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ASSESSMENT OF STRUCTURAL CHANGES AT IN-519 CAST STEEL REFORMER TUBES

ABSTRACT

Catalytic tubes are the most important parts in reformer furnaces at ammonia chemical plants. A steam reforming process converts hydrocarbons into mixtures of hydrogen, carbon monoxide and carbon dioxide. This reaction proceeds at a temperature range 800-900 °C and under pressure 3 - 4 MPa. This severe working condition causes a structural damage in the tubes. It is necessary to develop reliable methods for inspection of tube degradation and for realistic prediction of its residual life. The paper presents effects of long-term service at elevated temperatures on microstructural changes of the alloy IN-519 (24%Cr, 24%Ni, Nb).

Key words: *reformer tubes, residual lifetime, structural degradation*

INTRODUCTION

Steam reformer units provide hydrogen that is used for synthesis of ammonia, methanol and various other chemicals. The tubes made of alloy Cr-Ni cast irons are exposed to high temperature, stress and aggressive environment during service. Due to the complexity of factors influencing the lifetime of reformer tubes the estimation of degradation and life prediction methods are very limited. Prediction of residual lifetime of creep-resistant tubes and pipelines has been based on investigations performed during operation, including creep tests, tube deformation or deformation velocity measurements, metallographic examinations, mechanical properties tests (static, impact and fatigue) and physical properties examinations (radiological, ultrasonic, magnetic and electric properties measurements). The basic criterion for the evaluation of the suitability of creep-resistant material for future operation is creep strength, which depends on the material structure, and always decreases during the tubes lifetime. Creep tests are expensive and long term, so there are undertaken attempts to use more cost-effective methods instead of creep tests that also give useful and significant information [1,2].

Conventional non-destructive testing (NDT) techniques such as eddy current and ultrasonic, applied to reformer tubes examinations, are geared to detect creep damage in the form of internal cracking and are useful in the last stage of operation in reformer furnaces. Carburisation and oxidation of austenitic tubes surfaces create ferromagnetic layers. This phenomenon is frequently used as an indicator of tubes degradation. Measurements of magnetic permeability and low magnetic fields can give satisfactory information on effective tube wall thickness but cannot indicate creep failures unless microcracks appear [3].

The most recent techniques employ internal or external tube diameter growth as a material degradation indicator. Whenever catalytic tubes are operating under pressure in their creep temperature range, their diameters will increase in time. The laser mapping method referred as 'laser profilometry' allows to measure and quantification of tubes internal diameter [4]. The laser-mapping probe, inserted in a tube, can transmit several thousand diameter readings down its length. Recorded diameter increases in the range of 1-6% are potential indicators of certain stages of creep. This simple in principle and very convenient method does not assume other degradation mechanisms such as carburisation or oxidation of internal or external tube surfaces.

The method developed in the framework of EC NART project [5] assumes detecting of creep damage in catalytic tubes by two complementary examinations: ultrasounds testing and diameter measurements. The material structure, and the presence of voids can be assessed by means of ultrasounds testing. External diameter measurements of tubes deformation describe quantitatively creep damage. Information is added to database and converted in the life-assessment program, which calculates the probability of crack initiation and tube failure. Mentioned above methods are still in progress but due to the complexity of factors influencing the life of the catalytic tubes, current life prediction methods are limited and are not able to detect and quantify reliably of the damage existing in the tubes.

The structural criterion characterising tube degradation is very convenient but it can be accepted only when the structure evolutes continuously with the working time. This method, for example, is widely used for assessing quantitatively degradation of steel operated at elevated temperatures in power plants. Similar correlation can be observed for other metallic alloys working under creep conditions. Many investigations on heat resistant austenitic alloys reveal microstructure changes occurred during their operation in reformer units [1,6,7] but there are not any reliable structural factors proposed as degradation indicators so far.

In this current study, the centrifugal cast tubes made of alloy IN-519 after various working times are considered. The effects of long-term service at elevated temperatures on microstructural changes have been studied.

EXPERIMENTAL PROCEDURE

Investigations were performed on five tubes made of IN 519 cast steel taken from ammonia reformer furnace. The tubes worked at a temperature of 880°C and under 3,2 MPa pressure. Samples were taken below 4 m from the inlet end of the tubes where temperature during operation is stable. Tested tubes worked for various times from 24000 to 95000 hours. The tubes of a total length 12 meters (Fig. 1) were assembled together by welding from the 3-meter segments, so the chemical composition of the alloy could slightly differ along the tube.

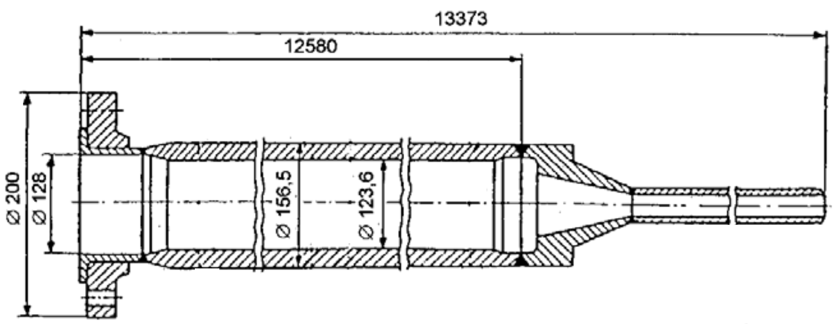

Fig. 1. The catalytic reformer tube

The table 1 shows he chemical composition of the samples. Since the new material was not available, the reference structure was detected on the sample "PM" taken from inlet end of the tube, where operational temperature did not exceed 540° C.

The microstructure of the material has been examined by optical microscopy and by scanning electron microscopy (SEM), and the chemical compositions of various phases have been detected by energy dispersive X-ray analysis (EDS). Metallographical samples were mechanically polished and etched by the Murakami reagent. Metallographical examinations were performed on the cross sections on the area near 1/3 tube wall thickness from the inner surface. The surface conditions of the tubes (carburisation, oxidation) are not discussed in this paper.

Table 1. *Chemical composition of tested tubes*

Sample designation	distance from the tube inlet	Working time	Chemical composition, wt %					
	m	h	C	Si	Mn	Cr	Ni	Nb
PM	0.2		0.297	0.598	0.557	23.3	26.0	1.38
24	6.5	24000	0.352	0.72	0.52	23.65	25.36	1.57
30	6.5	30000	0.435	0.71	0.61	23.40	24.66	1.8
44	4.0	44000	0.286	0.731	0.518	23.4	25.7	1.47
72	8.0	72000	0.318	0.86	0.365	23.9	24.9	1.46
95	5.0	95000	0.331	0.659	0.464	23.87	26.17	1.63

The microstructures of IN-519 cast steel specimens after various working times are presented in Fig. 2-4.

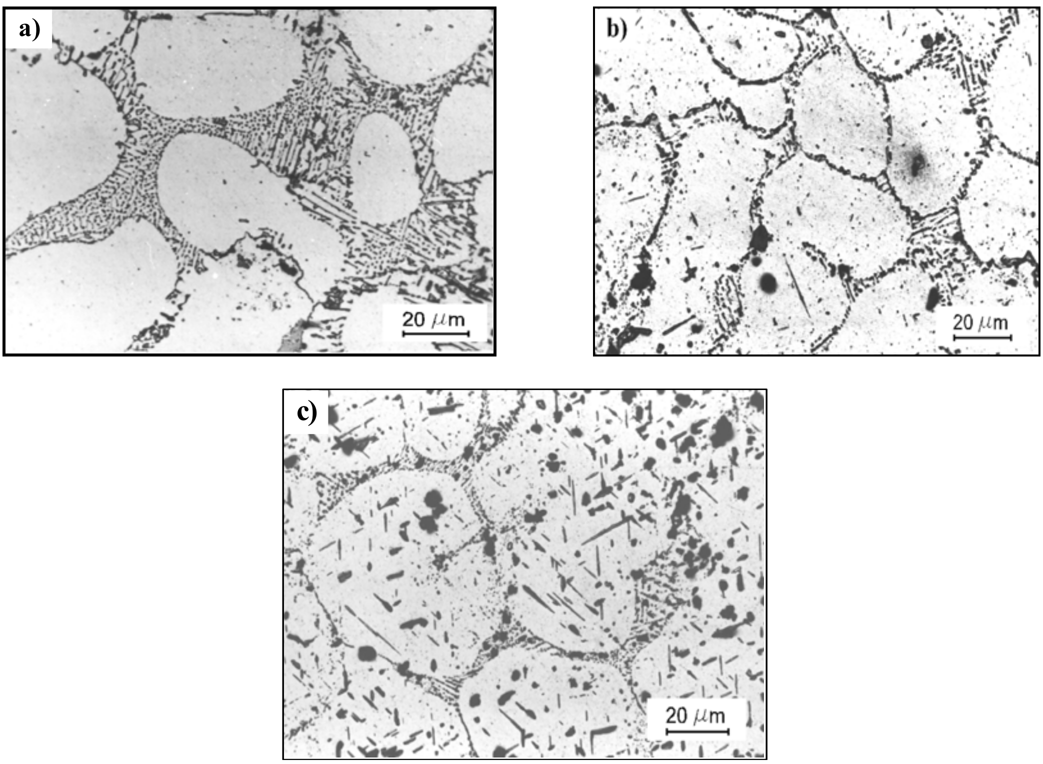

Fig. 2. Microstructures of IN-519 cast steel tubes, (a) non-degraded sample, after 24000 h (b) and 30000 h (c) operation in reformer furnace

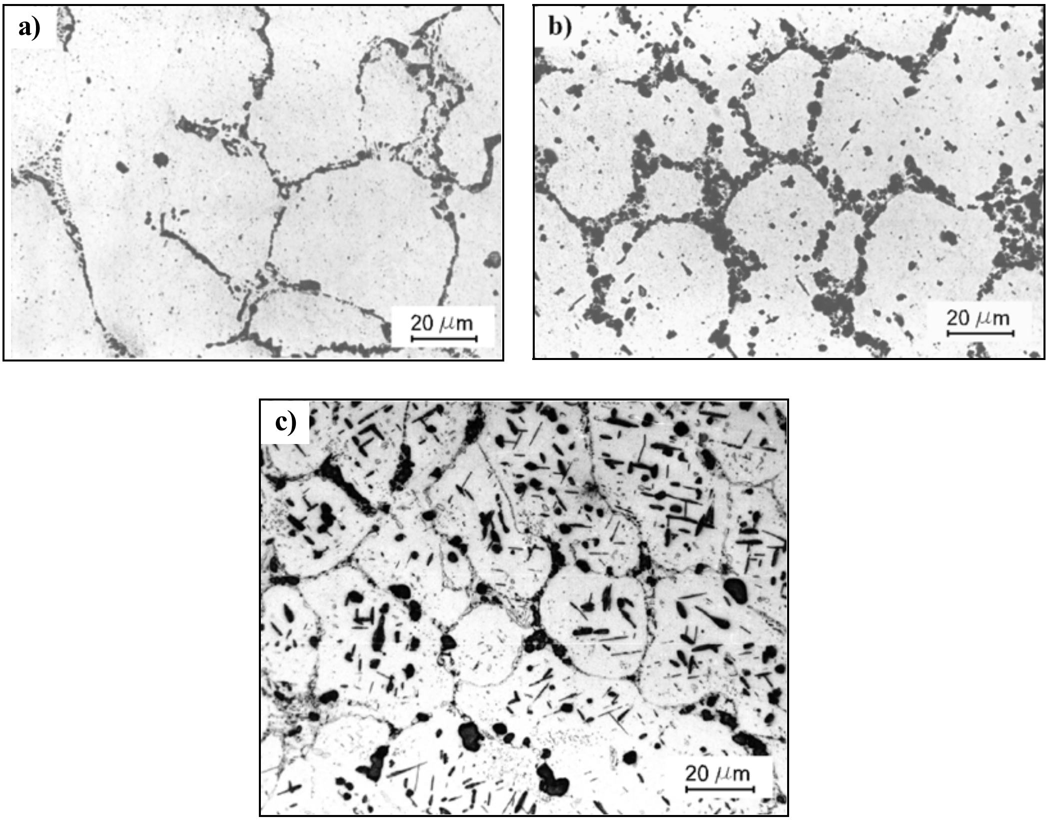

Fig. 3. Microstructures of IN-519 cast steel tubes after 44000 h (a), 72000 h (b), and 95000 h (c) operation in reformer furnace

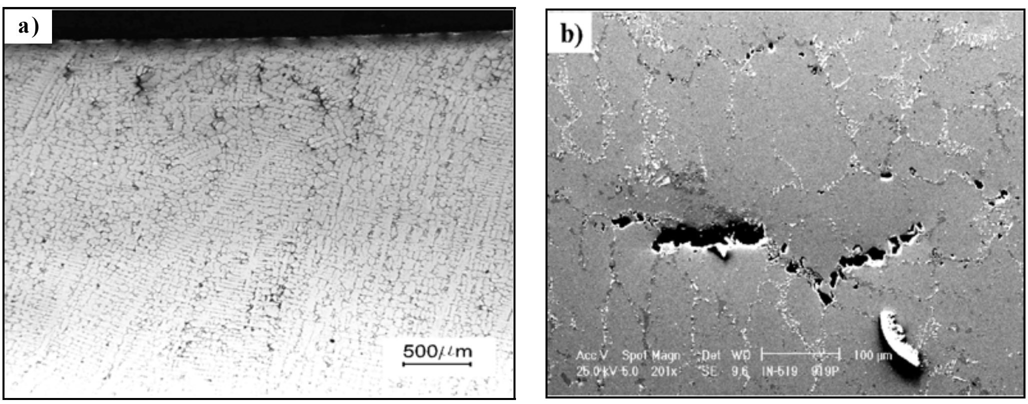

Fig. 4. Microstructures of IN-519 cast steel tubes. Voids aligned along dendrite boundaries

DISCUSSION

The non-degraded, reference structure of IN-519 alloy (PM), showed the dendritic columnar austenite grains located perpendicularly to tube walls. The structure consists of austenitic matrix with a proportion of primary inter-dendritic eutectic niobium carbides and chromium carbides. The thin semicontinous network of eutectic carbides can also be seen in the interdendric areas (Fig. 2a). The EDS analysis showed that some of eutectic carbides are Nb-carbides and others are Cr-carbides. The original morphology of eutectic carbides has been modified during the long time of operation at elevated temperatures when certain coalescence has taken place. The structure of samples after 24000 h still contain lamellar eutectic of primary carbides, but the coalescence process has formed incomplete continues network of primary carbides (Fig. 2b). Secondary carbides (mainly Nb carbides) were observed within the grains, but to a rather varying degree, both in size and amount. In addition to the small and round carbides inside austenite grains, also coarser and plate or needle-like precipitates of sigma phase were observed. Various amounts of sigma phase and degree of carbide coalescence were revealed.

The degree of structure degradation in the specimen after 30000 h operation was greater than in “24” samples (Fig. 2c). The carbide coalescence process was more advanced and quantity of lamellar eutectic decreased, but it still existed. The grain interiors were filled with needle-like sigma phase precipitates and dispersed NbC carbides.

The structure of the 44000 h sample consists of continuos network of coalesced carbides around austenite grains with only trace of primary eutectic structure. Little amount of sigma phase was detected inside the austenite grains (Fig. 3a).

The similar structure was found in 72000 h sample (Fig. 3b). In this case, the semi continuous coarse network along austenite grains consists of Cr and Nb carbides. Sigma phase was also present in the structure in the form of blocky precipitates. A small number of creep voids were found in the structure. The voids were formed at the interface between matrix and primary carbides or between matrix and the blocky sigma phase. The voids were rather small (up to 8 μm) and limited in number, scattered with no tendency to lining.

The structure of 95000 h (Fig. 3c) was similar to “72” sample, but unetched structure revealed a great number of creep voids. The voids are becoming aligned along dendrite boundaries. Aligned voids coalesced into fissures (up to 800 μm) were detected close to the inside surface of the tube (Fig. 4a,b).

The amount of primary and secondary phases (NbC, $M_{23}C_6$, σ) existing in the structures is presented in Fig. 5.

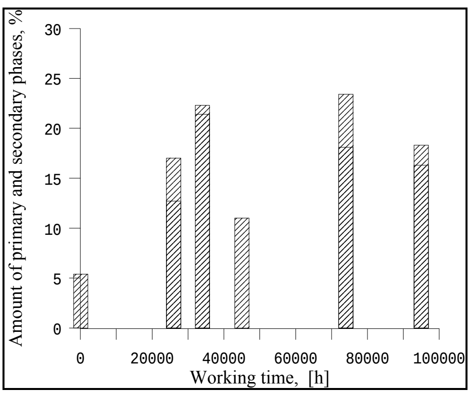

Fig. 5. Total amount of primary and secondary precipitates existed at IN-519 alloy structure after long term service at elevated temperatures

This simple quantitative description of the degree of structure degradation shows that structural changes during the operation time are not uniform and change in a non-monotonic manner with operating time. Moreover, the structures of the samples taken from the same reformer tube, used in the same conditions also can differ in quantity and form of precipitated phases. Generally, metallographic observations revealed that the various transformations took place in IN-519 cast steel tubes structure during operation time in the reformer furnace. These transformations are listed in Fig. 6.

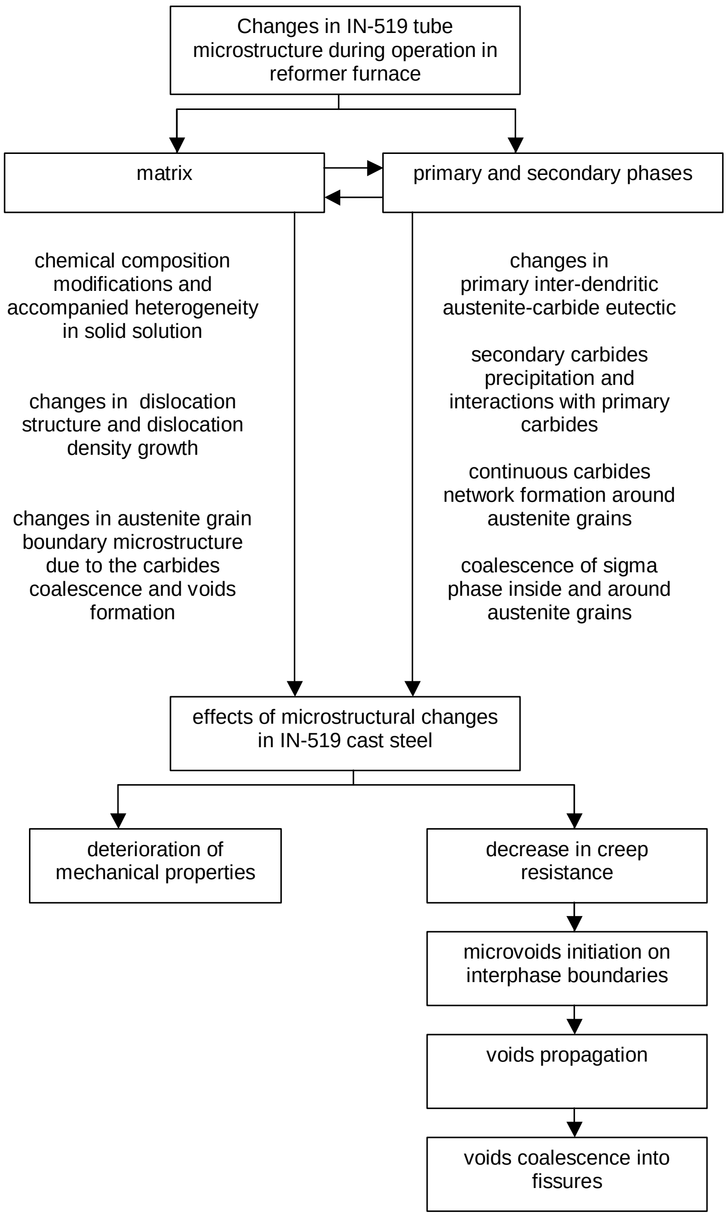

Fig. 6. Microstructural evolution of IN-519 cast steel tubes during operation time in reformer furnace [2]

CONCLUSIONS

1. Metallographic observations revealed the main transformations at IN-519 cast steel reformer tubes structure during their exploitation at elevated temperatures:
   a) coalescence of primary inter-dendritic austenite-carbide eutectic,
   b) formation of continuos network of primary and secondary carbides around austenite grains,
   c) sigma phase precipitation in the needle-like form,
   d) coalescence of sigma phase to the blocky shape.
2. Investigations showed that structural changes occur in non-monotonic way with operating time at elevated temperatures.
3. Estimation of tube degradation cannot be only based on the structure appearance.

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