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## **EFFECT OF LONG TERM SERVICE AT ELEVATED TEMPERATURES ON MECHANICAL PROPERTIES OF MANAURITE XM REFORMER TUBES**

### **ABSTRACT**

Microstructure transformations occur in the Manaurite XM cast steel tubes during long-term operation in the reformer furnace were revealed and described. The relationship between mechanical properties, an increase of internal diameter of the tube and microstructure degradation is discussed. Static tensile test was performed on two types of samples with different shapes. It has been shown differences in the results of tests and an explanation of this phenomenon.

*Keywords: Manaurite XM, reformer tubes, Fe-Ni-Cr alloy, static tensile test, mechanical properties*

### **INTRODUCTION**

Catalytic tubes are important parts of reformer units that convert hydrocarbons into mixture of hydrogen, carbon monoxide and dioxide. Chemical reactions proceed at a temperature range of 800-950°C and under pressure of 3.0-4.0 MPa. These severe working conditions cause a structural damage of tubes. The most widely used austenitic cast steel tubes are susceptible to creep at working temperature, and it is essential to be able to identify and localize such damage at its early stages [1,2,3]. Even small exceed of the nominal temperature of the tube surface results in rapid acceleration of degradation process in tube microstructure. The progress of creep processes can significantly reduce the operating time of the tubes. Overheating usually occurs as a result of incorrect regulation of gas burners, or due to the reduction in flow of process gas inside the tube and thereby reduction of the cooling tube's walls.

Series of diagnostic methods aiming to assess the tube condition during operation were developed. In industrial practice non-destructive methods indicating the progress of the degradation of tubes microstructure are desirable. Methods based on the use of eddy current or ultrasounds are effective in assessment of the advanced stages of the tubes degradation when targeted creep voids or microcracks are already present in the material. Assessment of the progress of structure degradation is not easy without the analyses of metallographic samples taken from the tubes [5,6,7].

Currently diagnostic methods involve the measurement of internal or external tube diameter growth as a material degradation indicator. Such measurements are carried out during the shutdown of the installation by scanning the outer surface of reformer tube along its length. Inner surface can be scanned only in the case of removal of the catalyst from the tube. Recorded diameter growth in the range of 1-6% are potential indicators of certain advancement of creep processes. These methods are reliable if the initial data of tube diameter are known. In work [4] the method for assessing the degradation level of tubes based on mechanical properties examinations at room temperature was proposed. A change of elongation values obtained in static tensile test was taken as a measure of tube material degradation.

In this study, the centrifugally cast tube made of Manaurite XM alloy is considered. The tube was removed from the methane reformer after 46000 hours of exploitation due to excessive growth of the inner diameter. The effect of long-term service at elevated temperature on microstructural changes, an increase of internal diameter, and mechanical properties of the tube have been investigated.

## EXPERIMENTAL

Investigations were performed on the centrifugally cast tube made of Manaurite XM (G-X45NiCrNbTi35-25) taken from reformer furnace. The tube of outer diameter 146 mm and wall thickness 10.0 mm was welded from 3 sections with total length of 15.8 m (Fig. 1). The chemical compositions of two investigated sections of the tube are presented in table 1. The tube worked at maximum temperature of 937°C under 3.0 MPa pressure. In such conditions the expected life time of Manaurite XM tubes is 100000 hours. Operational temperature was not equal on whole tube length and did not exceed 540°C at the upper section of the tube (nearest to the flange).

**Table 1.** Chemical composition of tested Manaurite XM cast steel tube

Sample	Chemical composition wt.%							
	C	Si	Mn	Cr	Ni	Nb	S	P
Manaurite XM	0.40	1.20	max	23.0	32.0	0.50	max	max
	0.45	2.00	1.50	27.0	35.0	1.00	0.030	0.030
Area I	0.44	1.63	1.16	24.7	36.2	0.67	0.001	0.012
Area III	0.53	2.06	1.18	24.1	37.0	0.71	0.001	0.008

Samples were taken from three different areas along the length of the tube. The first area (I) covered inlet zone of substrates to tube where the temperature does not exceed virtually 550°C. This area of the tube was considered as non-degraded. The second area (II), about 5500 mm from the flange, exhibited the largest diameter growth after exploitation, approximately of 2.90%. Area (III) about 12000 mm from the flange, also exhibited increase in diameter of circa 1.53%.

From each of the areas of the tube three sections of 25 mm, 100 mm and 300 mm were cut for metallographic and static tensile test examinations.

Static tensile tests were carried out on two types of samples. The first ones of 25.0 x 10.0 mm in cross section were machined from 300 mm sections and comprised full tube wall thickness. The second ones, round in cross section of 4.0 mm were machined from 100 mm

sections. From each section of reformer tube three specimens have been prepared. Static tensile tests were conducted according to PN-EN ISO 6892-1:2010 standard [8].

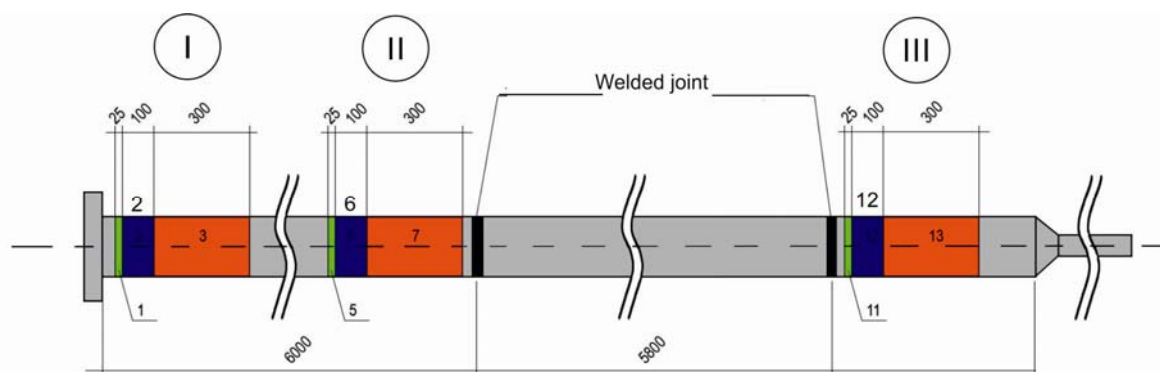


Fig. 1. Reformer tube with marked sections for research

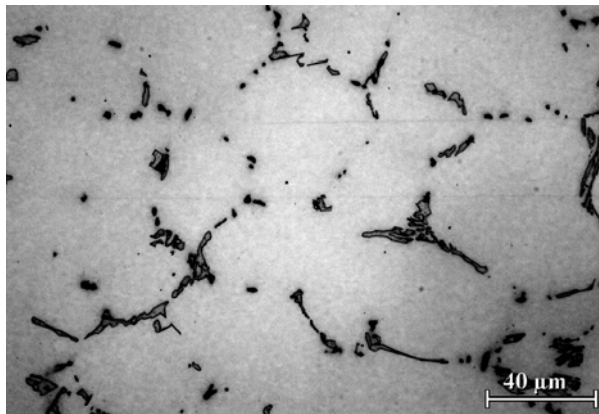
Microstructure of the alloy has been examined with the use of light optical microscopy. Samples were mechanically polished and etched by Murakami reagent (30g  $K_3Fe(CN)_6$ , 30g KOH, 60 ml water). Metallographic examinations were performed on the cross sections at the area near 1/3 tube wall thickness from the inner surface.

## RESULTS AND DISCUSSION

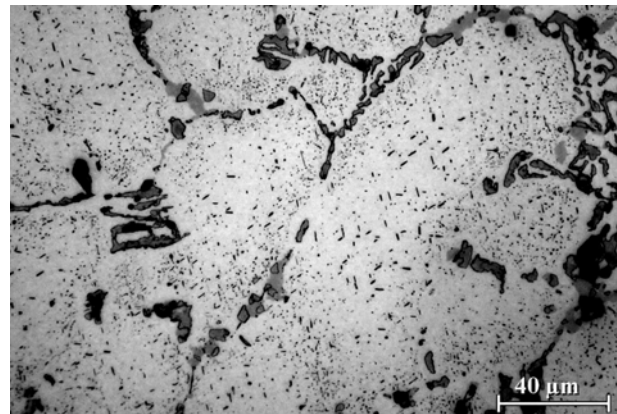
### *Metallographic examinations*

Non-degraded I-1 specimen showed the dendritic columnar austenite grains located perpendicularly to tube wall. The structure consists of austenitic matrix with a portion of primary inter-dendritic austenite-carbide lamellar eutectic, Fig. 2. Large primary carbides were randomly distributed along the grain boundaries. Structure of II-5 sample contains still lamellar eutectic of primary carbides, but the coalescence process has formed not complete continuous network around austenite grains. Secondary carbides are observed within the austenite grains in the shape of small and rounded precipitates as well as coarser plate or needle-like precipitates. Some carbide precipitations are greater in size due to initial stage of coalescence processes, Fig. 3. The similar structure was found in III-11 sample (Fig. 4), however there is no evidence of secondary carbides coalescence processes.

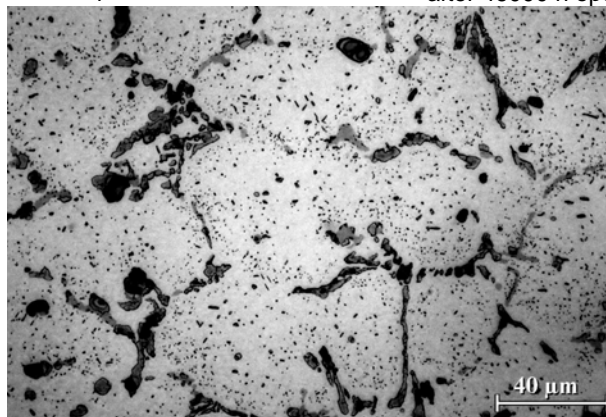
Metallographic examinations of II-5 and III-11 samples confirm the progress of degradation processes of tube microstructure. However, no creep voids were found in the microstructure at all tested sections.



**Fig. 2.** Non-degraded microstructure of Manaurite XM cast steel tube. Sample I-1



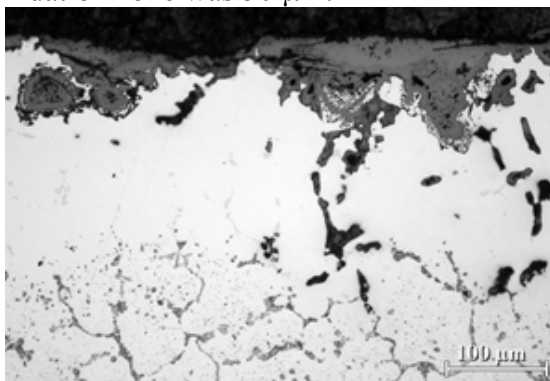
**Fig. 3.** Microstructure of Manaurite XM cast steel tube after 46000 h operation. Sample II-5



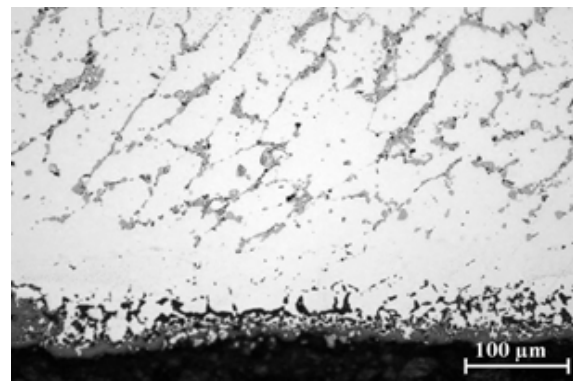
**Fig. 4.** Microstructure of Manaurite XM cast steel tube after 46000 h operation. Sample III-11

Fig. 5 and 6 show microstructure of the surface areas of the inner and outer tube segments. Progress of oxidation was found on both the inner and outer surfaces of the tube. Oxidation reduces an active cross-sectional area resulting in an increase stress in the remaining section, which can accelerate creep and crack initiation processes.

On the outer surface of the tube scale layer and the layer of oxidation are visible. Oxides progress into a tube wall along the austenite grain boundaries. The thickness of the scale reached 400  $\mu\text{m}$ , while the oxidation layer does not exceed 200  $\mu\text{m}$ . Oxidation of the inner surface of the tube was less advanced. Scale layer thickness was about 20  $\mu\text{m}$ , whereas the oxidation zone was 50  $\mu\text{m}$ .



**Fig. 5.** Microstructure of outer surface of the reformer tube. Sample I-1



**Fig. 6.** Microstructure of inner surface of the reformer tube. Sample II-5

### Static tensile tests

Static tensile tests were carried out on two sets of specimens. Samples with rectangular cross-section of 25 mm x10 mm containing the full thickness of the tube wall with raw inner and outer surfaces (set 1) and samples with circular cross section having a diameter of 4 mm and containing a central part of the material of the tube wall (set 2). Three samples were tested from each tube section. Average results of 0.2 proof strength ( $R_{p0.2}$ ), ultimate tensile strength ( $R_m$ ) and elongation (E) are shown in table 2.

**Table 2.** Static tensile test results at 20°C, average values

Tube section	0.2% proof strength [MPa]	Ultimate tensile strength [MPa]	Elongation [%]
Set 2 - circular cross section having a diameter of 4.0 mm			
I-2	303	526	12.8
II-6	357	462	1.1
III-12	315	445	2.9
Set 1 - rectangular cross-section of 25 mm x10 mm			
I-3	315*	417	6.9*
II-7	316*	319	1.4*
III-13	328*	344	1.7*
Manaurite XM	min. 250	min. 450	min. 8.0

\*approximate values

The results obtained on samples with round cross-section (set 2) well describe mechanical properties of the tube material at non degraded and degraded condition. Non-degraded material taken from the area near to the flange of the tube meets the requirements for minimum values of 0.2% proof strength, ultimate tensile strength and elongation for centrifugally cast tubes made of G-X45NiCrNbTi3525 steel (Manaurite XM). Tests show small decrease in ultimate tensile strength of 64 MPa and 81 MPa for II-6, III-12 samples in comparison to non-degraded I-2 samples. However, significant reduce in ductility has been observed in these areas. Elongation decreased from 12.8% (I-2 samples) to 1.1% and 2.9%. Changes in the elongation values are consistent with the values of the growth of the inner tube diameter.

The results of tensile tests carried out on samples with rectangular cross section containing full thickness of the tube wall (set 2) significantly differ from the results obtained on samples of round cross section (set 1). Tests showed significantly lower values of ultimate tensile strength and elongation (Table 2).

Generally, material of reformer tube shows low plastic properties. The compressive forces in the jaws of a testing machine caused cracking in samples curved heads (set 1) before test end. Hence samples heads has been milled to flat surface (Fig. 7). Due to cracking of specimens beyond measuring length, proof strength and elongation values should be treated as approximated.

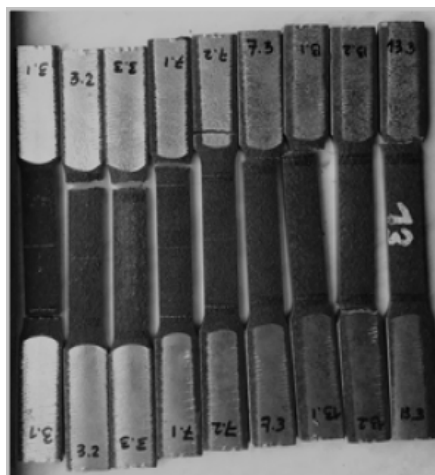


Fig. 7. Specimens with rectangular cross-section of 25x10 mm after tests

Differences in results of tensile tests obtained for two sets of specimens (set 1 and set 2) can be explained by the influence of the oxidized surface layers of samples containing the full thickness of the tube wall. Oxidized austenite grain boundaries behaved as initiators of brittle fracture, causing accelerated decohesion of specimens at lower tensile stresses. For this reason evaluation of mechanical properties of the material operated in creep conditions should be performed on the samples free from tube surface areas. On the other hand, the control of oxidation and carburization processes at the tube's surface during exploitation is essential.

## CONCLUSIONS

Research showed intermediate degree of degradation of tube microstructure, nevertheless uneven along the tube's length. It corresponds to the secondary, steady state of creep without evidence of any voids in microstructure. Uneven degradation of the tubes sections could be caused by local temperature differences along the tube length. It could be due to irregular heating by gas burners, however, more likely reason is the poor condition of the catalyst which can decrease the efficiency of the conversion reaction and reduce consumption of heat provided from the outside of the tube.

Uneven working temperature along the tube's length probably caused different diameter increase of the tubes sections at area II (2.90%) and III (1.53%). Greater increase in diameter of the tube is caused by more advanced microstructure degradation process. Research has also shown that the increase in inner diameter of the tube is correlated with a loss in ductility of cast steel measured at room temperature.

Moreover, it was found that:

- shapes of specimens taken from reformer tubes influence on the static tensile test results,
- specimens containing the full thickness of the tube wall with raw inner and outer surfaces exhibited lower strength and ductility compared to machined specimens containing only the central portion of the wall thickness of the tube.
- lower strength and ductility of full wall thickness specimens result from the presence of brittle oxidized surface layers where cracks initiation and further propagation is easier and occurs at lower tensile stresses.

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