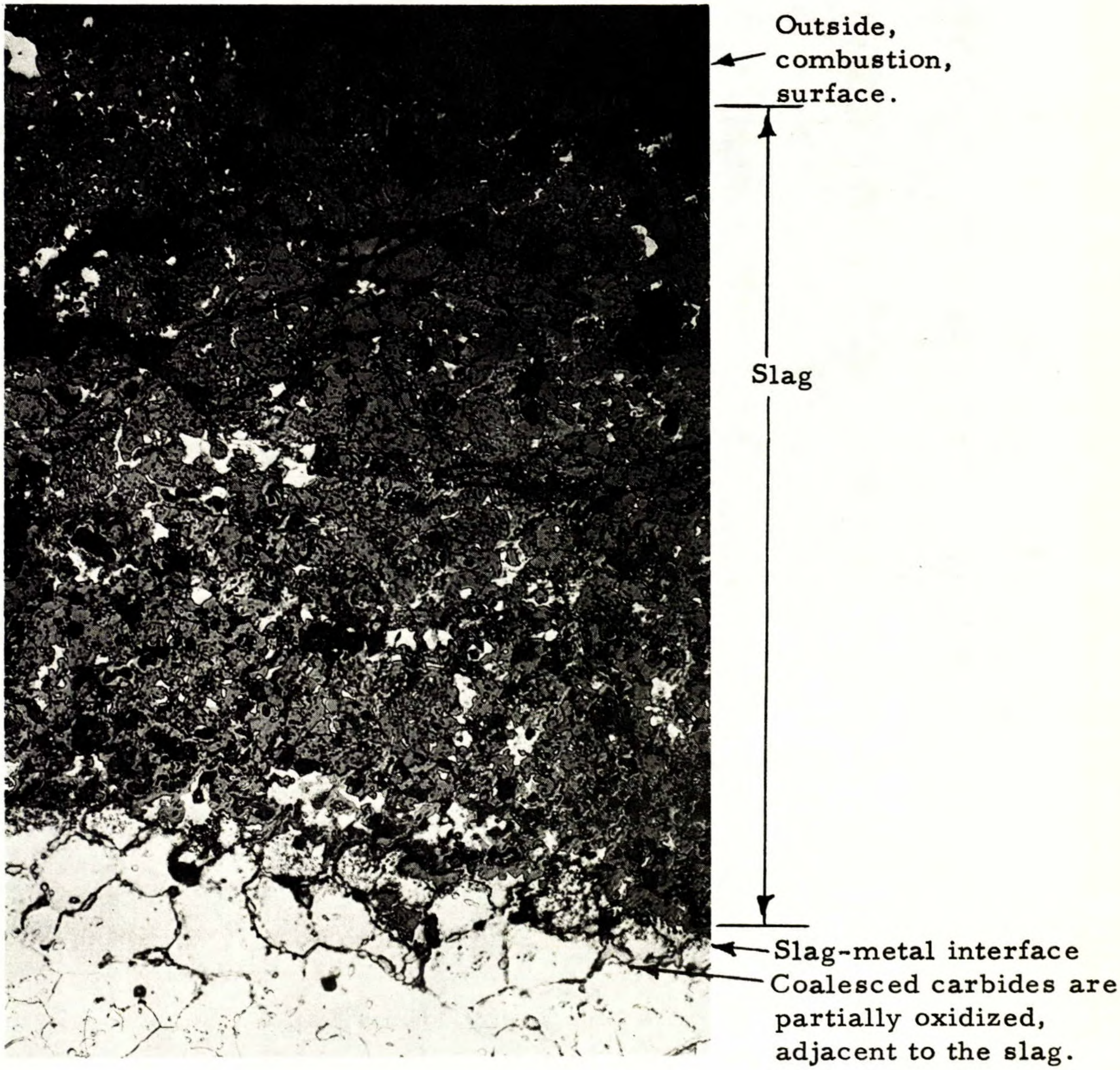
X500 etched 6% nital

Figure 5. Sample A. 180 degrees from section shown in Figure 1. This section of the tube was covered by furnace refractory and was 180 degrees from the exposed section illustrated in Figure 1. The carbide is partially spheroidized, but has not coalesced.



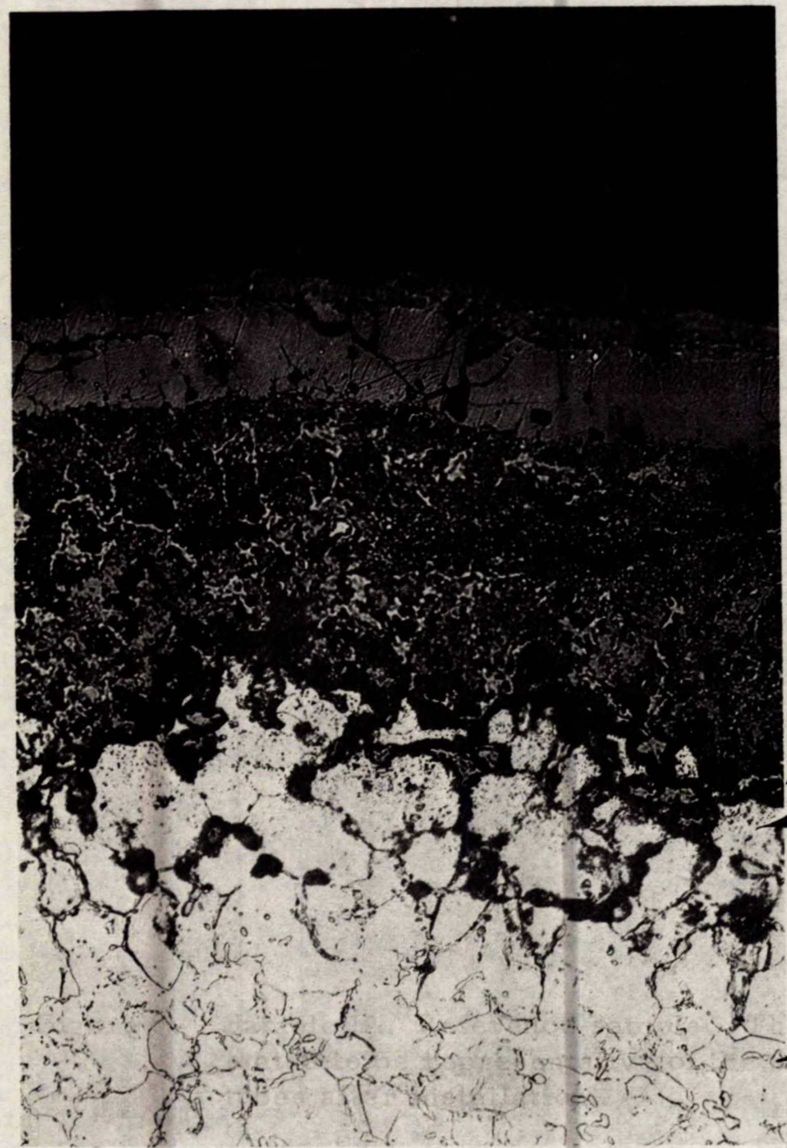
X500 etched 6% nital

Figure 6. Sample B. Reference sample. This section was stated to be representative of the structure of the tubes after installation.



X500 etched 6% nital

Figure 7. Sample A. Section at outside surface of reduced section illustrating the slag deposit and slag-metal interface. The slag contains metallic particles.



(Section thickness reduced to 1/8 in.)

Inside surface of tube.

Coke-metal interface.

Zone where carburization, solution and reprecipitation of carbide has occurred.

Coarse, coalesced carbides formed at 1300°-1400°F.

X500 etched in 6% nital

Figure 8. Sample A. Section taken at the inside surface in the region corresponding to maximum reduction of section.

The coke deposit and coke-metal interface are shown. The carbides have coalesced and are present as coarse particles, indicating service temperature of 1300°F-1400°F. Solution of coalesced carbide, accompanied by carburization and subsequent precipitation of small carbides, appears to have taken place in a narrow zone at the coke-metal interface.

The presence of this shallow zone is more consistent with tube temperature of 1400°F than 1300°F; whereas the residue of undissolved, coalesced carbide through the section indicates that the temperature has not exceeded 1450°F.

(4) Hardness Tests and Deep Etch Examination

The results of hardness tests made using the Rockwell "B" hardness tester on transverse ring sections, through samples A and B, are shown in Table 2.

TABLE 2

Rockwell "B" Hardness Measured at Centre of Transverse Sections

Identity	0°	90°	180°	270°
Sample A	* 60-65	65-67	65-67	65-67
Sample B	65-67	65-67	65-67	65-67

* reduced section.

The hardness at the centre of the section appears to be slightly lower in the region where coalescence of the carbides has occurred. However, all hardness values are considerably lower than maximum specified hardness.

Transverse ring sections through samples A and B were deep-etched for 20 min in 1:1 HCl:water solution at 160-180°F. No evidence of defect was observed in either ring section. The sections were free from lamination, seams and segregated inclusions. No weld was present, confirming that the tubes were of seamless manufacture. Etching caused some solution of slag adjacent to the surface of the tube but resulted in practically no solution of the coke layer from the inside tube surface.

(5) X-ray Diffraction and X-ray Fluorescence Examination of Slag and Coke Deposits.

X-ray diffraction (Debye Scherrer) patterns were obtained on slag and coke removed from the outer and inner tube surfaces, respectively, in the affected region. The slag was identified as α Fe_2O_3; $Na\ Al\ Si_3O_8$ and $Ca\ Al_2Si_2O_8$. X-ray fluorescence analysis detected iron and some vanadium. Chromium was not detected as a major trace element.

DISCUSSION

The presence of coalesced carbide, completely through the section in the region where the thickness had been reduced to 1/8 in. indicates that the tube operated at a temperature of 1300°-1400°F in this location. The inside surface temperature was sufficiently high to cause solution of the massive carbide. Subsequent precipitation caused formation of a shallow zone of metal at the inside surface where a dispersion of small carbides (dots) was observed, indicating that 1400°F was a more probable service temperature than 1300°F.

Similar changes in microstructure have been reported (1)(2), for 5% chromium steel tubes, in refinery service, in the presence of an internal deposit of coke.

Coalescence of carbide was not observed in the protected part of the tube directly opposite the reduced section or in the reference sample B, taken from a cooler location in the furnace.

The reduction in wall thickness at 1400°F appeared to be due to erosion, by siliceous (refractory) slag, of surface metal weakened by intergranular oxidation. Any contribution of the oil ash (V and S) or due to the nature of the burner flame (oxidizing, neutral or reducing) was masked by the dominant temperature effect. No sulphur compounds were detected in the slag. Iron was present as a major trace, vanadium was a minor trace element. Chromium was not detected.

CONCLUSIONS

1. The operating temperature was excessive. The microstructure observed at the reduced section was consistent with service temperature of the order of 1400°F.

2. Intergranular attack and change in appearance of carbide particles was observed in metal at the outside surface in close proximity to the slag. Erosion by siliceous slag appeared to assist in removal of surface metal.

3. Alteration of metal at the coke-metal (inside surface) interface was observed.

RECOMMENDATIONS

1. Reduce the operating temperature of the 5% chromium steel tubes in accordance with allowable stresses up to maximum service temperature of 1100°F.

2. After temperature is controlled, review burner and oil-ash character to obtain maximum tube life.

REFERENCES

1. "Properties of Carbon and Alloy Seamless Steel Tubing for High Temperature and High Pressure Service," Technical Bulletin, 6G, Pp 116-123, The Babcock and Wilcox Tube Company, Tubular Products Division, Beaver Falls, Pa.

2. C.T. Evans Jr, -"Oil Ash Corrosion of Materials at Elevated Temperatures", Symposium on Corrosion of Materials at Elevated Temperatures, ASTM Special Technical Publication 108, (June, 1950).

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