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Technical State Assessment of the Furnace Tubes from Oil Refineries and Petrochemical Plants by Examining Their Chemical Composition and Microstructure

Gheorghe Zecheru, Ibrahim Ramadan, Andrei Dumitrescu

Universitatea Petrol-Gaze din Ploieşti, Bd. Bucureşti 39, 100680, Ploieşti
e-mail: gzecheru@upg-ploiesti.ro

Abstract

This paper analyses the possibilities of assessing the technical state of the furnace tubes from the oil refineries and petrochimical plants by means of determining their chemical composition and microstructure, on samples taken on the occasion of performing the periodic technical inspections of these plants. The analysis takes into consideration the combined action of the main processes that lead to the progressive damage of the furnace tubes and to the limitation of their life duration: creep, activated by the long-term mechanical loading of the tubes at high temperatures, fatigue, determined by the time-dependent character of the mechanical and thermal loadings at which the tubes are subjected to and the modification of the tubes chemical composition and microstructure (accompanied, obviously, by the alteration of their mechanical strength and toughness properties), determined by their use in active environments (that can engender carburization / coking on the inside surface and oxidation / burning / decarburization on the outside surface of the tubes). The paper highlights the fact that the information obtained by the periodical examination of the chemical composition and microstructure, corroborated with the one obtained by other methods for the investigation of their technical state, allows for the prediction with an acceptable confidence level of the remaining life of the furnace tubes.

Key words: *furnace tubes, creep – fatigue damage, chemical composition & microstructural change, remaining life prediction.*

Introduction

The tubes (and the other components: elbows, return bends or headers, junction boxes, terminal or corner fittings, tube supports) from which the furnace tube coils in oil refineries and petrochemichal plants are made of (named in the followings PRFT) are subjected to severe usage conditions: a. high temperature, in the range in which their damage by creep takes place; b. multiple mechanical loads (having as main components the pressure of the fluid circulated through the coils, their own weight and the one of the transported fluid, the loads of thermal nature etc.), some of them with variable intensity, that can determine their damage by fatigue; c. active operating environment, the mixtures of hydrocarbons transported through the coils being able to cause carburization and/or coking on their inside surface and the atmosphere inside the furnaces being able to produce oxidation, burning and decarburization on their outside surface, the changes in the chemical composition (at the surface or, sometimes, extended in the whole cross-section of the tubes) being accompanied (obviously) by alterations of their microstructure and mechanical strength and toughness properties.

In order to correspond to these conditions during their standardized life (10…20 years), PRFT are manufactured (by means of heat forming or casting processes) from the heat resistant alloys indicated in Table 1 [1-6], at present existing however preoccupations regarding their manufacture also from other materials, such as ferritic and austenitic oxide dispersion strengthened alloys [7]. In the current paper only the materials listed in Table 1 will be taken into account: their use for the manufacture of the tube coils and tubular fascicles for the heating aggregates (furnaces, heaters, boilers) from the industrial technological plants, use which became traditional, because it is recommended by the most important Norms in force [2-4], have led to the accumulation of a consistent quantity of information regarding: a. the factors that influence their operational behaviour; b. their deterioration / damage mechanisms and failure modes.

Table 1. Main materials used for PRFT

Type of material	Material designation according to		Group of material a)	Werkstoffnr. [8]
	EN 10216-2,5	Grade – ASTM		
C–Mn Steel	P195, P235, P265	A–A 106	1.1	1.0348, 1.0345, 1.0425
0.5 Mo Steel	16Mo3	T1,T1a,T1b–A 209 P1–A 335	1.2	1.5415
1¼Cr–½Mo Steel	10CrMo5–5	T11–A 213 P11–A 335	5.1	1.7338
2¼Cr–1Mo Steel	10CrMo9–10	T22–A 213 P22–A 335	5.2	1.7380
5Cr–½Mo Steel	X11CrMo5	T5,T5b,T5c–A 213 P5,P5b,P5c–A 335	5.3	1.7362
9Cr–1Mo Steel	X11CrMo9–1	T9–A 213 P9–A 335	5.4	1.7386
9Cr–1Mo–V Steel	X10CrMoVNb9–1	T91–A 213 P91–A 335	6.4	1.4903
12Cr–1Mo–V Steel	X12Cr13 b)	409,410–A 268	6.4	1.4006
18Cr–8Ni Steel	X5CrNi18–10	304,304H–A 312	8.1	1.4301, 1.4948
16Cr–12Ni–2Mo Steel	X5CrNiMo17–12–2	316,316H–A 312	8.1	1.4401, 1.4919
18Cr–10Ni–Ti Steel	X6CrNiTi18–10	321,321H–A 312	8.1	1.4541, 1.4878
18Cr–10Ni–Nb Steel	X6CrNiNb18–10	347,347H–A 312	8.1	1.4550, 1.4961
Centrifugally Cast 25Cr–20Ni Steel	GX40CrNi25–20 c)	HK–40–A 351	8.2	1.4848
Ni–Fe–Cr Alloy	X8NiCrAlTi32–21 d)	8800,8810, 8811–B407	8.2	1.4876, 1.4958, 1.4959

a) according to CR ISO 15608; b) EN 10088-3 – martensitic corrosion resisting steel; c) EN 10295; d) other name: Incolloy 800, 800H, 800HP or Nicrofer 3220H, 3220HP

Due to their operational conditions, PRFT have a limited durability, and making an appropriate decision regarding their replacement involves: a. the definition of adequate methods and procedures for the assessment of their technical state; b. the continuos monitoring of their operating conditions; c. the periodic checking of their technical state; d. prediction of their remaining life. In this context, the present paper aims at to analysing: a. if the detemination of the PRFT chemical composition and microstructure, on samples cut on the occasion of performing the periodic technical inspections from the petrochemical technological plants and from the oil refineries, can be a suitable method for the assessment with a high confidence level of the PRFT technical state and for underlying the decisions regarding their maintenance in service or their replacement; b. how is it possible to correlate synthetically the characteristics regarding the PRFT chemical composition and microstructure, determined after a certain service life/period τ_f of the furnace in which they are used, with the parameters (with continuous variation during the period τ_f) describing the operating regime of the furnace (composition, pressure p_f and temperature t_f of the technological fluid processed in the furnace) and with the parameters that can synthetically describe the PRFT technical state: the cumulative damage (in the period τ_f) D_c and the remaining life τ_{re}.

Chemical Composition and Microstructure of the New PRFT

The assessment of the PRFT technical state based on the periodic determination of the characteristics regarding their chemical composition and microstructure implies the knowledge of the initial, reference state of these characteristics, defined on the ground of the information recording during the quality inspection of all the coils components (including the welded joints between them), performed on the occasion of putting into service each furnace from an oil refinery or a petrochemical plant. Because the furnace coils have a complex structure and a great number of components, in order to manage the information regarding their technical state, complete construction schemes must be prepared, in which every component is identified by a code and is assigned an individual folder, where there are included both its initial characteristics (design dimensions, chemical composition and microstructure at delivery, date of entry into service etc.) and the records of the parameters of the operating regime (pressure and temperature) along all the operating cycles / campaigns and the information obtained when checking its status on the occasion of the periodic technical inspections.

The chemical composition of the main types of materials intended for PRFT manufacturing (see table 1) is shown in Table 2. The delivery states and the specific usage conditions of the PRFT made from these materials are indicated in Table 3. The range of materials intended for PRFT manufacturing has been continuously developed, by modifying and adjusting the alloying recipes of the materials presented in Tables 1…3, so that it presently contains a significant number of materials types, each one having the quality characteristics imposed by its field of usage [5-13].

Table 2. Chemical composition of the main materials used for PRFT

Type of material	Chemical composition (cast analysis), % by mass [a)]						
	%C	*%Si*	*%Mn*	*%Ni*	*%Cr*	*%Mo*	Others
C–Mn Steel	b)	max 0.35	c)	max 0.30	max 0.30	max 0.08	d)
0,5Mo Steel	0.12-0.20	max 0.35	0.40-0.90	max 0.30	max 0.30	0.25-0.35	e)
1¼Cr–½Mo Steel	max 0.15	0.50-1.00	0.30-0.60	max 0.30	1.00-1.50	0.45-0.65	e)
2¼Cr–1Mo Steel	0.08-0.14	max 0.50	0.30-0.70	max 0.30	2.00-2.50	0.90-1.10	e)
5Cr–½Mo Steel	0.08-0.15	0.15-0.50	0.30-0.60	–	4.00-6.00	0.45-0.65	e)
9Cr–1Mo Steel	0.08-0.15	0.25-1.00	0.30-0.60	–	8.00-10.0	0.90-1.10	e)
9Cr–1Mo–V Steel	0.08-0.12	0.20-0.50	0.30-0.60	max 0.40	8.00-9.50	0.85-1.05	e),f)
12Cr–1Mo–V Steel	max 0.08	0.75-1.00	max 1.00	max 0.50	11.5-13.5	0.75-1.50	g)
18Cr–8Ni Steel	0.04-0.10	max 1.00	max 2.00	8.00-11.0	18.0-20.0	–	–
16Cr–12Ni–2Mo Steel	0.04-0.10	max 1.00	max 2.00	11.0-14.0	16.0-18.0	2.00-3.00	–
18Cr–10Ni–Ti Steel	0.04-0.10	max 1.00	max 2.00	9.00-13.0	17.0-20.0	–	h)
18Cr–10Ni–Nb Steel	0.04-0.10	max 1.00	max 2.00	9.00-13.0	17.0-20.0	–	i)
25Cr–20Ni Steel	0.35-0.45	max 1.75	max 1.50	19.0-22.0	23.0-27.0	max0.50	–
Ni–Fe–Cr Alloy	0.05-0.10	max 1.00	max 1.50	30.0-35.0	19.0-23.0	–	j)

a) For rolled PRFT $\%P \leq 0.025$; $\%S \leq 0.020$, and for cast PRFT $\%P \leq 0.040$; $\%S \leq 0.035$; b,c) for P195: $\%C \leq 0.13$; $\%Mn \leq 0.70$; for P235: $\%C \leq 0.16$; $\%Mn \leq 1.20$; for P265: $\%C \leq 0.20$; $\%Mn \leq 1.40$; d) microalloying with Al (max 0.02%), Nb (max 0.01%), Ti (max 0.04%), V (max 0.02%) for grain finishing; e) $\%Al \leq 0.40$ and $\%Cu \leq 0.30$; f) $\%V = 0.18\text{-}0.25$; it can also contain $\%Nb = 0.06\text{-}0.10$ and $\%N = 0.03\text{-}0.07$; g) $\%Ti \in [6\%C;\ 0.75]$; h) $\%Ti \in [4\%C;\ 0.65]$; i) $\%Nb + \%Ti \in [10\%C;\ 1,.0]$; j) $\%Cu \leq 0.75$; $\%Al = 0.15\text{-}0.60$; $\%Ti = 0.15\text{-}0.60$; $\%Fe \geq 39.5$.

The structures corresponding to the metallurgical states that can be obtained during PRFT manufacturing and/or of the delivery states of PRFT made of the materials previously specified are shown in Figure 1 [2, 4-6, 9-13]. For PRFT from C–Mn and Cr–Mo steels, which have solid – solid phase transformations, the structures defining these states, obtained by applying some heat treatments of the type annealing – A; isothermal annealing – I, normalizing – N, normalizing / quenching & tempering – N/Q + T, can be deducted by analysing the continuous cooling transformations diagram – CCTD, of the type of the ones shown as examples in Figure 2 [5-7, 11, 12]. For PRFT made of Cr–Ni steels and of Ni–Fe–Cr alloys, which do not have solid state phase transformations, the equilibrium structures are made of austenite and chemical compounds (of the type carbides, nitrides, carbonitrides, intermetallic compounds etc.), the quantity of carbon dissolved in austenite (and, therefore, the quantity of carbides and/or of carbonitrides from the structure) being able to de adjusted by applying the heat treatment named solution annealing – AT, which consist of heating the PRFT uniformly to a temperature t_i = 1050…1120 °C and cooling it rapidly (in water, oil or air) [2, 8].

Table 3. Delivery states and specific utilizations of the main PRFT types

PRFT material	Delivery state	Heat treatment conditions	Design metal temperature limit a)	Specific use b)
C–Mn Steel	+N	N(t_i = 880-940°C/air)	540 °C	CC, UB
0,5Mo Steel	+N	N(t_i = 890-950°C/air)	540 °C	CC, UB
1¼Cr–½Mo Steel	+NT	N(t_i = 900-960°C/air) + T(t_i = 650-750°C/air)	595 °C	CR, CC, UB
2¼Cr–1Mo Steel	+NT	N(t_i = 880-940°C/air) + T(t_i = 680-750°C/air)	650 °C	CR, CC, UB
5Cr–½Mo Steel	+I / +NT	I(t_i = 890-950°C/furnace); N(t_i = 930-980°C/air) + T(t_i = 730-750°C/air)	650 °C	CUAS, CUVS, DC, CH, CR
9Cr–1Mo Steel	+I / +NT	I(t_i = 950-980°C/furnace); N(t_i = 890-950°C/air) + T(t_i = 720-800°C/air)	705 °C	CUAS, CUVS, DC, CH, CR
9Cr–1Mo–V Steel	+NT	N(t_i = 1040-1090°C/air) + T(t_i = 730-780°C/air)	705 °C	DC, CH, CR
12Cr–1Mo–V Steel	+A / +QT	A(t_i = 745-825°C/air) Q(t_i = 950-1000°C/o,a) + T(t_i = 680-780°C/air)	705 °C	DC, CH, CR
18Cr–8Ni Steel	+AT	SA(t_i = 1000-1100°C/w,a)	815 °C	CUAS, CUVS
16Cr–12Ni–2Mo Steel	+AT	SA(t_i = 1020-1120°C/w,a)	815 °C	CUAS, CUVS,
18Cr–10Ni–Ti Steel	+AT	SA(t_i = 1020-1120°C/w,a)	815 °C	CH,
18Cr–10Ni–Nb Steel	+AT	SA(t_i = 1070-1125°C/w,a)	815 °C	DC, CH
Centrifugally Cast 25Cr–20Ni Steel	As – cast	–	985 °C	EPU
Ni–Fe–Cr Alloy	+A	A(t_i = 1120-1150°C/air)	1010 °C	EPU

a) API Std 530; temperature limit to define the creep range according to BS 7910 and API 579 – see [1]; b) CUAS – Crude-oil Unit Atmospheric Section; CUVS – Crude-oil Unit Vacuum Section; DC – Delayed Cokers; CH – Catalytic Hydrodesulfurizer; CR – Catalytic Reformer; CC – Catalytic Cracking; EPU – Ethylene Pyrolisis Unit; UB – Utilities Boylers [2]

The following statements imposes themselves: a. the microstructures shown in Figure 1 have been obtained by the examination of some metallographic samples at the optical microscope, considering that this manner of examination is the only one that could be accepted for the operative engineering assessment of the PRFT technical state, the high costs and long working durations making unfeasible the examination by electron microscopy (scanning electron microscopy – SEM or transmission electron microscopy – TEM); b. the reactives that has to be used for the preparation of the metallographic samples must be selected so that the microscopic examination can highlight all the microstructural features of PRFT (new or used) which can lead to the characterization of their quality or technical state; as an example, Figure 3 reproduces, from [24], the images of the microstructure of a heat-resistant alloy (from the range of the ones used to manufacture PRFT), obtained by examination at the optical microscope of some samples etched with various metallographic reactives.

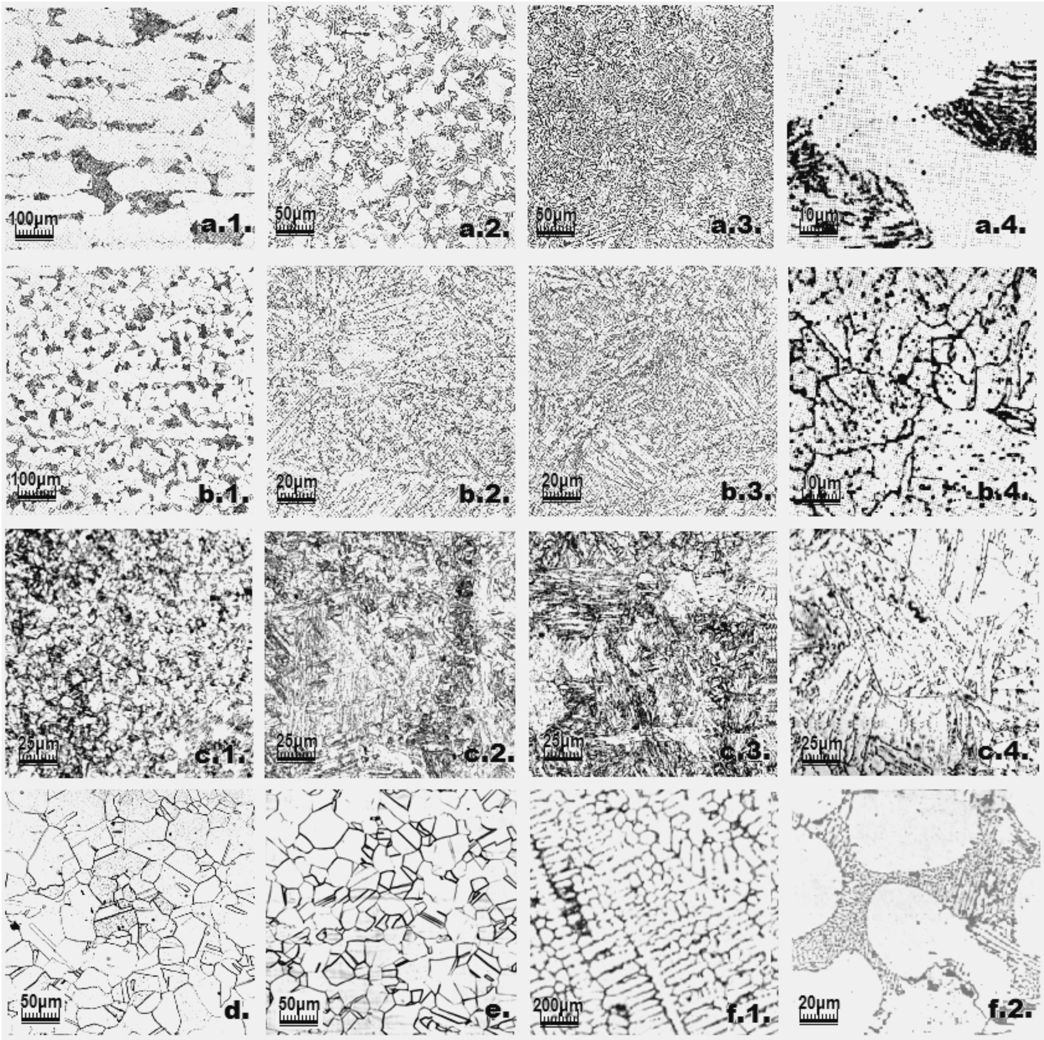

Fig. 1. The metallographic structure (at room temperature), for the usual states, of PRFT manufactured from various materials [5-7, 10]:
a) 1¼Cr–½Mo Steel: a.1. A (t_i = 920ºC, τ_m = 10 min, furnace to 500 ºC → air) – ferrite and pearlite / HV 146; a.2. N (t_i = 920 ºC; τ_m = 10 min; air) – ferrite and bainite / 237HV; a.3. N (t_i = 920 ºC; τ_m = 10 min; ventilated air) – ferrite and bainite / 265HV; a.4. N (t_i = 930 ºC; τ_m = 10 min; air) + T (t_i = 700 ºC; τ_m = 1 h; air) – ferrite, bainite and carbide particles; b) 2¼Cr–1Mo Steel: b.1. A (t_i = 920ºC, τ_m = 10 min, furnace to 500 ºC → air) – ferrite and pearlite / 160HV; b.2. N (t_i = 920ºC, τ_m = 10 min, air) – bainite and only a small amount of pro-eutectoid ferrite / 256HV; b.3. N (t_i = 920ºC, τ_m = 10 min, air) – bainite and a little martensite (no pro-eutectoid ferrite) / 340HV; b.4. N (t_i = 930ºC, τ_m = 10 min, air) + T (t_i = 750ºC, τ_m = 2 h, air) – ferrite and granular carbide particles / 175HV; c) 9Cr–1Mo–V Steel: c.1. N (t_i = 1040 ºC; τ_m = 2 h; air) + T (t_i = 690ºC, τ_m = 2 h air) – tempered martensite; c.2. N (t_i = 1040 ºC; τ_m = 2 h; air) + T (t_i = 745ºC, τ_m = 8 h, air) – tempered martensite; c.3. N (t_i = 1040 ºC; τ_m = 4 h; air) + T (t_i = 725ºC, τ_m = 2 h, air) – tempered martensite; c.4. N (t_i = 1040 ºC; τ_m = 8 h; air) + T (t_i = 790ºC, τ_m = 20h, air) – ferrite grains and granular carbide particles; d) 18Cr–8Ni Steel – austenite; e) 16Cr–12Ni–2Mo Steel – austenite; f) Centrifugally Cast 25Cr–20Ni Steel: f.1. as cast – dendritic carbides within an austenitic matrix; f.2. as cast – austenitic matrix with inter-dendritic eutectic carbides.

As it can be ascertained by analysing the information above, the microstructures of new PRFT correspond to some stable structural states (with phases and constituents that do not have the tendency of rapid transformation during the maintenance of PRFT at the operating temperature), with precipitates whose properties (shape, dimensions, distribution pattern and dispersion degree) ensure a good creep strength and durability, and without phases (of the type σ – phase) having embrittlement effects.

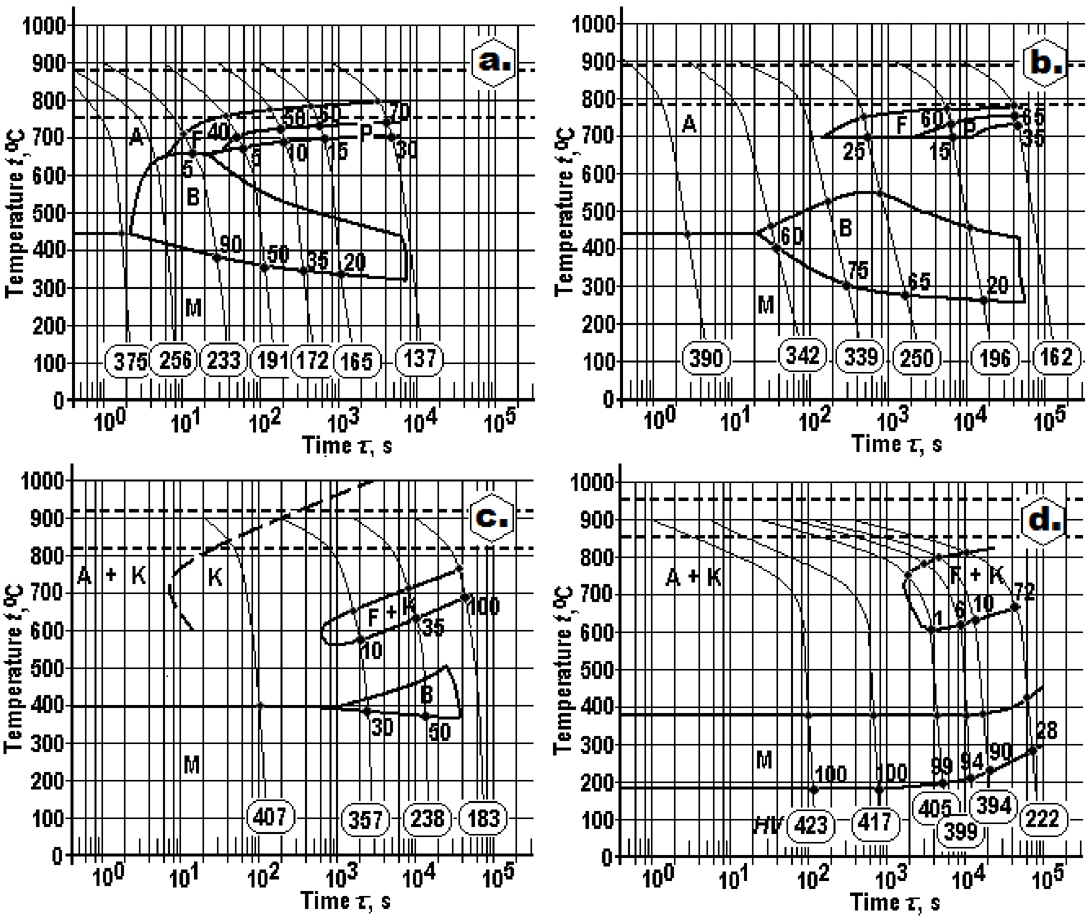

Fig. 2. CCTD of the main types of Cr – Mo steels used to manufacture PRFT:
a) 1¼Cr–½Mo Steel; b) 2¼Cr–1Mo Steel; c) 5Cr–½Mo Steel; d) 9Cr–1Mo–V Steel

Alterations of Composition and Microstructure during the PRFT Use

The long-term usage of PRFT at high temperatures, in the range of manifestation of the creep phenomenon, determines the ocurrence of some alterations of the chemical composition and microstructure that can influence to an important extent the life duration of the furnace coils from the oil refineries and petrochemical plants. If the atmospheres from the furnaces and/or the fluids circulating through the coils are active, the changes in the chemical composition and microstructure (at their surface or in their volume) that PRFT endure in the course of their use increase in intensity and complexity and will become the factors with the highest weight of influence for the PRFT life; obviously, together with these factors, the factors that define the loading regime will also evince their influence: the PRFT working temperature, the intensity and the triaxiality degree of the mechanical stresses generated within the PRFT.

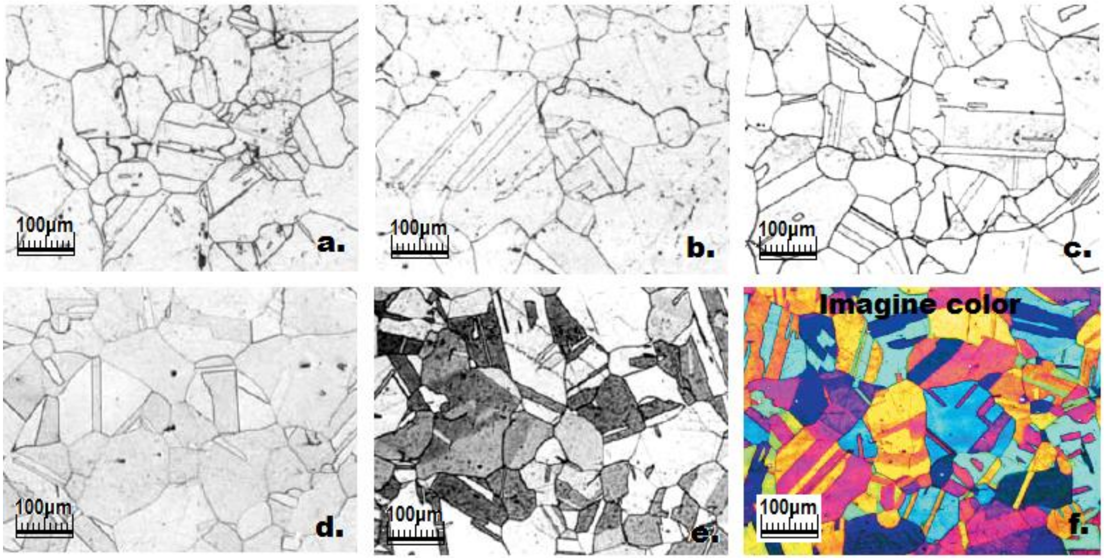

Fig. 3. Microstructures of a heat-resistant alloy based on Ni (with 0.04 %C; 15.5 %Cr; 7 %Fe; 2.5 %Ti) obtained by the examination at the optical microscope of some samples etched using: a) Glyceregia (2 parts glycerol, 3 parts HCl, 1 part HNO_3); b) Kalling's reagent 2 (5g $CuCl_2$, 100 ml HCl, 100 ml ethanol); c) Marble's reagent (10 g $CuSO_4$, 50 ml HCl, 50 ml H_2O distilled); d) Aqua regia (20 ml HNO_3, 60 ml HCl); e) HCl +1% Na_2O_2; f) Tint etched in 50 ml HCl, 50 ml H_2O,1 g $K_2S_2O_5$

The matrix of PRFT microstructure does not suffer essential changes throughout their use, remaining ferritic, in the case of PRFT from Cr-Mo steels, or austenitic, in the case of PRFT from Cr-Ni stainless steels or from super-alloys of the type Ni-Fe-Cr; if the matrix of PRFT structure (from Cr-Mo steels) in the delivery state (NT or QT) also contains bainitic or martensitic formations, these undergo (during the long-term maintenance at a high temperature) tempering processes that transforms them in ferrite and spheroidal carbides. Likewise, in the case of low alloy steels (C-Mn steel or 0.5Mo steel), which are delivered in the state N, with a ferritic – pearlitic structure, a long-term maintenance at a high temperature produces globular cementite from pearlite, followed, in some cases (if Si and Al have been used in unfit quantities for deoxidation when elaborating these steels), by the cementite decomposition in ferrite and graphite. As a consequence, the structural changes throughout the PRFT use refer mainly to the phases and/or constituents, with small percentage weights, which are distributed at the edge of or inside the crystals of the ferritic or austenitic matrix (named in the followings, generically, secondary phases or precipitates): carbides, nitrides or carbonitrides (of the main alloying elements: Cr, Mo or of some supplementary alloying elements, introduced in small quantities, for the improvement of the PRFT utilization features, such as: Ti, Nb, V, W, Si, B), intermetallic compounds; usually, in the PRFT microstructures, there are distributed carbides M_3C, $M_{23}C_6$, M_6C, MC, M being Fe, Cr, Mo, V, Nb (for instance, Fe_3C, $Cr_{16}Fe_5Mo_2C_6$, Fe_3Nb_3C, $(Fe,Cr)_{21}Mo_3C_4$, Cr_5SiC, TiC, NbC), nitrides MN, M being Cr, Nb, Ti (as an example, NbN, TiN, $(Cr,Fe)_2N$, Cr(V,Nb)N ≡ Z-phase or $Cr_2(V,Nb)_2N_2$ – modified Z-phase) and intermetallic phases / compounds / combinations of the type Laves phases (for instance, Fe_2Mo, Fe_2Nb, Fe_2W), in the microstructures with an austenitic matrix (but sometimes also in the ones with ferritic matrix) being also possible to appear precipitates of σ-phase, which are compounds of the type (Ni,Cr,Mo)Fe, of G-phase, which are compounds of the type $Ni_{16}Nb_6Si_7$ or $Ni_{16}Ti_6Si_7$ or of χ-phase, which are compounds of the type $Fe_{36}Cr_{12}Mo_{10}$ or $(FeNi)_{36}Cr_{18}(Ti,Mo)_4$ [17, 18]. The structural alterations, that are attained by mechanisms based on the diffusion of the alloying components (C, Cr, Mo, Ni, Ti, Nb, N etc.) and on their thermodynamic activity (which determines the possibilities that they form chemical compounds), presents the following features: a. they are dependant on the temperature ranges in which PRFT are used and, respectively, in which the phases (carbides, nitrides etc.) from the PRFT structure are stable (see table 4 [17-22]); b. they are influenced by the activity of the fluids circulating through PRFT and/or the atmosphere from the furnace where PRFT are used, which can engender carburization on their inside surface and/or oxidation and decarburization on their outside surface (see fig. 4 [20]), determining high gradients of carbon concentration in the PRFT wall, which triggers and intensifies the processes of generating and transforming the secondary phases; c. the secondary phases with globular form and small sizes, uniformly distributed in the matrix crystals, improve the creep behaviour of PRFT, while the secondary phases disposed under the form of a network at the edge of the matrix crystals have an embrittlement effect and speed up creep cracking and failure of PRFT; d. long-term maintenances at high temperature of PRFT determine the coalescence of secondary phases particles (decreasing the number of particles and increasing the particles sizes and the distances between the secondary phases particles distributed in the matrix, respectively obtaining some continuous inter-crystalline networks of secondary phases) and accelerates the creep failure of PRFT.

Table 4. The temperature ranges for the stability of the secondary phases from the PRFT structure

Matrix of PRFT microstructure	Type of secondary phase	Chemical formula of secondary phase	Temperature range, °C
Ferrite / Austenite	Carbide $M_{23}C_6$	$Cr_{16}Fe_5Mo_2C_6$	600-950
Ferrite / Austenite	Carbide M_6C	Fe_3Nb_3C	700-950
Ferrite	Ti carbonitride	Ti(C,N)	700-t_s a)
Ferrite	Nb carbonitride	Nb(C,N)	700-t_s a)
Ferrite	Cr-Fe nitride	$(Cr,Fe)_2N$	650-950
Austenite	Z – phase	Cr(V,Nb)N	700-1000
Ferrite / Austenite	Laves phase	Fe_2Mo / Fe_2Nb	550-900
Ferrite / Austenite	σ – phase	(Ni,Cr,Mo)Fe	550-1050
Ferrite / Austenite	χ – phase	$Fe_{36}Cr_{12}Mo_{10}$ or $(FeNi)_{36}Cr_{18}(Ti,Mo)_4$	600-900

a) Melting point of steel

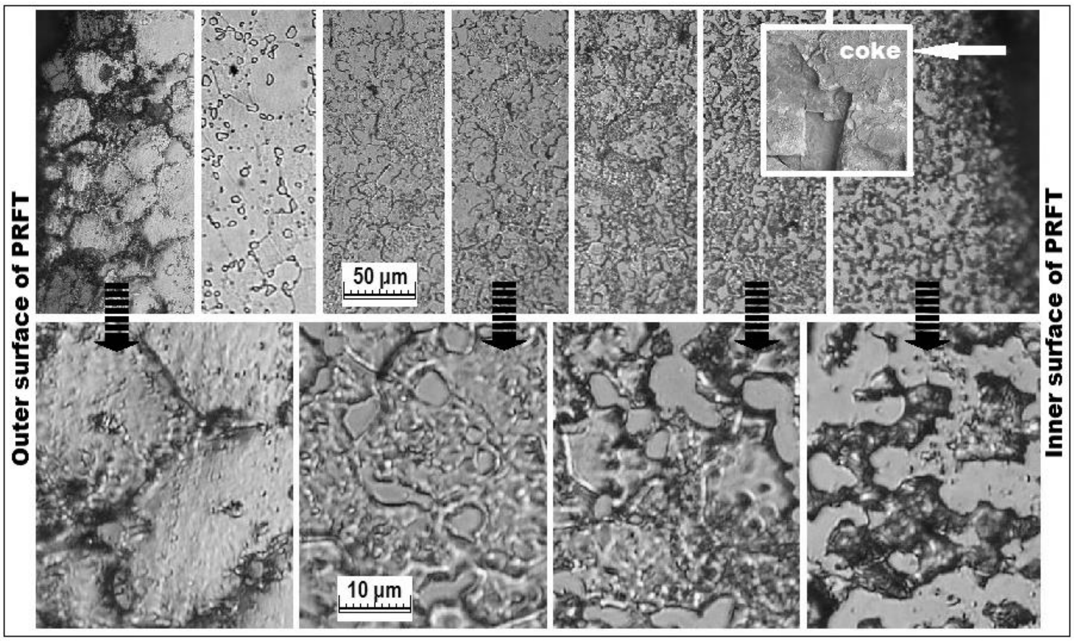

Fig. 4. Effects of the technological fluid (mixture of hydrocarbons) and of the atmosphere from the furnace 02-H1 from Petrotel LukOil Refinery upon PRFT, made of X11CrMo9–1 steel, used for a long time (over 110000 h): carburization (in the whole section: on the inside surface 1.40 %C, on the outside surface 0.57 %C), coking (on the inside surface) and inter-crystalline oxidation (on the outside surface) [20]

The structure changes described above can be noticed by comparing the microstructures shown in Figure 5, corresponding to some PRFT used for a long time at high temperatures, with PRFT microstructures in their delivery status (see fig. 1).

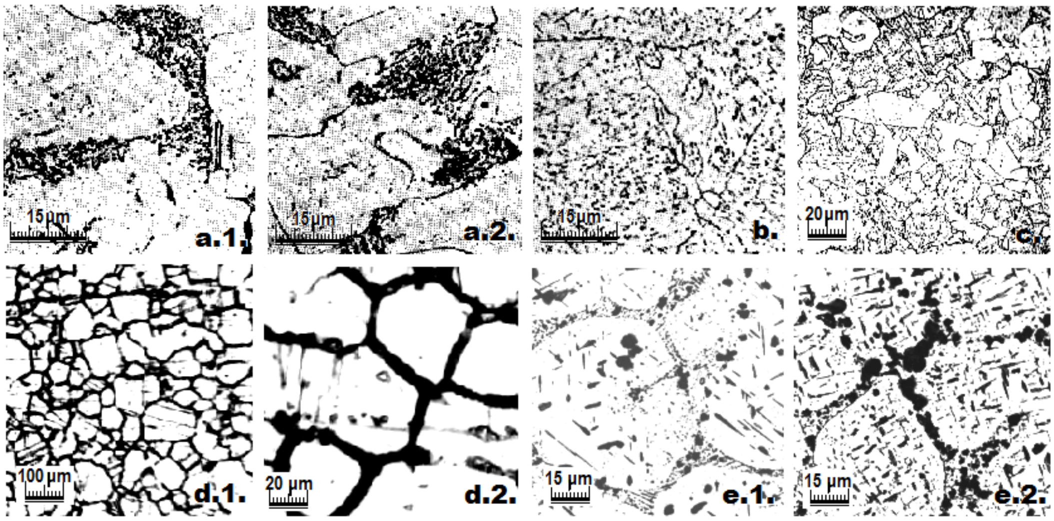

Fig. 5. The metallographic structure (at room temperature), after usage, of PRFT manufactured from various materials [6, 9, 10, 13-19, 21-24]:
a) 1¼Cr–½Mo Steel: a.1. initial structure: ferrite, bainite and carbide particles – fig. 1.a.4; creep-rupture test: temperature t_c = 500 ºC; stress σ_c = 150 MPa; time τ_c = 52058 h; structure: precipitates with an irregular distribution in ferrite and spheroidised carbide particles in bainite; a.2. initial structure – fig. 1.a.4; creep-rupture test: t_c = 550 ºC; σ_c = 120 MPa; τ_c = 3588 h; structure: similar to a.1;
b) 2¼Cr–1Mo Steel: initial structure: ferrite and granular carbide particles – fig. 1.b.4; creep-rupture test: t_c = 550 ºC; σ_c = 150 MPa; τ_c = 18194 h; structure: ferrite and spheroidised carbide particles;
c) 9Cr–1Mo–V Steel: initial structure: ferrite and granular carbide particles – fig. 1.c.4; long-term service: t_c = 550-590 ºC; σ_c = 100 MPa; τ_c = 143000; structure: ferrite and spheroidised carbide particles; d) 18Cr–8Ni Steel: d.1. initial structure: austenite – fig. 1.d; long-term service; heavy carbide precipitation at the austenite grain boundaries; d.2. – similar to d.1, but at higher magnification;
e) Centrifugally Cast 25Cr–25Ni Steel: e.1. initial structure: austenitic matrix with inter-dendritic eutectic carbides – fig. 1.f.2; long-term service in the reformer furnace: t_c = 880 ºC; σ_c = 14 MPa; τ_c = 24000 h; the structure contains lamellar eutectic of primary carbides, but the coalescence process has formed not completely a continuous network of primary carbides / secondary carbides are observed within the grains / in addition to the small and rounded carbides inside the austenite grains, coarser and plate or needle-like precipitates (carbides and sigma phase) are observed; e.2. initial structure: similar to e.1 – fig. 1.f.2; long-term service in the reformer furnace: t_c = 880 ºC; σ_c = 14 MPa; τ_c = 72000 h; semicontinuous coarse network along austenite grains consists of carbides / sigma phase is also present in the structure in the form of blocky precipitates / there is a small number of creep voids in the structure, the voids are formed at the interface between matrix and primary carbides or between matrix and the blocky sigma.

Assessment of the PRFT Technical State on the Basis of their Composition and Structure

The assessment of the PRFT technical state based on the determination of their chemical composition and microstructure (performed periodically, on the occasion of the technical inspections or current repairs, on samples taken from PRFT, or using non-destructive methods, with the help of mobile spectrometers and the examination of some metallographic replicas [4-6, 9, 10, 21-24]) implies the knowledge of some pertinent experimental correlations between the following categories of factors: a. the chemical composition, microstructure and mechanical properties of PRFT; b. the technological regime of the PRFT operation, defined by: temperature t_f, pressure p_f, nature and chemical activity / aggressiveness of the technological fluid transported; c. nature and chemical activity / aggressiveness of the atmosphere from the furnace in which PRFT are used; d. creep durability / life duration τ_f of PRFT (in the conditions defined by the previously described categories of factors).

For the (ideal) case in which, during their operation, PRFT does not change its chemical composition, and the temperature and pressure conditions are maintained constant (t_f = const. and p_f = const.), the Z – parameter method can be applied [14-16]. The application of the method for PRFT made of a certain heat-resistant steel grade, with a certain interval of the operational temperature $t_f \in [t_{f\min};t_{f\max}]$ and a certain regime of mechanical loading, characterized by a certain interval of the stresses (maximum or equivalent, determined by applying an adequate strength theories) $\sigma_f \in [\sigma_{f\min}; \sigma_{f\max}]$, generated in the PRFT wall during their use, presupposes the completion of the following stages (described by considering the information from [14-16] regarding PRFT made of a heat-resistant steel of the type 10CrMo5–5, with 0.08-0.15 %C; 0.90-1.20 %Cr; 0.25-0.35 %Mo and 0.10-0.35 % V):

- determination, on the samples cut from PRFT specimens, of the microstructures in the delivery status (new PRFT) and in the states obtained as a result of their damage by creep (with different maintenance durations τ_{tf}, at different loading regimes (t_{tf} =ct; σ_{tf}=ct), $t_{tf} \in [t_{f\min}; t_{f\max}]$, $\sigma_{tf} \in [\sigma_{f\min}; \sigma_{f\max}]$), for each of the determined microstructures being assigned an indicator of the level of creep damage $E = 1,2\ldots n_E$; in the case of PRFT made of 10CrMo5–5 type steel, it has been considered for the delivery status (with ferritic – pearlitic structure, without spheroidised carbides) level 1 – no spheroidization, with E = 1, and for the states obtained consequently to the creep damage of the structure from the delivery state, with different degrees of spheroidization of the carbides from the ferritic matrix, it has been considered: level 2 – slight spheroidization, with E = 2, level 3 – medium spheroidization, with E = 3, level 4 – complete spheroidization, with E = 4 and level 5 – serious spheroidization, with $E = n_E = 5$;
- execution, on samples cut from the specimens whose microstructures have been determined in the previous stage (each one having attached an indicator $E = 1, 2 \ldots n_E$), of creep-rupture tests, with different working regimes ($t_{f(E)}$; $\sigma_{f(E)}$), $t_{f(E)} \in [t_{f\min}; t_{f\max}]$, $\sigma_{f(E)} \in [\sigma_{f\min}; \sigma_{f\max}]$, on the basis of which the creep-rupture times (in hours) $\tau_{f(E)}$ are determined and the statistical correlations are defined:

$$F(t_{f(E)}, \sigma_{f(E),}\, \tau_{f(E)}) = 0; \quad (1)$$

for the case of PRFT made of 10CrMo5-5 type steel, it has been considered $t_{f(E)} \in [400^{o}C; 600^{o}C]$, $\sigma_{f(E)} \in$ [50MPa; 200MPa] and the following correlation has resulted:

$$[t_{f(E)} + 273{,}15]\,[20 + \lg\tau_{f(E)}] = Z(E) - 2490\lg\sigma_{f(E)} - 10\sigma_{f(E)}, \quad \text{with} \quad Z(E) = 27220 - 540E, \quad (2)$$

in which the microstructure resulting from the creep damage of PRFT is characterized by assigning a value to the indicator E and intervenes in the equation of the statistical correlation by means of the parameter $Z(E)$;

- prediction of the PRFT remaining life $\tau_{f(E)}$, with state of damage due to their previous use characterized by the value of the indicator E, in the conditions of operation with a regime ($t_{f(E)}$;$\sigma_{f(E)}$), by solving equation (1); in the case of PRFT made of steel of the type 10CrMo5–5, by processing the equations from the group (2), one obtains:

$$\tau_{f(E)} = 10^{\,G(t,\sigma,E)}, \quad \text{with} \quad G(t,\sigma,E) = -20 + [27320 - 540E - 2490\lg\sigma_{f(E)} - 10\sigma_f\,] \,/\, [t_{f(E)} + 273.15]. \quad (3)$$

The diagram for the use of the Z – parameter method for the case of PRFT from 10CrMo5–5 type steel is shown in Figure 6, on which there are also indicated (as an example) the data of a case study regarding the prediction of the remaining life $\tau_{f(E)}$ of some PRFT (from steel of the type 10CrMo5–5), for which, at the last technical inspection performed, based on the microstructure examination, the value E = 3.5 has been assigned to the indicator of the level of creep damage, and their future operating regime is ($t_{f(E)}$ = 525 °C; $\sigma_{f(E)}$ = 130 MPa); it can be noticed that the PRFE considered for the case study have a remaining life $\tau_{f(E)} \cong 3000$ h.

The *Z* – parameter method (as well as other methods proposed in literature: the method based on the concept of free energy [19] or the method based on the use of charts with the microstructures of PRFT that have failed by creep at different operating regimes (t_f; σ_f) [9]) cannot be applied for the assessment of the technical state of PRFT from the furnaces from oil refineries and petrochemical plants, because these are operated with regimes (t_f; σ_f) having the parameters t_f and/or σ_f variable in time. In order to be able to assess the remaining life of the PRFT operated in such conditions, the authors propose the creation and use of some charts with the microstructures of PRFT, new and with different degrees of use, each microstructure having attached the following categories of information: a. the chemical composition of the material from which PRFT has been made; b. the phases and constituents that are noticed in the PRFT microstructure; c. the cumulative damage D_c of PRFT, ascertained using the procedure described in [1], by taking into consideration the parameters (t_f; σ_f) and durations τ_f of all the operational sequences of PRFT before the determination of the microstructure.

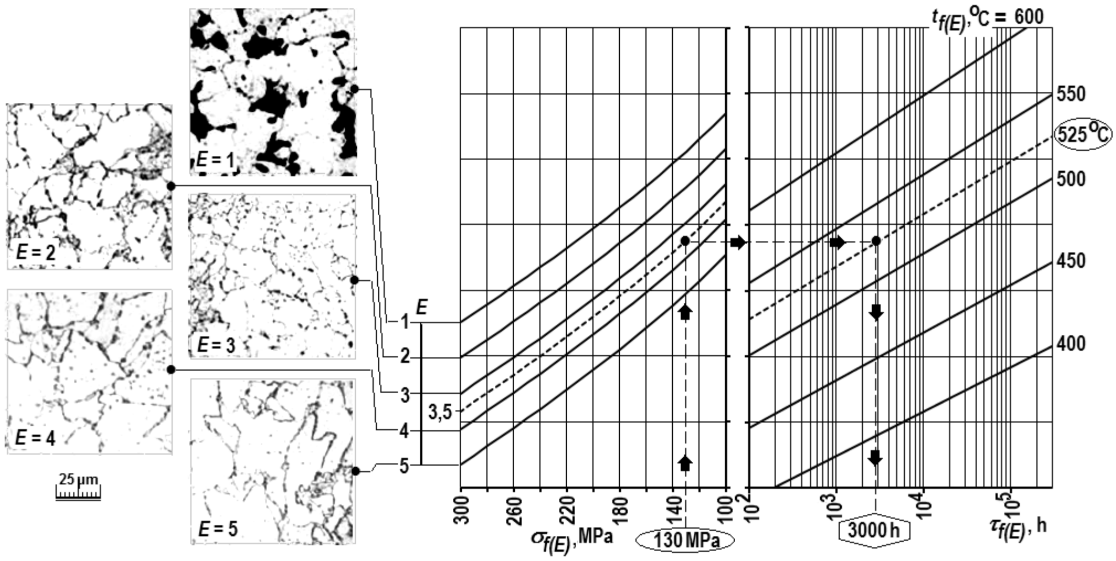

Fig. 6. Diagram for using the *Z* – parameter method for the prediction of the remaining life of PRFT

Conclusions

The issues analysed and treated in the present paper have led to the following conclusions, regarding the possibilities of assessment of the technical state of the furnace tubes from the oil refineries and petrochemical plants by detemining their chemical composition and microstructure:

- the comparison of the tubes microstructure in the delivery status and after their usage, with known operating regimes (temperature – pressure) and on well-defined periods, in the furnaces of the plants for hydrocarbons processing can lead to the assessment of their technical state, in order to underlie the decisions regarding continuation of their operation or the execution of some maintenance works;
- the structural changes during the use of the tubes refers mainly to the nature, dimensions, distribution pattern and dispersion degree of the phases and/or constituents, with small percentage weights, which are distributed at the edge of or inside the crystals of the ferritic or austenitic matrix: carbides, nitrides or carbonitrides, intermetallic compounds;

- the assessment of the technical state of the tubes by means of examining their microstructure is more difficult in the cases in which the fluids circulating through the tubes and/or the atmosphere from the furnace in which they are used generate phenomena of carburization and coking on their inside surface and/or of oxidation and decarburization on their outside surface; in such cases, the periodical estimation of the tubes technical state shall provide for both the microstructure examination and the determination of the chemical composition alterations;
- the precision of the assessments based on the microstructure examination with the optical microscope is limited, imposing the suitable preparation of the metallographic samples or replicas and the existence of some charts with reference images; the high costs and long working durations make unfeasible the use of advanced methods for the microstructures examination (scanning electron microscopy – SEM or transmission electron microscopy – TEM);
- for the evaluation of the technical state of the tubes which have utilization regimes with parameters (temperature, pressure) variable in time, it is recommended to build charts with the microstructures of the tubes in the delivery states and in the states corresponding to different levels of their cumulative damage;
- the confidence level of the assessments regarding the tubes technical state can be considerably increased if, besides the determinations of the chemical composition and the microstructure examinations, other methods are also used (especially tests able to assess their remaining mechanical strength after different service periods in the furnaces).

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Aprecierea stării tehnice a ţevilor cuptoarelor din rafinării şi instalaţii petrochimice prin examinarea compoziţiei chimice şi microstructurii acestora

Rezumat

Lucrarea analizează posibilităţile de evaluare a stării tehnice a ţevilor cuptoarelor din instalaţiile de rafinare a petrolului şi petrochimice prin deteminarea compoziţiei chimice şi microstructurii acestora, pe eşantioane prelevate cu ocazia efectuării reviziilor tehnice periodice ale acestor instalaţii. Analiza ia în considerare acţiunea combinată a principalelor procese care conduc la degradarea progresivă a ţevilor cuptoarelor şi la limitarea duratei lor de viaţă: fluajul, activat de solicitarea mecanică îndelungată a ţevilor la temperaturi ridicate, oboseala, determinată de caracterul variabil în timp al solicitărilor mecanice şi termice la care sunt supuse ţevile şi modificarea compoziţiei chimice şi microstructurii ţevilor (însoţită, evident, de modificarea caracteristicilor lor de rezistenţă mecanică şi tenacitate), determinată de utilizarea lor în medii active (care pot produce carburarea/cocsarea la interior şi oxidarea/arderea/decarburarea la exterior a ţevilor). Lucrarea evidentiază faptul că informaţiile obţinute prin examinarea periodică a compoziţiei chimice şi microstructurii, coroborate cu cele obţinute prin alte metode de investigare a stării lor tehnice, pot asigura estimarea cu un nivel de încredere acceptabil a duratei de viaţă reziduale a ţevilor cuptoarelor.