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Effect of solution heat treatment on mechanical properties of Manaurite XM reformer tubes after long term service at elevated temperatures

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ABSTRACT

The results of microstructure and mechanical properties changes of tubes made of Fe-Ni-Cr alloy G-X45NiCrNbTi35-25 after long term operation in methane reformer at elevated temperatures are presented. A method of tube regeneration by using solution heat treatment is proposed. Examinations included metallographic analysis with the use of light microscope (LM), scanning electron microscope (SEM), microanalysis of the chemical composition of precipitates (EDS) and static tensile tests. It was shown that solution heat treatment significantly affects the microstructure of the alloy, restoring the mechanical properties like tensile strength, yield strength and elongation of the tubes close to the values for the delivery condition, over 540 MPa, over 300 MPa and over 12%, respectively. The greatest improvement was observed in elongation, for samples after long-term operation at elevated temperature it was a minimum of 1.1% and after heat treatment 12.1% for the minimum requirement of 8% declared by producer (as cast).

Keywords: Manaurite XM; reformer tubes; creep degradation; Fe-Ni-Cr alloy; microstructure; mechanical properties; solution heat treatment.

INTRODUCTION

To ensure energy security the use of advanced construction materials, qualified manufacturing technologies and appropriate quality control methods of construction elements and devices is required [1-3]. This applies primarily to installations used in the extraction and oil processing industries, as well as the generation of electricity and heat [4-6]. Currently, due to the degradation of installations used for many years, more and more attention is being paid worldwide to the development of effective methods for predicting the operational durability of devices and structures and to the development of economic methods for their maintenance, including post-failure repairs [7-9].

Creep-resistant cast steel G-X45NiCrNbTi35-25 (trade name – Manaurite XM) is a fifth-generation alloy that uses the synergistic effect of niobium and titanium microadditives on the creep resistance of the alloy. Manaurite XM cast steel is used in the production of centrifugally cast catalytic methane reformer tubes. The chemical composition is characterized by an increased content of chromium and nickel in relation to the previous generation alloys, Table 1 [10, 11]. Chromium content in the range of 23–27% and nickel in the range of 32–35% as well as the presence of niobium and titanium microadditions create fine-dispersed carbides within microstructure, stable at high temperatures, which ensures high creep resistance at temperatures exceeding 900 °C. The specially selected chemical composition of G-X45NiCrNbTi35-25 alloy protects microstructure against the formation of a brittle sigma phase, the presence of which contributes to alloy brittleness and deterioration of creep resistance. At the sigma-austenite phase boundary, due to the difference in structures, microdiscontinuities may appear, the development of which may lead to the formation of macrocracks [12-15].

Acc. to ASTM	Acc. to Manoir	С	Mn	Si	Ni	Cr	Additions	R _m min.	R _{p0,2} min.	A min.
	Industries		MPa		%					
HK-40	Manaurite 20	0.35–0.40	1.00–1.50	1.0–2.0	18–22	24–28	Nb, W	449	242	10
IN-519	Manaurite 24/24 Nb	0.25-0.50	0.50–2.0	1.0–2.0	23–25	23–25	0.8-1.8 Nb	450	220	8
HP-Nb	Manaurite 36X	0.35–0.45	max. 1.5	max. 2.0	32–35	23–27	max. 1.5 Nb	450	250	8
HP-NbW	Manaurite 25-35W	0.40-0.45	max. 1.5	1.2–2.0	32–35	23–27	0.50-1.0 Nb, 4.0-5.0 W, Ti + Zr	450	250	8
HP-MA	Manaurite XM	0.45-0.50	max. 1.5	1.2–2.0	32–35	23–27	0.50-1.0 Nb, Ti, Zr, W	450	250	8

Table 1. Chemical composition and mechanical properties of creep-resistant steel used for the production of catalytic tubes of different generations [10, 11]

The maximum operating temperature of catalytic tubes made of fifth-generation alloys is about 940 °C at a pressure of about 3 MPa. During long-term operation at elevated temperatures, changes occur in the microstructure, which leads to a deterioration of the alloy's creep resistance. Numerous studies have shown that during the ageing of the alloy the carbide-austenitic eutectic disintegrates, secondary carbides initially precipitated as fine particles coagulate and grow in the form of blocks or acicular form. Changes in the microstructure cause a decrease in the mechanical properties of the tubes both at operating temperature and at room temperature. The tensile strength and yield strength of cast steel are reduced. The brittleness of the material increases, which is manifested by a decrease in impact strength and elongation in static tensile tests carried out at room temperature [10, 16-18, 19].

The problem of safe operation of catalytic tubes is extremely important and still relevant. The costs associated with replacing tubes in a methane reformer are very high and therefore efforts are made to operate the tubes as long as possible, but still safely. Over the years, actions have been taken to renew catalytic tubes, mainly related to restoring their original geometry. In secondgeneration Fe-Cr-Ni alloys (IN-519), attempts have been made to regenerate the microstructure of the tubes by long-term solution heat treatment at high temperatures [20, 21]. In principle, solution heat treatment of cast steel should cause dissolution of secondary and partially primary carbides, as a result of which the austenitic matrix will be enriched with alloy elements. The next stage of operation of such tubes at high temperatures will cause the precipitation of fine secondary carbides again. This change in microstructure will increase creep resistance of the tube material and will allow for their further operation. However, it should be clearly noted that this method of pipe regeneration can be effective only when no large clusters of creep voids and microcracks appear in the microstructure [22, 23].

The motivation for undertaking the research was to check how solution heat treatment would affect the change in the microstructure of the fifth generation alloy (Manaurite XM) after long-term use. Changes in the mechanical properties of the tubes will be determined only at room temperature and on this basis conclusions will be drawn about the possibility of improving the creep resistance of the alloy.

EXPERIMENTAL

The tests were carried out on a catalytic tube with an internal diameter of 125.0 mm, external diameter of 146.0 mm, wall thickness of approx. 9.8 mm, total length of 15.8 m. The tube made of austenitic cast steel grade G-X45NiCrNbTi35-25 was removed from a methane reformer after 46 000 hours of operation at a temperature of 937 °C and an internal pressure of 30.5 bar.

The catalytic tube consisted of three sections connected by circumferential welds. The pipe diagram is shown in Figure 1. Samples were cut from each section (I, II and III) of the catalytic tube for microscopic metallographic examinations, chemical composition analysis and static tensile tests. The microstructure and material properties of the tube from areas I, II and III differed due to different operating temperatures. Area I of the tube – close to the substrate inlet – was operated at the lowest temperature. The further from the flange, the temperature of the tube increased and reached the nominal value at 1/3 of the height counted from the end of the tube.



Figure 1. Diagram of the catalytic tube with marked places where samples were taken for testing

The analysis of the chemical composition of the tube sections was carried out on a Spectrolab optical spectrometer type LAB 05 S/N 45/263. Table 2 presents the average content of elements obtained from four trails and the requirements for centrifugally cast steel tubes Manaurite XM according to the company standard of Manoir Industries.

The summary presented in Table 2 shows that all tested tube sections have a similar chemical composition and were probably made from one melt.

Two sets of samples were prepared for the tests. The samples were taken parallel to the tube axis. The first set of samples was tested in the state after operation – samples from sections I-2, II-6, III-12 (Fig. 1), the second set of samples was subjected to heat treatment by solution heat treatment – samples from sections I-3, II-7, III-13. Both sets of samples for the static tensile test contained three samples from each section. A total of 18 samples with a circular cross-section of \emptyset 5.0 mm and an initial measuring length of Lo = 30 mm were prepared, taken from the central part of the catalytic tube wall material. Static tensile tests were carried out in accordance with the PN-EN ISO 6892-1:2016-09 standard.

The microstructure of the material has been examined by light optical microscopy and by scanning electron microscopy (SEM), and the chemical compositions of various phases have been examined by energy dispersive X-ray spectroscopy (EDS). Metallographic samples were mechanically polished and etched by Murakami reagent $30 \text{g K}_3\text{Fe}(\text{CN})_6$, 30 g 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.

The samples were solution heat treated in a chamber furnace. The samples were placed in a cold furnace. The heating was carried out in two stages. In the first stage, the furnace was heated to 700 °C and the samples were kept there for 1 hour. Then, the furnace temperature was raised to 1220 °C, the samples were kept at this temperature for 2 hours and then cooled using a stream of compressed air. Solutioning parameters were selected based on the patent description [21].

RESULTS AND DISCUSSION

Figures 2–4 show LM microstructures of the catalytic tube in the after-service conditions and in the state after solution heat treatment. In sample I-2 (Fig. 2a) an undegraded structure characteristic for high-carbon austenitic cast steel in the as-cast state was observed. It is composed of austenitic matrix and carbide-austenitic eutectic of characteristic lamellar composition located on the boundaries of austenite grains. Apart from the eutectic structure, there are also elongated primary carbides distributed along the austenite boundaries. Massive primary carbides Nb and Cr occur only within the eutectic

Table 2. Results of the control analysis of the chemical composition of the tested catalytic tube

Section	Element content, wt. %										
Section	С	Si	Mn	Р	S	Cr	Мо	Ni	Nb	Ti	
Manaurite XM	0.40 0.45	1.20 2.00	max 1.50	max 0.030	max 0.030	23.0 27.0	max 0.50	32.0 35.0	0.50 1.00	+	
I	0.53	2.05	1.30	0.012	0.001	25.2	0.10	36.7	0.67	0.05	
II	0.53	2.01	1.24	0.018	0.001	25.3	0.08	36.5	0.65	0.02	
III	0.53	2.00	1.30	0.015	0.001	25.2	0.00	36.3	0.667	0.04	



Figure 2. Microstructure of sample: a) I-2 in the post-service state, b) I-3 after solution heat treatment

and along the austenite grain boundaries. The interiors of austenite grains are free of precipitates.

The original morphology of eutectic carbides has been changed during the long time of operation at elevated temperatures during which certain coalescence has taken place. The structure of II-6 (Fig. 3a) and III-12 (Fig. 4a) samples contain still lamellar eutectic of primary carbides, but the coalescence process has formed not completely continuous network of carbides. Secondary carbides in great amount are observed within the austenitic grains. No acicular precipitates were observed within the austenite grains characteristic for the intermetallic sigma phase. The size, shape and distribution of secondary carbides were similar in samples II-6 and III-12.



Figure 3. Microstructure of sample: a) II-6 in the post-service state, b) II-7 after solution heat treatment



Figure 4. Microstructure of sample: a) III-12 in the post-service state, b) III-13 after solution heat treatment

After solution heat treatment, significant changes in the alloy microstructure were observed. In sample I-3 (Figure 2b), the disappearance of the austenitic-carbide eutectic and coagulation of eutectic carbides, which formed compact precipitates along the austenite grain boundaries, were observed. Some of these carbides formed large clusters inside the austenitic matrix. In samples II-7 and III-13, the disappearance of secondary carbide precipitates was observed, which dissolved in the matrix, Figure 3b and 4b. Coalescence of primary carbides and some secondary carbides occurred, which formed a thick network along the austenite grain boundaries.

The observations from light microscope were confirmed by examinations using a scanning electron microscope (SEM). Figure 5a shows the microstructure of sample III-12 in the post-service state. A large number of small spherical secondary carbides are visible inside the austenitic matrix. Figure 5b shows the same structure obtained using the backscattered electron technique (BSE), which allows for qualitative differentiation of structural components with various chemical composition. It can be seen that the carbides forming a compact network around the austenite grains are not homogeneous. Some of the compact carbides are light in color, while others are dark.

Figure 6a and 6b show the SEM-BSE microstructure of sample III-13 after solution heat treatment. Areas of austenitic matrix without secondary carbide precipitates are visible. The network of coagulated carbides on the austenite grain boundaries shows a structure composed of different types of carbides. Higher magnification in Figure 6b reveals the presence of a network of fine cracks in the austenitic matrix and on the austenite-carbide boundaries. Such cracks were not observed in the microstructure of the tube in the post service state, before solution heat treatment.

Figure 7a shows the morphology of secondary carbides precipitated in the austenitic matrix in sample III-12 after service. The diameter of globular precipitates or the width of elongated precipitates does not exceed 1 μ m. There are no signs of



Figure 5. Microstructure of sample III-12 in the post-service state: a) SEM, b) SEM – BSE mode



Figure 6. Microstructure of sample III-13 after solution heat treatment: a) SEM - BSE, b) SEM – BSE Close-up of the crack network



Figure 7. Microstructure of sample: a) III-12 in the post-service state, b) III-13 after solution heat treatment

coagulation of secondary precipitates. No acicular precipitates characteristic of the σ phase were found. Figure 7b shows an enlarged SEM image of sample III-13 after solution heat treatment.

Microanalysis of the chemical composition of the austenitic matrix and carbide precipitates was performed using a scanning electron microscope coupled with an energy dispersive X-ray spectrometer (EDS). Examples of the obtained spectra for the analyzed areas are presented in Figure 8 a–c (a – dark precipitates, b – light precipitates and c – austenitic matrix) from the areas as indicated in Figure 7b, respectively.

The results of chemical composition microanalyses are presented in Table 3. The obtained results indicate that the dark precipitates (Fig.



Figure 8. Spectra (EDS) of the areas of sample III-13 after solution heat treatment, a) dark precipitate area, b) light precipitate area, c) austenitic matrix

Place of applysis	Chemical composition, wt. %								
	Si	Cr	Fe	Ni	Nb	Ti	V	Mn	
Dark precipitation	1.45	71.92	18.47	8.16	_	_	_	_	
Bright precipitation	1.55	12.31	18.03	16.28	47.94	3.16	0.10	0.63	
Acicular precipitation (Fig. 5a)	1.33	47.58	27.53	22.90	-	_	_	0.66	
Austenitic matrix I-3 in the post-service state	1.9	24.5	38.6	34.2	-	_	_	0.8	
Austenitic matrix III-13 in the post-service state	2.0	22.7	39.2	34.9	_	_	_	1.2	
Austenitic matrix III-13 after solutionizing	2.7	23.6	38.51	36.0	0.2	-	_	1.2	

Table 3. Results of chemical composition microanalysis (EDS) of microstructure elements of Manaurite XM alloy

5a) are conglomerates of chromium carbides of the M23C6 type, while the adjacent light precipitates are niobium carbides and probably niobium-rich phases of the Nb6Ni16Si7 type. The spherical precipitates inside the austenite grains in sample III-12 in the post-service state (Fig. 6a) are M23C6 carbides containing mainly chromium. The tests did not detect any precipitates with a composition characteristic for the σ type intermetallic phase.

Microanalysis of the chemical composition of the austenitic matrix indicates a decrease in the chromium content from 24.5% to 22.7% during long-term service of the tube, which should be associated with the formation of secondary chromium carbide precipitations and a decrease in the chromium content in the matrix. The solution heat treatment caused the dissolution of some of the secondary carbides, which increased the Cr content in the matrix to about 23.5%.

The results of the static tensile test at room temperature are presented in Figure 9. The

minimum values of yield strength ($Rp_{0.2}$), tensile strength (Rm) and percentage elongation after break (A) declared by the manufacturer are marked as horizontal lines on the graphs in the corresponding colors and are 250 MPa, 450 MPa and 8%, respectively. It is noticeable that the strength and plasticity of the tube material from the areas operated at high temperatures (II-6, III-12) are significantly reduced compared to the area of the tube near the flange, where the temperature did not exceed 550 °C (I-2).

Solution heat treatment at temperature of 1220 °C caused structural changes in the microstructure of the cast steel and a significant improvement in the mechanical properties tested at room temperature. An increase in the tensile strength (Rm) and percentage elongation after fracture (A) was observed in all tested areas of the tube (I, II, III). The obtained values of tensile strength and elongation meet the requirements of the cast material declared by the manufacturer.



Figure 9. Results of the static tensile test carried out at 20 °C, a) 0.2% proof strength (Rp0.2) and tensile strength (Rm), b) percentage elongation after fracture

CONCLUSIONS

The article presents the results of research on mechanical properties and changes in the microstructure of centrifugally cast catalytic tubes after long-term operation under creep conditions and after revitalization by solution heat treatment.

- 1. The tests showed a significant degree of degradation of the tube microstructure after long-term operation (45,000 h) at a temperature of 937 °C.
- 2. The changes in the microstructure resulted in a significant reduction in the strength properties (Re, Rm) and plasticity of the tube material tested at room temperature.
- 3. No creep voids, microcracks or intermetallic phase (Cr-Fe) were found in the microstructure of the tubes in the post-service state.
- 4. In order to improve the mechanical properties of the tubes and their creep resistance, it was proposed to carry out a solution heat treatment at a temperature of 1220 °C.
- 5. Solutionizing caused changes in the microstructure of the tested G-X45NiCrNbTi35-25 alloy. Most of the secondary precipitations of chromium carbides dissolved, which enriched the austenitic matrix in Cr.
- 6. After solutionizing, the tensile strength (Rm) and percentage elongation after fracture (A) were restored to values that met the manufacturer's requirements.
- 7. After heat treatment, small cracks were observed in the austenitic matrix and at the austenite-carbide boundaries. Therefore, the tubes should be subjected to non-destructive testing (NDT) after solutionizing to exclude the presence of cracks that threaten further safe operation.
- 8. The mechanical properties of the tubes assessed at room temperature can be an indirect measure of the material's creep resistance. In order to determine the rate of degradation of the regenerated microstructure, additional tests of the tubes should be carried out under creep conditions.

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