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Evaluation of reformer tubes degradation after long term operation

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Properties

ABSTRACT

Purpose of this paper is to show the effect of long-term service at elevated temperatures on microstructural changes of cast steel reformer tubes made of the alloy IN-519 (24%Cr, 24%Ni, Nb). The relationship between mechanical properties and microstructure degradation is discussed.

Design/methodology/approach: Investigations were performed on five tubes taken from ammonia reformer furnace. Tubes worked at temperature of 880ºC and 3.2 MPa pressure. The operation time varied from 24000 to 95000 hours. Microstructure of the material has been examined with the use of light optical microscopy and scanning electron microscopy (SEM). The energy dispersive X-ray analysis (EDX) was used for phase identification. The mechanical properties have been evaluated in static tensile tests at room temperature.

Findings: Metallographic investigations of IN-519 cast steel catalytic tubes show that structural changes occur in non-monotonic way with operating time at elevated temperatures. For this reason the evaluation of tube degradation can not be based only on the microstructure examinations. The presence of a good correlation between mechanical properties of the catalytic tubes and service conditions, i.e. temperature, time, and internal stress was confirmed.

Research limitations/implications: The surface condition of the tubes walls like carburization and oxidation is not considered in this study.

Practical implications: The method for assessing the current degradation level and for predicting residual lifetime of creep-resistant tubes has been established. The method uses elongation values as the main factor characterizing structural degradation of catalytic tubes. It respects all degradation mechanisms involved in tubes degradation, and can give reliable information on reformer tube condition through almost whole period of operation.

Originality/value: Microstructure transformations occur in the IN-519 cast steel tubes during long-term operation in the reformer furnace were revealed and described

Keywords: Creep-resistance; Structure degradation; Reformer tubes; IN-519 cast steel

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1. Introduction

Catalytic tubes are important parts of reformer units at ammonia, methanol, hydrogen and gas process plants. They are the most expensive parts of reformer equipment. A steam reforming process converts hydrocarbons into mixture of hydrogen, carbon monoxide and dioxide. Chemical reactions proceed at a temperature range of 800-900°C and under pressure of 3-4 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 locate such damage at its early stages. The ammonia plant users postulate strong needs to develop reliable methods for inspection of tubes degradation and for realistic prediction of theirs residual life. Uncertainty about residual life frequently leads to conservative operation, beneath of nominal productivity of reformer units or premature replacement of the tubes [1-3].

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 [4-11].

Reliable criterion describing the amount of degradation in creep resistant reformer tubes has not been established so far. Conventional non-destructive testing (NDT) techniques such as eddy current and ultrasonic, currently applied to reformer tubes, 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 micro cracks appear [2,3].

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 quantify the tubes internal diameter [12]. 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 described in [13] 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.

Methods mentioned above 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 characterizing tube degradation is very convenient but it can be accepted only when the structure changes 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 [1,13-15] but there are not any reliable structural factor proposed as degradation indicator so far.

In this 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. The relationship between operation time and mechanical properties is discussed. The method for assessing the degradation level of tubes based on mechanical properties examinations at room temperature was proposed.

2. Experimental

Investigations were performed on five tubes made of IN 519 cast steel taken from ammonia reformer furnace. The tubes worked at 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 varying lengths of time 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.

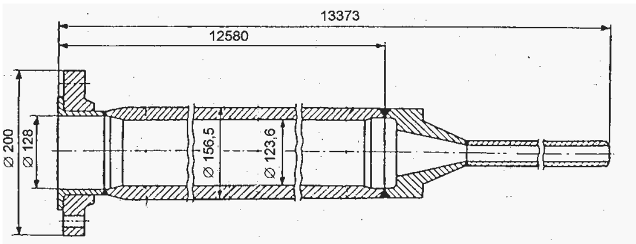

Fig. 1. Catalytic tube used in reformer unit

Table 1 shows the 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.

Microstructure of the alloy has been examined with the use of light optical microscopy and by scanning electron microscopy (SEM) Chemical compositions of various phases have been examined by energy dispersive X-ray analysis (EDX). Samples were mechanically polished and etched in Murakami reagent (30 g $K_3Fe(CN)_6$, 30 g KOH, 60 ml water). The mechanical properties at room temperature have been determined in static tensile tests. Metallographic examinations were performed on the cross sections at the area near 1/3 tube wall thickness from the inner surface. The surface condition of the tubes walls (carburisation, oxidation) is not discussed in this paper.

Table 1.
Chemical composition of tested IN-519 cast steel tubes

Sample designation	Distance from the tube inlet	Working time	Chemical composition wt.%							
	m	h	C	Si	Mn	Cr	Ni	Nb	S	P
PM	0.2		0.297	0.598	0.557	23.3	26.0	1.38	0.005	0.029
24-1	6.2	24000	0.351	0.62	0.53	23.42	25.59	1.46	0.003	0.021
24-2	6.5	24000	0.352	0.72	0.52	23.65	25.36	1.57	0.002	0.020
30-1	6.2	30000	0.309	0.79	0.68	23.79	25.17	1.47	0.002	0.024
30-2	6.5	30000	0.435	0.71	0.61	23.40	24.66	1.8	0.001	0.008
44	4.0	44000	0.286	0.731	0.518	23.4	25.7	1.47	0.003	0.023
72-1	4.0	72000	0.354	0.833	0.467	24.7	24.9	1.50	0.009	0.025
72-2	8.0	72000	0.318	0.86	0.365	23.9	24.9	1.46	0.012	0.023
95	5.0	95000	0.331	0.659	0.464	23.87	2 6.17	1.63	0.006	0.013

3. Results and discussion

3.1. Metallographic examinations

The non-degraded (PM) specimen showed the dendritic columnar austenite grains located perpendicularly to tube walls. The structure consists austenitic matrix with a proportion of primary inter-dendritic eutectic niobium carbide and chromium carbide. These massive lamellar carbides closely resemble pearlite. The thin semicontinous network of eutectic carbides can also be seen in the iterdendric areas, Fig.2.

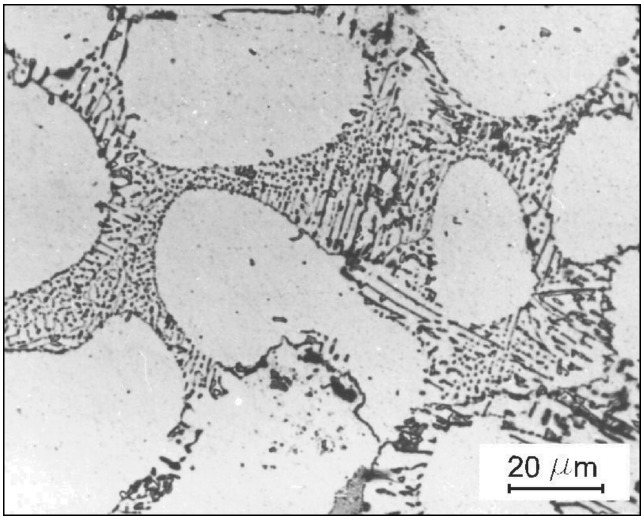

Fig. 2. Non-degradated structure of IN-519 cast steel, specimen PM

An EDX analysis showed that some of eutectic carbides are Nb-carbides and others are Cr-carbides. The two types of carbides cannot be distinguished from each other in the optical microscope The microstructures of IN-519 cast steel specimens after various working times are presented in Figs. 3-10.

The original morphology of eutectic carbides has been modified during the long time of operation at elevated temperatures during which certain coalescence has taken place.

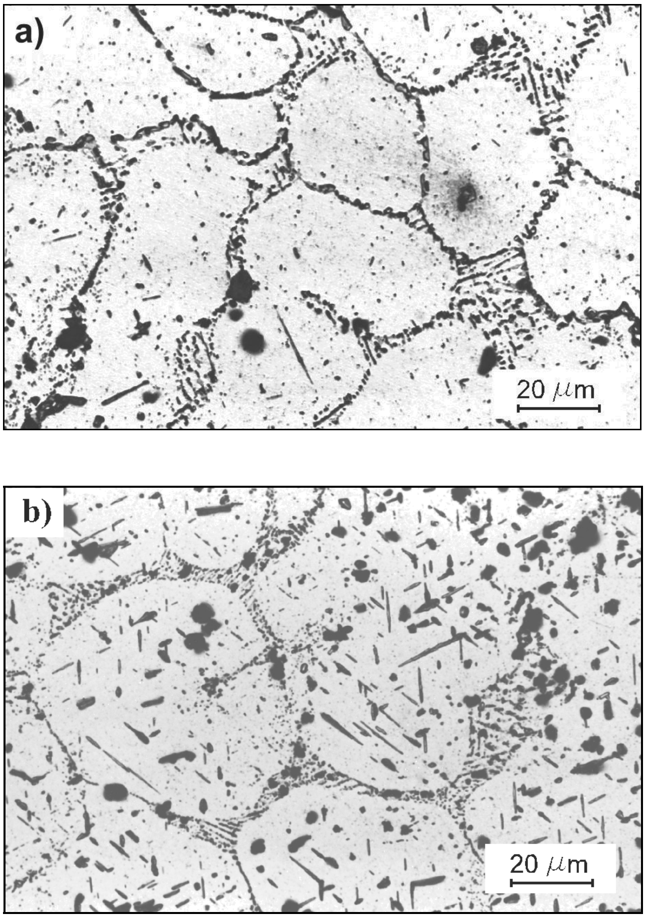

Fig. 3. Microstructure of IN-519 cast steel tubes after 24000 h operation in reformer furnace, (a) 24-1 and (b) 24-2 specimen

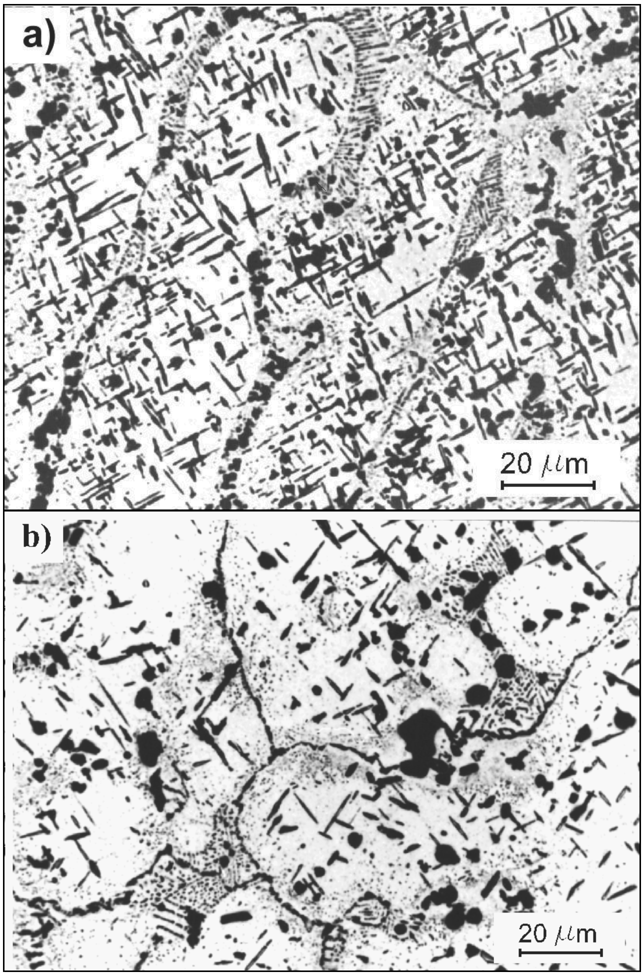

Fig. 4. Microstructure of IN-519 cast steel tubes after 30000 h operation in reformer furnace, (a) 30-1 and (b) 30-2 specimen

The structure of 24-1 and 24-2 samples contains still lamellar eutectic of primary carbides, but the coalescence process has formed not completely continuous network of primary carbides. Secondary carbides (mainly Nb carbides) are observed within the grains, but to a rather varying degree, both in size and amount. In addition to the small and rounded carbides inside the austenite grains, coarser and plate or needle-like precipitates are observed. An EDX analysis revealed that these precipitates have a chemical composition close to the sigma phase.

Presence of this phase in the alloy structure was unexpected because IN-519 cast steel has low susceptibility to formation of this embrittling phase in the temperature range of 600-950°C.

To ensure low susceptibility to sigma phase formation, the chemical composition of the alloy was modified to conform to the upper limit of 1.0% silicon and to maintain the nickel/chromium ratio at unity or above. The amount of sigma phase and degree of carbide coalescence was different in samples 24-1 and 24-2 (Fig. 3). These two samples were taken from different segments of one reformer tube but very close to each other (0.2 m) separated by welding joint. Obviously, the working conditions in this area of the furnace were the same, the manufacturing technology was also similar, so the structural difference could only be explained through slightly different chemical compositions of tube segments.

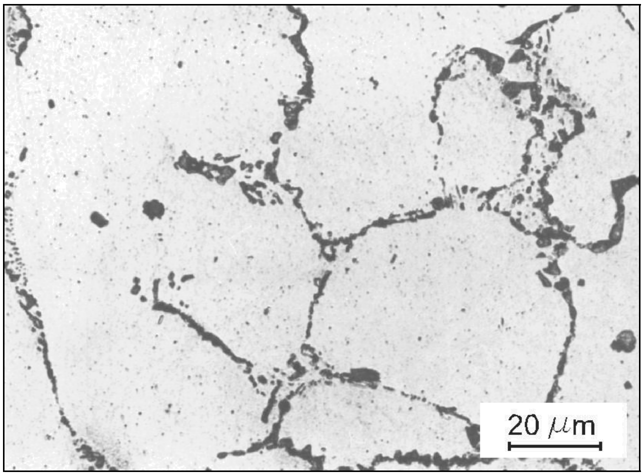

Fig. 5. Microstructure of IN-519 cast steel tubes after 44000 h operation in reformer furnace

The degree of degradation in the 30-1 and 30-2 specimens (30000 h) was greater than in “24” samples (Fig. 4). The carbide coalescence process is more advanced and quantity of lamellar eutectic decreased, but it still exists in both samples. The grain interior was filled with needle like sigma phase precipitates and dispersed NbC carbides. These two samples were taken from two segments of one reformer tube very close to each other and also in these structures the considerable differences in the amount of secondary phases were observed.

The structure of 44 sample (44000 h) consists continuous network of coalesced carbides around austenite grains with only the trace of primary eutectic structure. Very small amounts of sigma phase were detected inside the austenite grains.

The similar structure was found in 72-1 sample (72000 h). In this case, the semicontinuous coarse network along austenite grains consists of Cr and Nb carbides. Sigma phase is also present in the structure in the form of blocky precipitates. In 72-2 (Fig. 6b) sample, the corresponding coarse network of coalesced carbides existed but grain interiors were filled with great amounts of needle-like sigma phase precipitates. A small number of creep voids were found in “72” samples structure. The voids were formed at the interface between matrix and primary carbides or between matrix and the blocky sigma. The voids were round and rather small (up to 8 μm in diameter) and limited in number. They are scattered with no tendency to lining.

The structure of 95-1 was similar to 72-2 sample (Fig. 7), but unetched structure revealed a great number of creep voids. The voids were located mainly on the inside surface of the tube and at the midwall. Voids are becoming aligned along dendrite boundaries. Aligned voids coalesced into fissures (up to 800 μm in length) were detected close to the internal surface of the tube (Fig. 8).

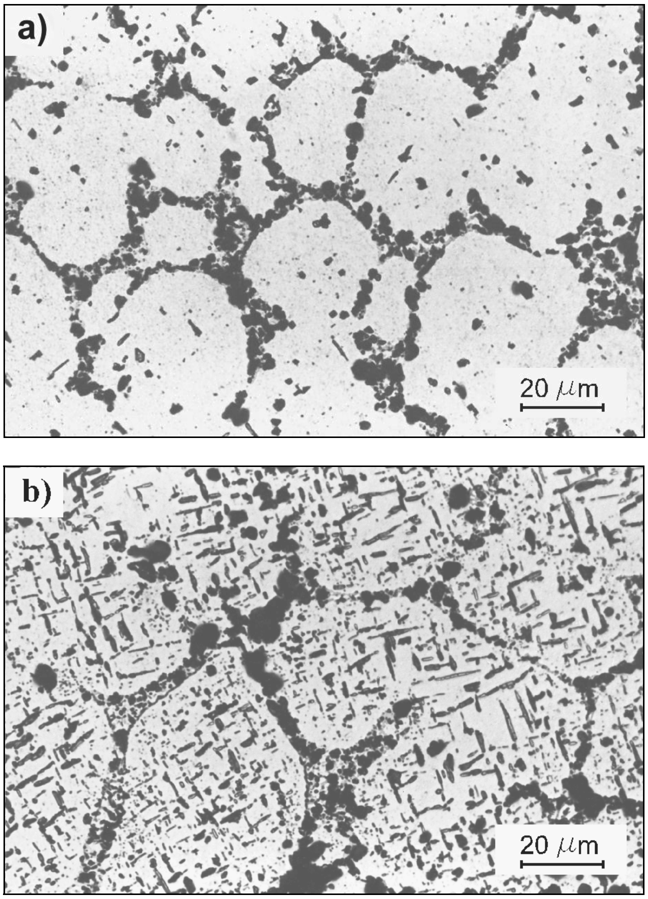

Fig. 6. Microstructure of IN-519 cast steel tubes after 72000 h operation in reformer furnace, (a) 72-1 and (b) 72-2 specimen

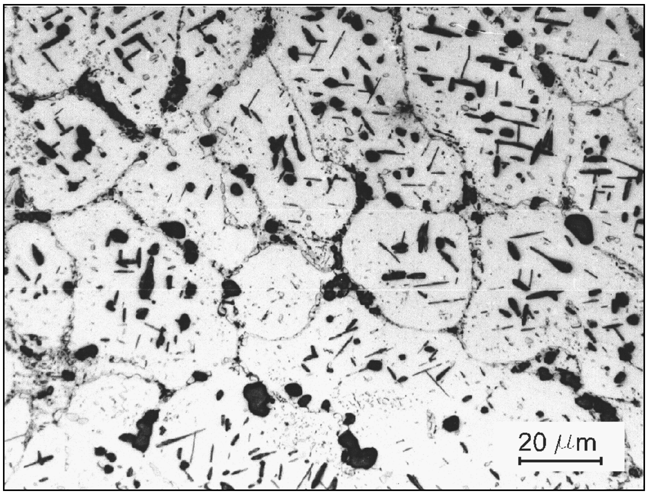

Fig. 7. Microstructure of IN-519 cast steel tubes after 95000 h operation in reformer furnace

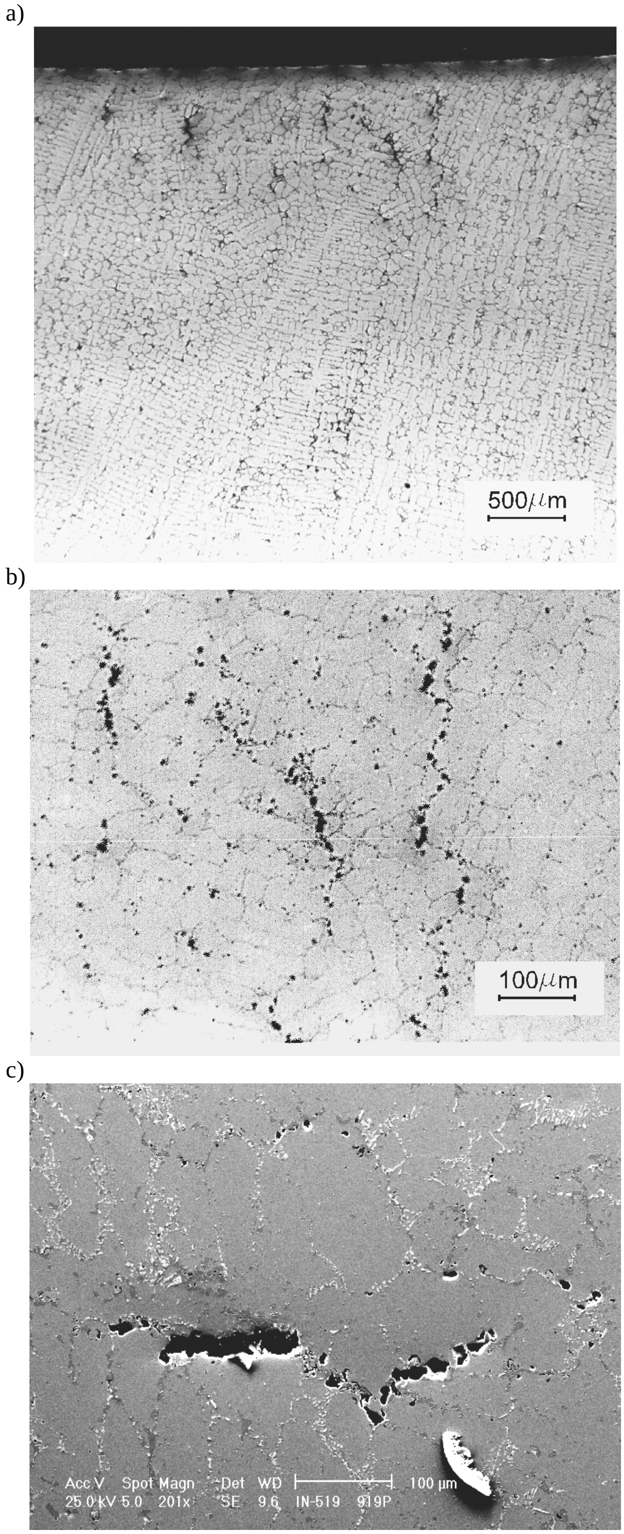

Fig. 8. Microstructures of IN-519 cast steel tubes. Sample 95, a), b), c) voids aligned along dendrite boundaries

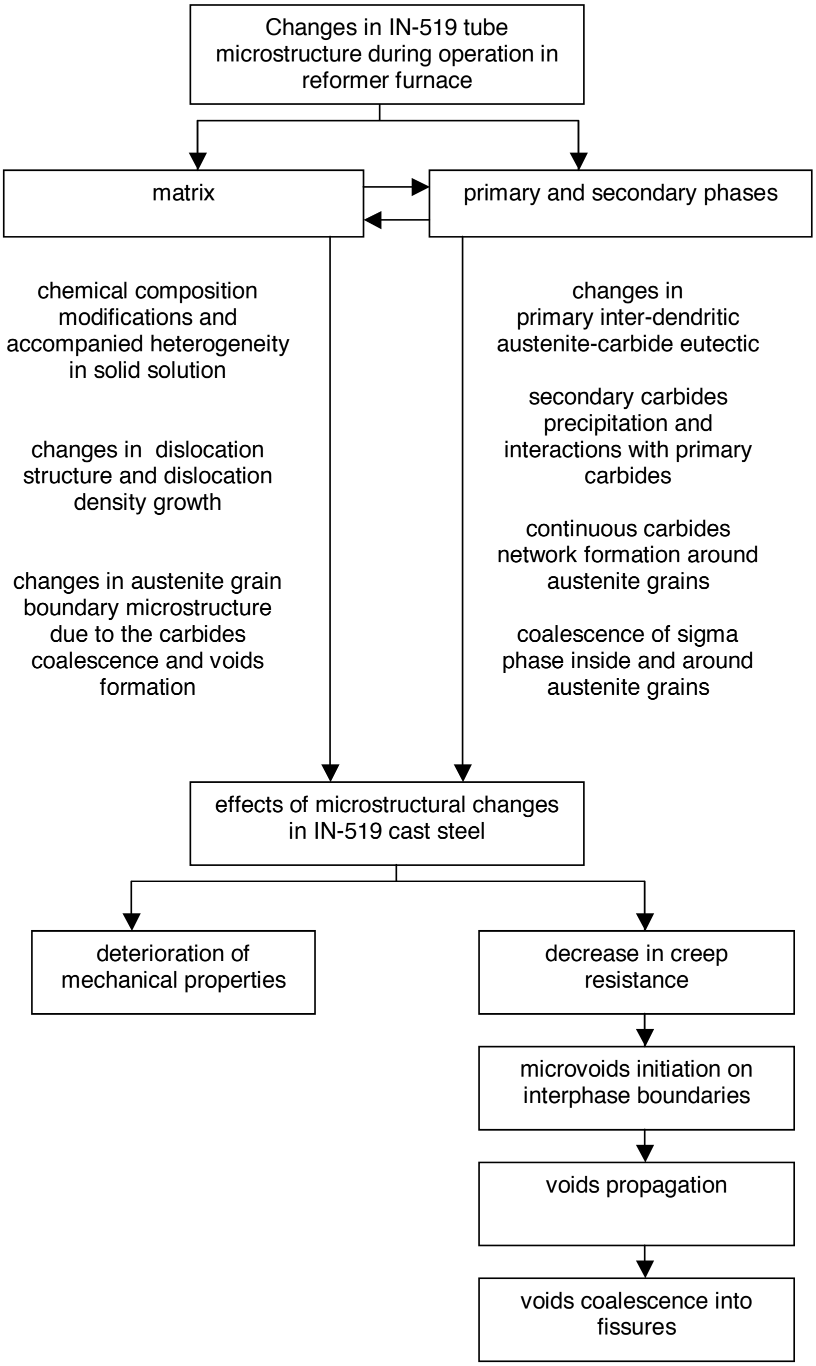

Fig. 9. Microstructural evolution of IN-519 cast steel tubes during operation time in reformer furnace [2]

Metallographic observations revealed that the following transformations took place in the structure during tube exploitation [2,15]:

- coalescence of primary inter-dendritic austenite-carbide eutectic,
- formation of continuous network of primary and secondary carbides around austenite grains,
- sigma phase precipitation in the needle-like form,
- coalescence of sigma phase to the blocky shape.

The amount of primary and secondary phases (NbC, $M_{23}C_{6}$, σ) existing in the structures is presented in Fig. 10.

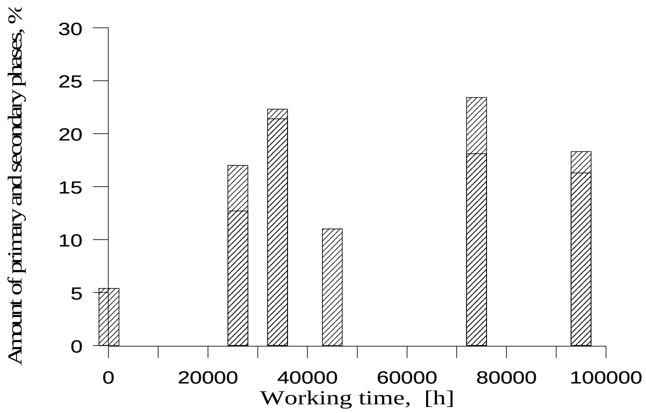

Fig. 10. Total amount of primary and secondary precipitates existed in the IN-519 alloy structure after long term service at elevated temperature

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, exploited in the same conditions also can differ in quantity and form of precipitated phases.

3.2. Mechanical properties examinations

Excluding application of microstructure factor for degradation level description of reformer tubes, the mechanical properties should be considered. The literature data indicate that mechanical properties obtained in static or dynamic tests at room temperature can not be used as measure of cast steel tube microstructure degradation mainly due to the non-monotonic changes after various operation periods. That theory was confirmed in investigations [4] but only for the first, short period of tubes utilization (up to 20000 h). Further operation can provide linear relationship between specific mechanical property and working conditions.

Results of hardness tests and tensile tests performed at room temperature on flat test specimens are shown in Fig. 11. The specimens were taken parallel to longitudinal axis of the tubes and contained the whole tube wall thickness. The time axis at the charts is plotted in logarithmic scale in order to obtain the straight line and estimate correlation between mechanical properties and tube working time.

The hardness test results show a large scatter (Fig. 11a) and it seems that this method is not suitable for estimating reformer tube degradation.

Results of tensile tests (Fig.11b,c) indicate that the most significant is reduction of plastic properties measured by unit elongation (E) at room temperature. The E values show the best correlation with working time logarithm. Taking this into account, the degree of E values reduction could be useful for determining the tube's degradation level and for estimating its residual lifetime.

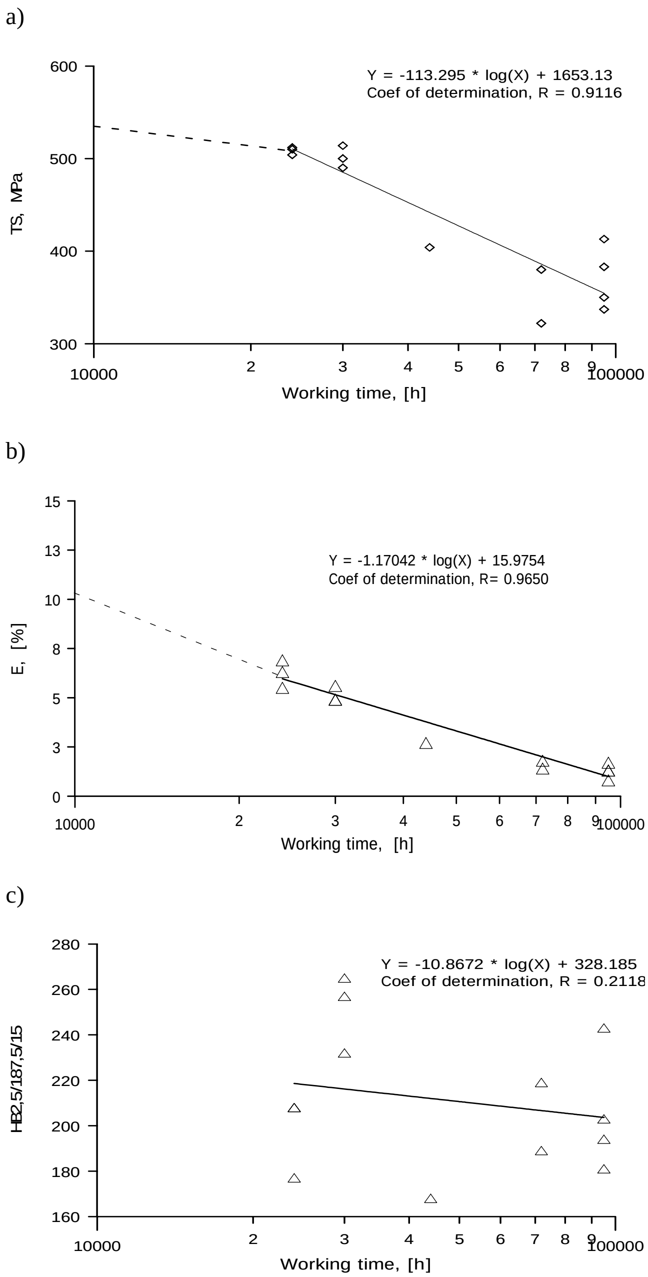

Fig. 11. Mechanical properties of IN-519 alloy after long-time service at 880°C in reformer furnace, a) tensile strength, b) elongation, c) Brinell hardness

3.3. The method for life time prediction of reformer tubes

The method employing mechanical property changes can be applied for assessing the current degradation of the tube's material after considering working parameters, e.g. stress and temperature. Working conditions can be representing in Larson-Miller parameter (P_{LM}). Standard relationship between tubes elongation (E) and P_{LM} was established after analysis of several dozen investigations results taken from available literature. The good correlation of regression equation was obtained. Practical verification of E =F(P_{LM}) relationship was confirmed in examinations performed on IN-519 tubes (Fig. 12).

Correlation between mechanical properties and service conditions allows on predicting residual lifetime of creep-resistant tubes.

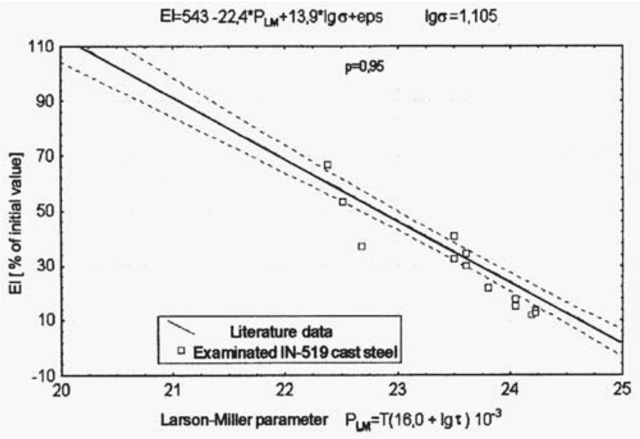

Fig. 12. Elongation of IN-519 alloy in dependence of working parameters in reformer furnace [4]

The method was developed on the base of IN-519 cast steel investigations, and uses elongation values as the main factor characterising structural degradation of catalytic tubes. The proposed method respects all degradation mechanisms involved in tubes degradation, i.e. creep, oxidation, carburisation, thermal fatigue and can give reliable information on reformer tube condition through almost whole period of operation.

4. Conclusions

1. Investigations of IN-519 cast steel reformer tubes revealed that structural changes occur in non-monotonic way with operating time at elevated temperatures, thus the evaluation of tube degradation cannot be based only on structure appearance.
2. Changes of elongation values for IN-519 cast steel reformer tubes obtained in tensile tests show the best correlation with the working parameters.
3. The method for assessing the current degradation level and for predicting the residual lifetime of creep-resistant tubes based on mechanical properties examinations performed at room temperature was proposed.

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