SOLUTIONIZING OF IN 519 SUPERALLOY AFTER LONG-TERM EXPOSURE

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S u m m a r y

Hydrogen used for ammonia synthesis in chemical plants is received as a result of endothermic thermal–catalytic decomposition of methane with water steam. The process is carried out in reformer pipes made from austenitic cast steel with nickel catalyst under pressure up to 4.0 MPa and temperature up to 900 °C [1]. The mechanical properties and phase composition of these tubes changed during a long service. The precipitation of intermetallic phases in alloyed austenite matrix and at grain boundaries are spheroidizated. The stable dendritic microstructure disappears. This results in a decrease of mechanical properties of the pipe material as well as in the intensification of creeping. In order to regenerate the tube material a solution heat treatment was applied. The author presents results of LMA, XRD and mechanical property investigation of IN 519 samples taken from a centrifugal cast pipe which worked in a catalytic reformer for 120760 hours and was solutionized.

Keywords: reforming, IN519 superalloy, phase transformation, solutionizing, G phase

Przesycanie nadstopu IN 519 po długotrwałej eksploatacji

S t r e s z c z e n i e

Wodór do syntezy amoniaku w zakładach chemicznych uzyskuje się w endotermicznym procesie cieplno-katalitycznego rozkładu metanu parą wodną pod ciśnieniem do 4 MPa w temperaturze do 900 °C. Proces prowadzi się w reformerze wykonanym z nadstopu IN 519 z rur odlewanych odśrodkowo i wypełnionych katalizatorem niklowym. Długotrwała eksploatacja powoduje przemiany fazowe i strukturalne w austenitycznej osnowie nadstopu: sferoidyzację wydzieleń faz międzymetalicznych oraz w eutektyce na graniach ziarn. Odlewnicza mikrostruktura dendrytyczna ulega zanikowi. Następuje koagulacja wydzieleń faz międzymetalicznych, powodując zmiany właściwości mechanicznych nadstopu IN 519, także intensyfikując proces pełzania. W celu regeneracji materiału rury (IN 519) prowadzono jego przesycanie. W pracy przedstawiono wyniki badań właściwości mechanicznych, metalograficznych i rentgenograficznych nadstopu IN 519 pobranego z rury po 120760 h eksploatacji i przesycaniu.

Słowa kluczowe: reformer, nadstop IN 519, przemiany fazowe, przesycanie, faza G

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1. Introduction

Catalytic pipes are used in chemical and petrochemical industry to obtain hydrogen. In service conditions in the temperature range of 550÷900 °C, at the inside pressure up to 4 MPa, the material of the pipes undergoes creeping which can result in the destruction of the pipe [2-20]. The tubes applied in steam reforming, of a total length of 12 meters, were assembled together by welding of their segments. The tubes' segments were made by means of centrifugal casting of austenitic chromium-nickel cast steels stabilized with additions of niobium. A long–term exposure of tube material to elevated temperatures and stress causes changes in their microstructures, generation and growth of creeping processes and, in consequence leads to a deterioration of their functional properties. The microstructure of IN 519 superalloys in delivery states contains alloys austenite as well as carbides $(Cr,Fe)_{23}C_6$ and NbC. After a long-term service a decrease of the hardness and the plasticity of steels was observed as a result of disappearance of dendrite structure, changes of NbC carbides in TCP phase – $Ni_{16}Nb_6Si_7$, precipitation, spheroidization and coagulation of intermetallic phases. In the zone of a temperature below 815 °C, an increase of the hardness and a decrease of the plasticity of tube material were observed as result of intermetallic σ phase precipitation [8-20].

A great number of Polish reformer units have attained or exceeded their design life of 100,000 hours in service. A gradual exchange of the second generation catalytic pipes (24% Cr, 24% Ni, 1% Nb) into the third generation pipes (25% Cr, 35% Ni, 1% Nb + Ti / Zr) is taking place. A growth in the price of catalytic pipes from 6,000 EUR in 2004 to 11,000 EUR in 2006, costs of exchange and losses suffered when it is necessary to stop production led to attempts to modernize reformers. Diagnostic methods of catalytic pipes had to be perfected and new catalysts had to be introduced. The equipment of the reformers in spring system of every pipe, monitoring and the providing for stable parameters of operation, lead to the situation that catalytic pipes are exploited over their design life. For example in chemical works "POLICE" in 2004 200 catalytic pipes IN 519 were exchanged after 120,760 hours of operation into the 3rd generation Manaurite XM pipes. In an identical reformer, the second generation pipes IN 519 after 143,300 hours of operation were exchanged in 2007 into the third generation 4852 Micro pipes manufactured by Schmidt + Clemens firm. A question arises what is the remaining life of the exchanged pipes and if there is a possibility to restore the microstructure and properties of these catalytic pipes?

The earlier investigations carried out after 74,200 h working hours showed the possibility of restoration of useful features of the IN 519 tube material [9, 13, 14]. To check the possibility of restoration material of the same kind of tubes after 120,760 hr of service the solution heat treatment procedures at 1000 ^{o}C/6h, 1100 ^{o}C/4h and 1200 ^{o}C/2h were carried out.

2. Experimental details

The test sections were taken to examinations from the inlet area, the areas 1.65 m from the inlet where the maximum hardness and minimum plasticity of tube material were observed and the areas 8.5 m from the inlet of substrates where the maximum deterioration of mechanical properties and plasticity of tube material was observed. The tensile, hardness and impact tests, metallographic and X-ray examinations were performed. The specimens for tensile and impact tests have been made so as to ensure the location of axis sample at the area near 1/3 tube wall thickness from the inner surface. As a reference structure, the structure from the inlet end of the tube was used, where the service temperature did not exceed 550^{o}C. The tensile test was performed three times for each measuring point using Instrom type 8500/8800 at the load range of 100 kN. The Charpy impact tests were performed three times for each measuring point at a temperature of 20^{o}C and six times for the measuring point at a temperature of 830^{o}C. The microstructure of the material has been identified by light optical microscopy (LMA) and by scanning electron microscopy (SEM), and chemical compositions of various phases have been examined by energy dispersive X-ray analysis (EDX). Metallographical examinations were performed on the cross sections perpendicular to the tube axis or along the axis of tube. After mechanical polishing the specimens were etched with Murakami reagent dyeing σ phase and chromium carbide brown.

3. Experimental results

Metallographical investigations of the received specimen (from the inlet substrates area) showed dendritic columnar austenite grains located almost perpendicularly to the tube walls. The structure consists of austenitic matrix with a network of eutectic carbides which precipitated initially during the solidification process and which were distributed at the dendrite and grain boundaries (Fig. 1). X-ray analysis showed that the eutectic carbides were niobium carbides and chromium carbides [4-15].

As a result of a long time of operation at an elevated temperature the structure in the matrix and grain boundaries was modified. In the region 1.65 m from the inlet, after 120,760 h of operation, fine secondary carbides precipitated

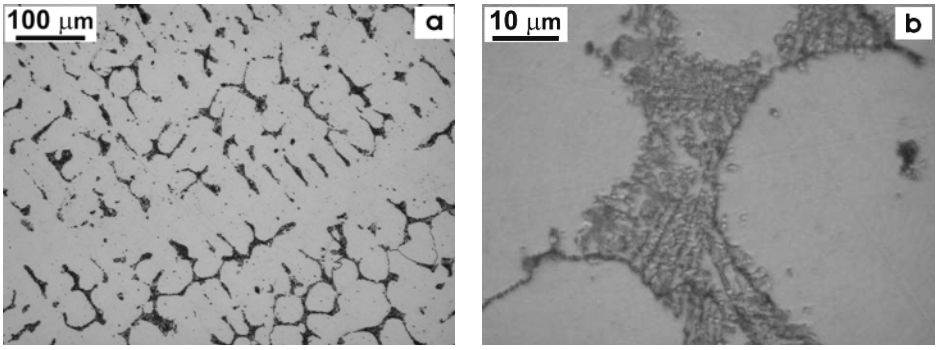

Fig. 1. Microstructure of the wall centrifugally casted pipe IN 519. Murakami etched

heterogeneously and σ phase within the dendrites and grains from as cast supersaturated matrix were found in the structure (Fig. 2). The σ phase is present not only in the shape of "needles" but also in the globular form. An EDX analysis reveals a significant amount of chromium in the precipitates of σ phase which is higher than the amount of chromium found in the matrix, and a slightly higher amount of silicon [11]. X-ray diffraction spectra from this area showed phases of: σ, Ni_3Nb, TCP phase type G ($Nb_6Ni_{16}Si_7$) and a disappearance of NbC (Fig 3). In the region 8.5 m from the inlet, after 120,760 h of operation, the carbides, precipitated Ni_3Nb and $Nb_6Ni_{16}Si_7$ phase showed a tendency to coarsen and to coalescence. Fig. 4 shows the semicontinuous network of coalescend carbides and a precipitated phase around and inside the grains of austenite. X-ray diffraction samples from this area showed an increase in the amount of Ni_3Nb, $Nb_6Ni_{16}Si_7$ and a decreased quantity of NbC phases (Fig. 5). The σ phase was not found in this region.

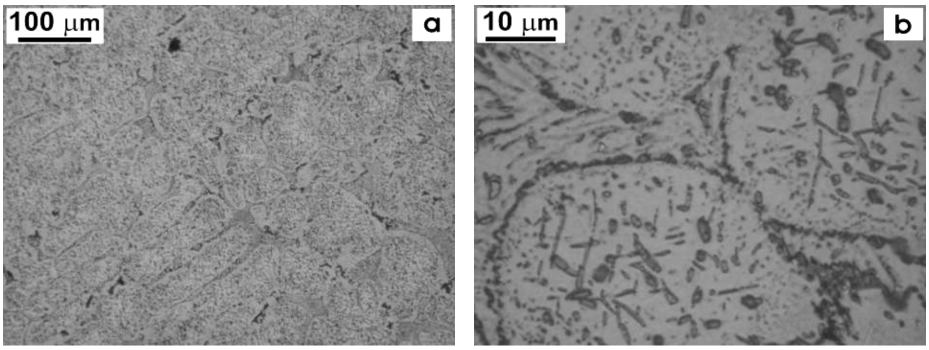

Fig. 2. Microstructure of the wall centrifugally casted pipe IN 519 at 1.65 m from the inlet after 120,760 hr of operation. Murakami etched

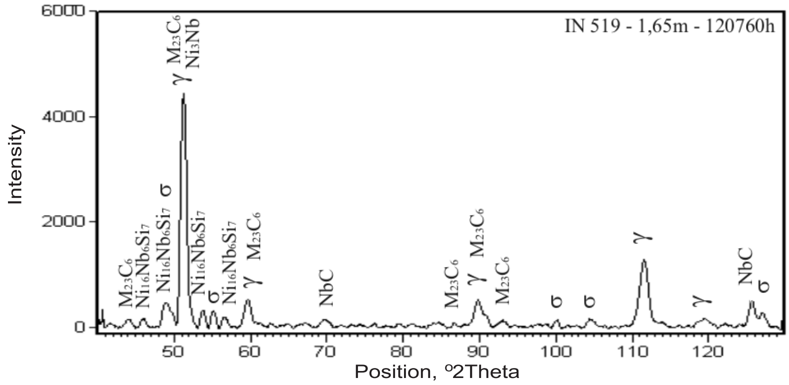

Fig. 3. X-ray diffraction pattern of tube material at a distance of 1.65 m from the inlet parent substance after 120,760 hr of operation.

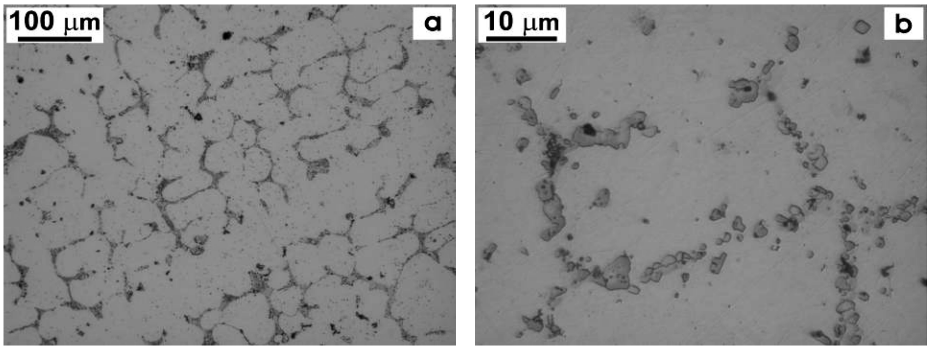

Fig. 4. Microstructure of the wall centrifugally casted pipe IN 519 at 8.5 m from the inlet after 120,760 hr of operation, Murakami etched

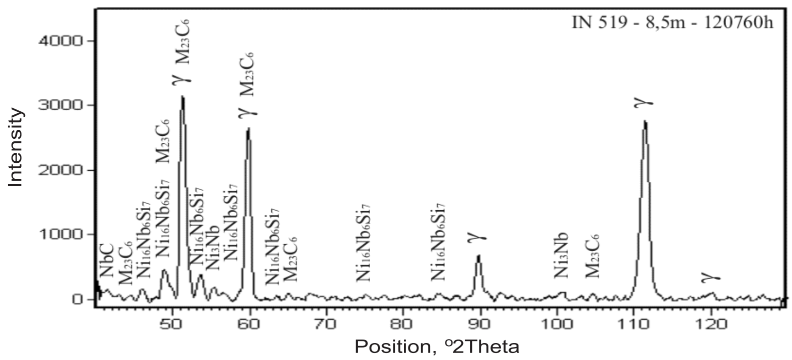

Fig. 5. X-ray diffraction pattern of tube material at a distance of 8.5 m from the inlet parent substance after 120,760 hr of operation

Annealing at a high temperature leads to a dissolution of intermetallic phases σ, Ni_3Nb, $Nb_6Ni_{16}Si_7$ and $M_{23}C_6$ in the austenite (Fig. 6). X-ray analysis confirms the lowering intensity reflexes from, σ, Ni_3Nb, $Nb_6Ni_{16}Si_7$ and $M_{23}C_6$ phases and increasing reflexes from NbC carbides (Fig. 7).

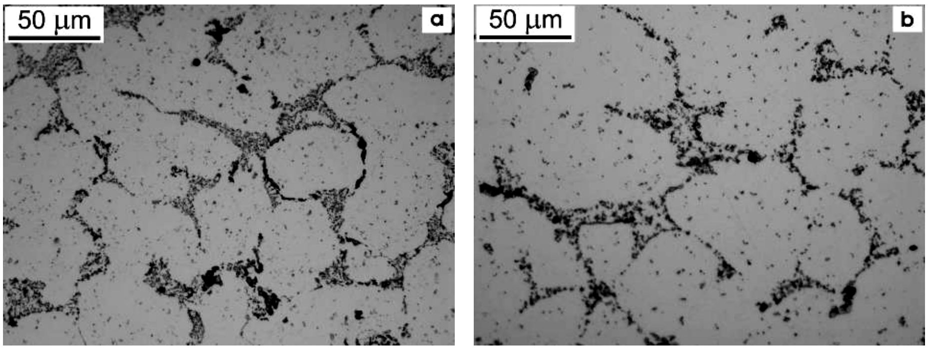

Fig. 6. Microstructure of tube material after 120,760 hr of operation and solutionizing at 1200 °C for 2 hr at distances from the inlet of: a) 1,65 m, b) 8,5 m, respectively

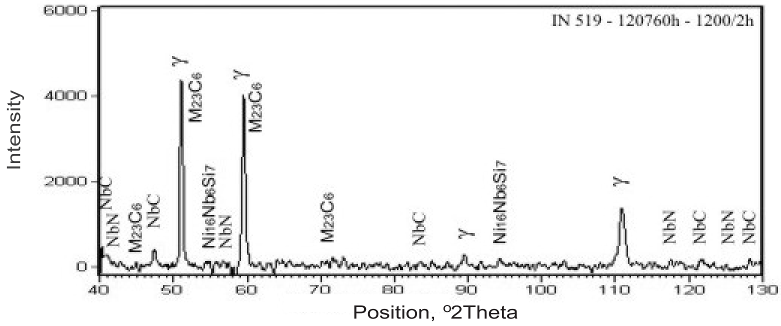

Fig. 7. X-ray diffraction pattern of tube material at a distance of 8,5 m from the inlet after 120,760 hr of operation and solutionizing at 1200 °C for 2 hr

The tensile and hardness tests of tube material after 120,760 hr of operation show a minimum tensile strength and Brinella hardness at 8,5 m from the inlet of substrates [15]. The average mechanical properties of the tube material as received and after 120,760 hr of operation are presented in Tab. 1.

The changes of average mechanical properties of the tube material after solution heat treatment versus temperature are shown in Figs. 8-11.

Table 1. Mechanical properties of IN 519 superalloys after 120,760 hr of operation

Test section	**Mechanical properties**				
	R_m MPa	**HB 2,5/187,5/15**	**A_5 %**	**$KU2_{20}$ J**	**$KU2_{830}$ J**
As received	630.1	194	23.8	29	59
1.65 m from inlet	606	253	3,2	4,0	14
8,5 m from inlet	368.4	186	2.6	3.8	15

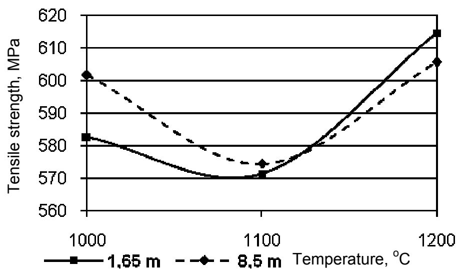

Fig. 8. Tensile strength versus temperature of solutionizing

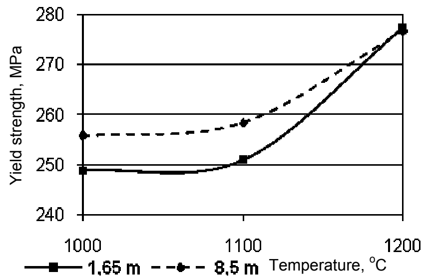

Fig. 9. Yield strength versus temperature of solutionizing

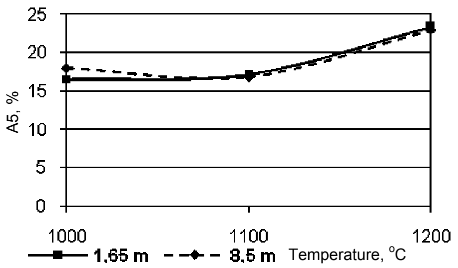

Fig. 10. Unit elongation versus temperature of solutionizing

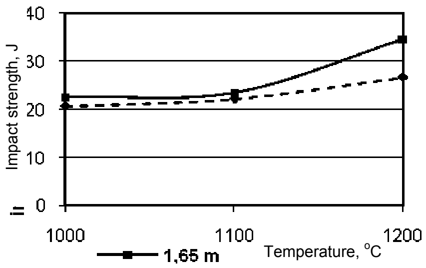

Fig. 11. Impact strength verus temperature of solutionizing

The results obtained by means of X-Ray analyses were confirmed with EDX microanalysis. For example the data obtained from EDX analysis performed in the eutectic region showed a stabile distribution of alloy elements in the matrix and a high concentration of niobium and chromium in undissolved intermetallic phases (Fig. 12).

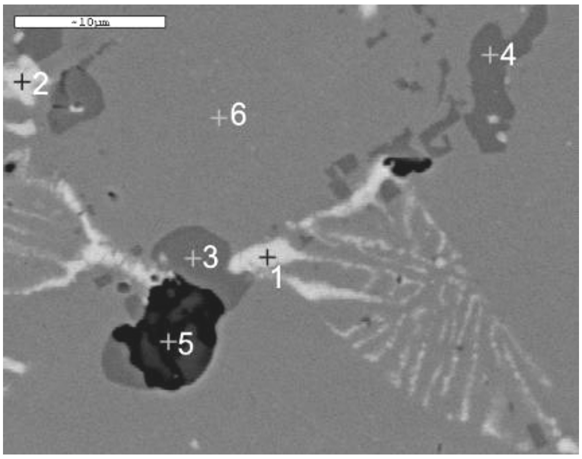

Fig. 12. Distribution of elements in the structure of tube material at a distance of 1,65 m from the inlet after 120,760 hr of operation and solutionizing at 1200°C for 2 hr

The analysis of the elements' distribution in the structure at 1,65 m from the inlet is presented in Table 2. A high content of chromium and iron at points 3 and 4 indicates the presence of $M_{23}C_6$ carbides. A low content of silicon and increased amounts of niobium at points 1 and 2, indicates dissolution and transformations of σ, Ni_3Nb and $Nb_6Ni_{16}Si_7$ into niobium carbides. The results of the analysis at this point comprise the average values for refined NbC carbides and the austenite which surrounds them. The sulphide of manganese was found at point 5. The same content of chromium and nickel in the matrix in as received and after solutionizing state at point 6 suggests a correct selection of parameters of heat treatment solution.

Table 2. Microanalysis at points 1÷6 – Fig. 12

Element	Content of element, % weight.					
	1	2	3	4	5	6
Chromium	3.18	3.92	78.07	76.21	35.91	25.55
Iron	2.40	3.34	16.37	18.79	3.57	47.20
Nickel	1.20	1.47	4.49	4.36	2.26	25.64
Niobium	92.72	90.23	0.08	0.05	4.08	0.20
Silicon	0.27	0.33	0.33	0.25	0.78	0.95
Manganese	0.23	0.29	1.10	0.35	24.87	0.46
Sulphur	-	-	-	-	25.17	-

The analysis of the elements' distribution in the structure at 8,5 m from the inlet (Fig. 13), is presented in Table 3. A high content of chromium and iron

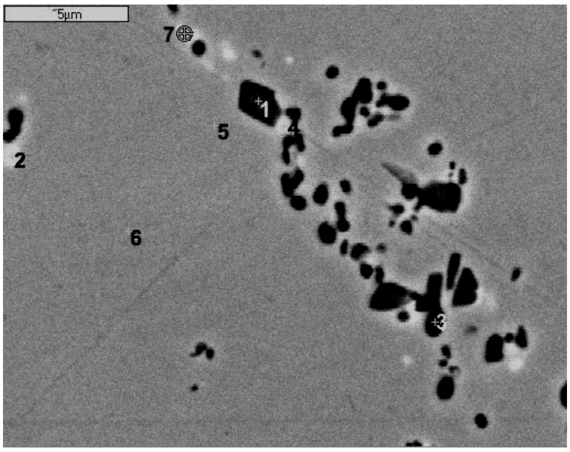

Fig. 13. Distribution of the elements in the structure of the tube material IN 519 at distance of 8,5 m from inlet after 120,760 hr of operation and solutionizing at 1200°C for 2 hr, x5000

Table 3. Microanalysis at points 1÷7 – Fig. 13

Element	Content of element, % weight.						
	1	2	3	4	5	6	7
Chromium	65.78	13.96	26.02	19.99	25.47	25.77	17.57
Iron	25.62	22.49	38.53	38.70	48.71	47.20	32.34
Nickel	7.64	11.41	17.80	20.94	24.47	25.01	16.76
Niobium	0.48	50.97	16.57	18.86	0.01	0.17	32.34
Silicon	0.26	0.61	0.63	0.96	0.98	1.18	1.03

at point 1 indicates that undissolved $M_{23}C_6$ carbides are present in the microstructure. A low content of silicon and increased amounts of niobium at points 3, 4, 7 and 2 suggest that Ni_3Nb and $Nb_6Ni_{16}Si_7$ phases dissolve and transform into niobium carbides. The result of the analysis at these points are the average values of element contents in the NbC carbides and austenitic matrix. The same contents of chromium and nickel in the matrix in as received (casted) and solutionized state (points 5 and 6) indicate a correct selection of parameters of heat treatment solution.

4. Solutionizing in situ

A high price of new pipes and the possibility to regenerate the microstructure and properties of long-lasting explicated catalytic pipes by solution heat treatment led to the introduction of semi-industrial regeneration of the pipes [21, 22]. High costs of disassembly, transportation, solution heat treatment and re-assembly of the pipes in the reformer limit the dissemination of the technology of catalytic pipes regeneration.

Investigations of catalytic pipes operated for dozens of days in closed holes' state after they lost their leaktightness showed the possibility of regeneration of their microstructure, and their proprieties, in situ (in place of operation). At the lack of flow of reacting substances the temperature of the pipe in reformer reaches 1200°C, which is the optimum temperature of solutionizing of pipes used for a very long time and made from superalloy IN 519.

An account of the X-ray analysis of IN 519 tube samples in as delivery state, after 143,300 hr of operation in closed holes' state at the end of the operation period is presented in Fig. 14. The phase $Ni_{16}Nb_6Si_7$ and Ni_3Nb underwent total, and the phase $(Cr,Fe)_{23}C_6$ and NbC partial dissolution in time of holding at 1200°C. The lack of reflex of phase $(Cr,Fe)_{23}C_6$ in state of delivery results from fast cooling during centrifugal casting. The ratio of surface of reflexes of NbC to γ in state as delivery amounts to 0.0263 and it diminishes to 0.0106 after 143300 hr of exploitation.

As a result solutionizing in situ ratio grows up to 0.044 which confirms the presence of metastable state after centrifugal casting.

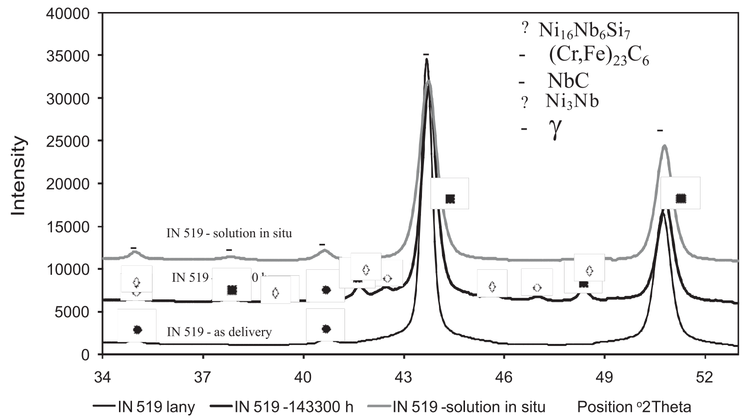

Fig. 14. Combinations X-ray diffraction pattern of tube material at a distance of 8.5 m from the inlet parent substance after 143,300 hr of operation

5. Discussions

A long–lasting operation of catalytic tubes at a raised temperature causes structural and phase changes, spheroidization precipitation of the intermetallic phases in alloyed austenite matrix and at grain boundaries. This results in a decrease of the mechanical properties of the pipe material as well as in the intensification of the creeping, especially in the region of the areas 8.5 m from the inlet of substrates. In order to regenerate tube material solution heat treatment was applied. As a result of solutionizing at the temperature range of 1000°C÷1200°C, its structure has changed profoundly – Fig. 6. The globular Ni_3Nb, $Nb_6Ni_{16}Si_7$ and $M_{23}C_6$ phase underwent dissolution, and also the eutectic grain refining took place. The eutectic grain refining took place as a result of dissolving and the phase transformations of its components. The analysis of the distribution of the elements shows that previous correlation between occurrence of niobium, nickel and silicon ceased to exist. The conclusions drawn from the distribution of the elements and local analysis are confirmed by X-ray Diffraction – Fig. 3. After solutionizing at the temperature range of 1000°C÷1200°C, the reflexes from NbC carbides were observed in the diffraction pattern, and the higher was the temperature of solutionizing the more intense were the reflexes. The reflexes from Ni_3Nb, $(Cr,Fe)_{23}C_6$ and $Nb_6Ni_{16}Si_7$ phase disappeared. In the eutectic NbC carbides there was also a small amount of undissolved chromium carbides. X-ray diffraction samples from tube in closed holes' state confirms the presence of NbC and $(Cr,Fe)_{23}C_6$ carbides and disappearance of $Nb_6Ni_{16}Si_7$ and Ni_3Nb phases.

6. Conclusions

A solution heat treatment, especially at 1200°C/2hr, leads to a considerable improvement of the mechanical properties and plasticity of tube material deteriorated during long service at a raised temperature in the reformer. The excessive embrittlement of superalloy IN 519 is removed. In the region of the maximum deterioration, after solutionizing, the elongation, impact strength and tensile strength were almost the same as when cast, whereas the hardness decreased below the initial state. As a result of solutionizing the brittle intermetallic phases $(Cr,Fe)_{23}C_6$, Ni_3Nb and $Nb_6Ni_{16}Si_7$ are dissolved and in their place the nucleation of NbC carbides occurred. The same phase transformation processes take place in material tube during solutionizing in situ. The stability of the structure and properties of the solutionizing in situ superalloy in reforming environment will have to be verified.

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