

Materials for Reformer Furnace Tubes. History of evolution

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Abstract

The paper discusses progress that has been made over the past sixty years in increasing the service life of centrifugally cast, creep-resistant tubes operating in reformer furnaces. Attention was mainly focused on the principles of selection of the chemical composition of castings to improve their creep behaviour. The reasons accounting for withdrawal of tubes from service were indicated. Examples of chemical composition and mechanical properties obtained in creep-resistant Ni-Cr cast steel used by the leading European tube manufacturers were stated. Trends in current research aiming at further improvement of the tube performance characteristics were mentioned.

Keywords: Innovative Foundry Technologies and Materials, Damages in Reformer Furnace Tubes, Ni-Cr Austenitic Cast Steel

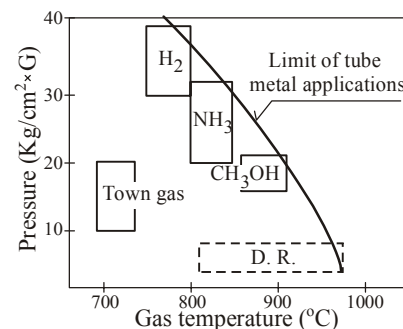
1. Introduction

Creep-resistant tubes are used in many branches of the industry, but their main application is in the chemical and petrochemical industry (Fig. 1). No matter where they are applied, one and the same fact is always stressed, namely that the stability of tube operation determines the reliability and efficiency of the operation of the whole installation [1–7].

Since the beginning of the 60-ties of the past century, in installations whose operating conditions require the use of tubes characterised by high creep resistance, the centrifugally cast tubes made from different grades of the creep-resistant, nickel-chromium austenitic steel have been used [1–9].

The use of the above mentioned material and technology guarantees to the currently running installations a trouble-free operation for over 100 000 hours [6, 7]. Here it should be emphasized that so long life on performance could be obtained due to the, running for over 50 years, scientific research and

industrial tests, successfully carried out to improve the casting production technology and recommend the best chemical composition of materials cast (Tab. 1).



Rys. 1. Different applications of tubes [8]

This article discusses the most important achievements in research and development works aiming at a maximum increase of the life of creep-resistant tubes operating in reformer furnaces.

Table 1.
Increased creep resistance of the centrifugally cast tubes [3]

Date	Chemical composition, wt%			Others elements	Relative strength
	Cr	Ni	Nb		
1960s	25	20	—	—	1,0
1970s		24	1		1,4
Early 80s	23	22		Ti	1,7
Mid 80s	25	35		Ti, Zr, W, Cs	1,9
Late 80s			2,2		

2. Degradation of tube properties on performance

The causes of the degradation of the properties of tubes during their operation were discussed on the example of catalytic tubes used in steam reformers [7]. The catalytic tube has a length of 12 to 13 m, a 70 - 160 mm diameter, and wall thickness of 10 - 20 mm. It consists of several, centrifugally cast segments 3 to 6 m long, joined by butt welding. The tube is operating in a vertical position, in a relatively wide field of temperatures (Fig. 2) [6, 7].

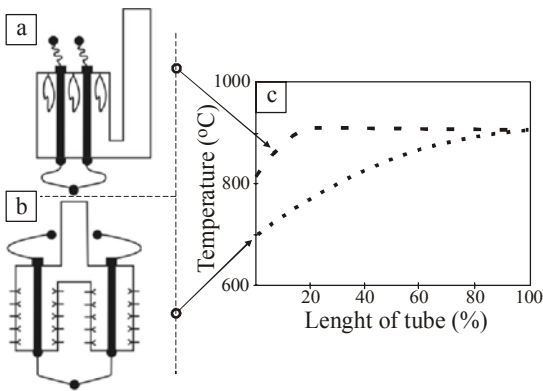


Fig. 2. The setup of tubes and burners in reformer furnace with upper (a) and lateral (b) heating system and temperature distribution along the tube length (c) [9]

The final result of the degradation of the properties of the tube during its operation is the formation of a longitudinal crack (Fig. 3). The decohesion of the tube wall is the result of a series of the interrelated events that ultimately lead to a drop of the mechanical and physical properties and change the tube geometry. These events mainly involve [1-7]:

- aging and creep rupture, and
- thermal fatigue resulting from uneven temperature distribution in the tube wall in both lengthwise (Fig. 2) and crosswise direction, and in parts of the furnace directly cooperating with this tube.

The microstructure of the cast steel of which the tube is made is in the initial state composed of an austenitic matrix (supersaturated solid solution of austenite) and carbide-austenite eutectic distributed in interdendritic spaces (Fig. 4a).

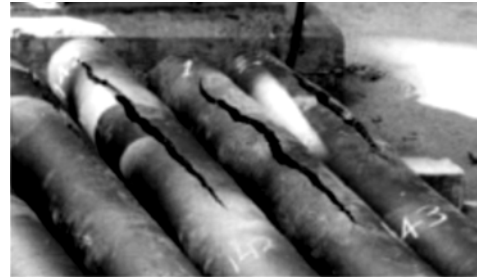


Fig. 3. Longitudinal cracks in catalytic tubes [7]

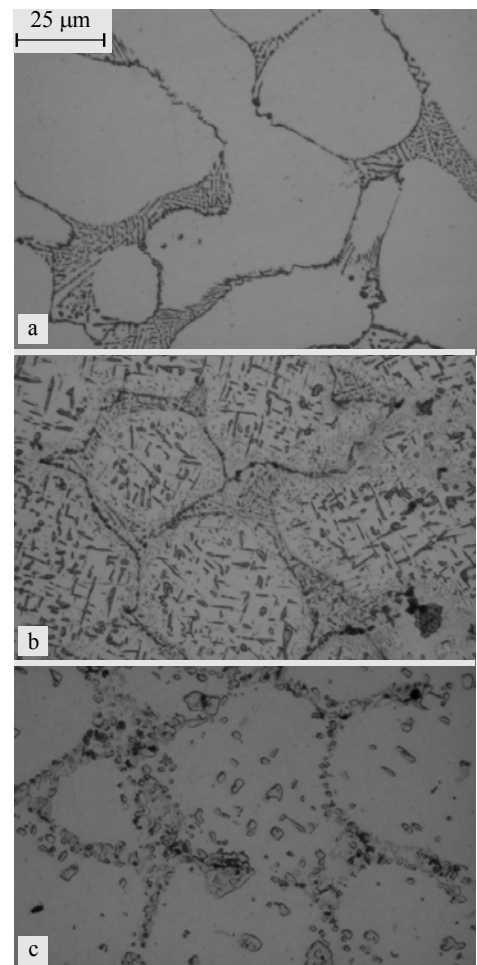


Fig. 4. Microstructure of IN519*^{*/} cast steel [7]: a) as-cast state, b, c) after 120,760 hours of operation - differences observed in particle morphology are the result of different temperatures of the tube wall (Fig. 2) from which samples were taken for analysis; *^{*/} chemical composition of the cast alloy is given in further part of this article

In the tube material during operation, numerous disadvantageous changes take place, extending through several, spread in time, characteristic stages which include [10, 11]:

- precipitation of high-dispersed particles of the intermetallic phases inside austenite grains (Fig. 4b),
- coalescence and coagulation of primary and secondary phases (Fig. 4c),
- formation of micropores and microcracks (Fig. 5),
- deformation of the tube wall combined with macrocrack formation (Fig. 3).

The described changes proceed at a rate directly proportional to the increasing temperature of the examined tube section (see Fig. 2 and Fig. 4b and c).

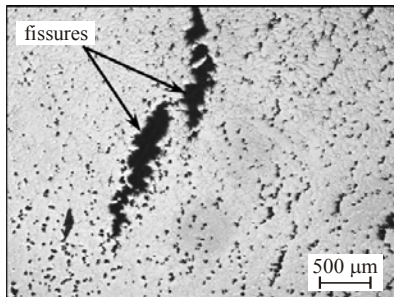


Fig. 5. Cracks on the external tube surface [13]

In the process of tube destruction, a significant share has also the high-temperature corrosion, mainly oxidation and carburisation taking place in the subsurface tube area [6, 7].

3. Manufacture of tubes

Extending the reformer failure-free operating cycle is possible, first of all, through the use of tubes offering higher creep resistance [1–7].

From studies of the creep resistance it follows that when tubes are made from a material with coarse grain structure, this greatly improves the creep behaviour. In practice, this objective is achieved by simultaneous control of the tube solidification conditions during the process of centrifugal casting and proper selection of the cast material chemical composition [6, 7, 13].

Under given operating conditions, high strength of tubes also enables their wall thickness to be reduced, thus ensuring:

- better process efficiency owing to a large inner diameter of the tube, and
- better resistance to thermal fatigue owing to a temperature gradient reduced on the tube cross-section.

3.1. Tube casting technology

In the process of centrifugal casting, the grain size mainly depends on the cooling rate during casting solidification. Extensive studies of this subject were conducted in the 70-ties of the past century [13]. The results of tests published in the

aforementioned work are still cited in the reference literature as fully valuable data.

Generally, it can be stated that creep resistant tubes are characterised by the highest quality, when the manufacturing technology allows producing the dendritic zones of columnar shape on the entire cross-section of the casting wall (Fig. 6), or at least in 80% of that cross-section [7].

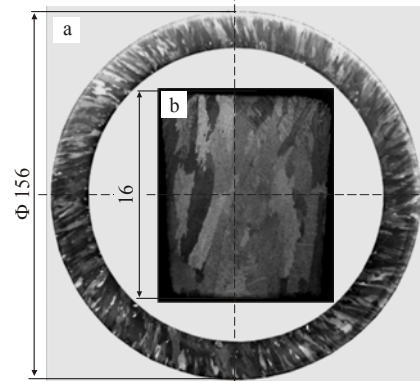


Fig. 6. Macrostructure of catalytic tube made of IN519 cast steel [7]: a) cross-section, b) fragment of the casting wall

3.2. Chemical composition of cast steel used for reformer tubes

Changes that have occurred over the last 60 years in selection of the chemical composition of the austenitic steel used for a variety of the centrifugally cast tubes can be ordered according to the growing number of the added alloying elements and their proportional share in the cast material.

Cast steel of the 1st generation has been used in the industry from the 50-ties of the past century (Tab. 1). A standard for classification of the designations and grades of this cast steel was developed by American Casting Institute (ACI) (Tab. 2). Some of the cast steel grades having high content of the alloying elements are compared in Table 1. The main alloying constituents are nickel, chromium, and silicon. Individual grades of this cast steel (e.g. HK, HT, HP) have always been and still are an inspiration to develop the next generations of this cast material (see Tab. 3, Fig. 10).

Cast steel of the 2nd generation differs from the cast steel of the 1st generation mainly in the addition of carbide-forming elements stronger than chromium (niobium in the first place). Its industrial use began in the 70-ties of the past century. Studies evaluating the effect of niobium on the cast steel creep resistance have indicated that, in this particular respect, the content most advantageous is comprised in a range of 0.8–1.2% (Fig. 7). The cast steel may also contain cobalt and tungsten (Fig. 10) [6, 7]. The addition of these elements enhances the effect of both solution and precipitation hardening, having also an important and beneficial influence on the cast steel creep resistance [5–7]. Studies were also carried out on the combined effect of niobium and titanium on the cast steel creep behaviour (Fig. 8).

Table 2.

Designations and chemical composition (wt.%) of selected grades of austenitic cast steel according to ASTM A 297/A 297M – 97 [5]

ACI	UNS	C	Si	Mn	P	S	Cr	Mo	Ni
HK	J94224	0,20-0,60	1,00-2,00	max 2,00	max 0,040	max 0,040	24,00-28,00	max 0,50	18,00-22,00
HT	N08605	0,35-0,75	1,00-2,50				15,00-19,00		33,00-37,00
HU	N08004						17,00-21,00		37,00-41,00
HP	N08705						24,00-28,00		33,00-37,00

Adding both these elements jointly results in an approximately 1.7-fold increase of the cast steel creep resistance, compared to the grade without an addition of these elements (Fig. 8). The best combined effect of the joint addition of niobium and titanium is obtained when the proportional share of the atomic content of these elements (Ti+Nb)/ C (determines the morphology of secondary carbides) and Ti/ (Ti+Nb) (determines the morphology of primary carbides) amounts to about 0.5 [14].

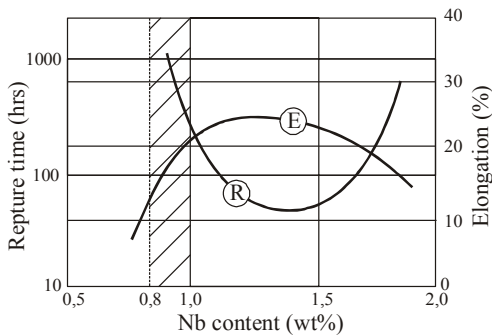
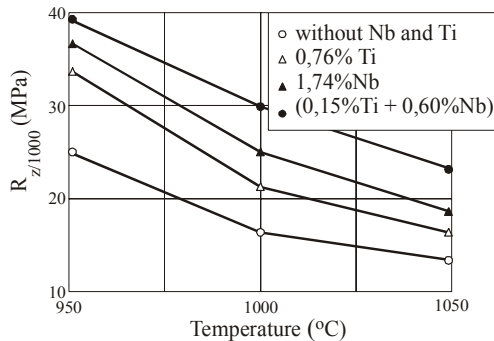


Fig. 7. Influence of the Nb content on the creep properties of HP cast steel [15]



Rys. 8. Influence of the Nb and/ or Ti content on the creep rupture of HK cast steel [14]

During that period, studies were also undertaken to know the degree and type of effect of all alloying elements on the creep resistance of cast steel (Fig. 9).

Cast steel of the 3rd generation started being used in the industry in the 80-ties of the past century (Tab. 1 and 3). One can risk the statement that the results disclosed in [16], regarding the introduction of niobium, titanium and zirconium to austenitic steel for the centrifugally cast tubes, mark a starting point in studies of the austenitic alloys with additions of niobium and

microalloying elements from groups III and IV of the periodic table (Ti, Ta, Zr), and also with rare earth elements (Ce, Nd, Pr, Hf). In investigations of the chemical composition of the cast steel of the 3rd generation, the phenomenon of synergism was used. It was noted that several alloying elements, each of which individually increases the resistance to creep, taken jointly give a much better effect at lower concentrations. The amount of the introduced microalloying elements usually does not exceed 0.5%. The outcome is strong refinement of the alloy structure and improved stability of simple MC type carbides [16–18].

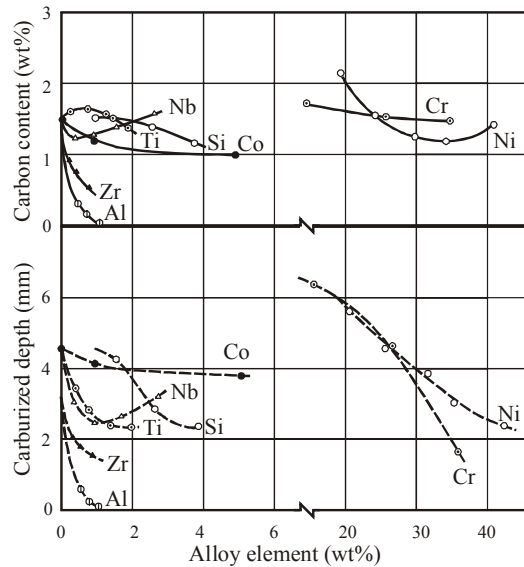


Fig. 9. Influence of alloy elements on carburization resistance of HK cast steel [19]

Changes in cast steel chemical composition included not only the introduction of the above mentioned microalloying elements, but also carbon content reduced to a level of 0.10-0.15% (Tab. 3 and 4). This part of the research focused mainly on the cast steel used for parts of installations cooperating with tubes. Studies of the possibility to reduce carbon content were done mainly to increase the plastic properties of this material. Cast steel with an addition of aluminium was also introduced into service (Manaurite XO and Manaurite 40XO cast steel) [20]. Despite some technological difficulties associated with the production of castings containing high levels of aluminium and heavy brittleness of cast steel caused by the structure including phases containing this element, the chemical composition was elaborated for a family of alloys offering high resistance to carburisation.

Table 3.

Nominal chemical composition (wt%) of centrifugal cast materials for reformers [1]

Material	S+C Märker [®] G / Centralloy [®] CA	Fe	Ni	Cr	Carbid forming elements
High-carbon alloys for radiant tubes (typically 0,40-0,45% C)					
HK 40	4848	<52	20	25	—
IN 519	4855	<47	24	24	Nb
HP Nb	4852	<37	35	25	
HK MA	4848 micro (new S+C alloy)	<52	20		Nb, Ti, Zr
HP MA	4852 micro	<37	25		Nb, W, Ti, Zr
Low-carbon alloys for outlet components (typically 0,10-0,15% C)					
32/20 + Nb	4859	<45	32	20	Nb
HP LC	H 101	<35	37	25	Nb, Ti, Zr
HP LC MA	H 101 micro (new S+C alloy)				

Table 4.

Minimum 10⁵ hours creep rupture strength (MPa) for low-carbon alloys [1]

Material	S+C name	Temperature, °C				
		800	850	900	950	1000
Alloy 800HT	wrought	20,0	13,6	9,6	5,5	—
32/20 + Nb	4859	37,6	27,2	18,8	12,2	7,0
HP LC	H 101	27,0	18,2	12,1	8,0	5,0
HP LC MA	H 101 micro	36,9	26,5	19,0	13,6	9,7

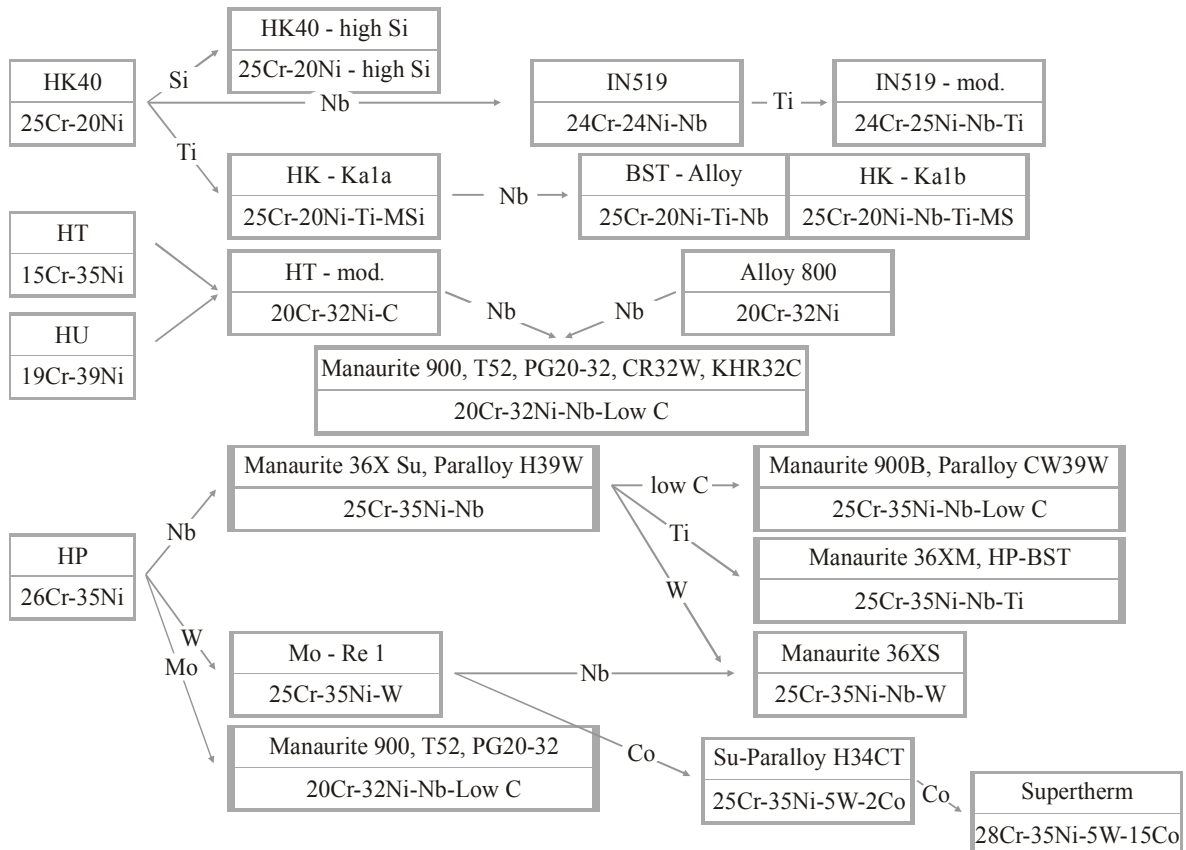


Fig. 10. Evolution in chemical composition of the austenitic cast steel for reformer tubes [8]

As a result of intensive studies, the creep resistance of tubes produced from the cast steel of the 3rd generation has by now more than doubled, compared to the creep resistance of tubes of the 1st generation (Tab. 1). The microadditions introduced to cast steel gather mainly in the MC carbide precipitates [15–18]. It should be remembered, however, that any attempts at a wider presentation of the results of the research done on both laboratory and industrial scale on the cast steel from this family must fail because of restricted access to more detailed information. At this stage of studies and industrial applications, the data are still considered confidential. In spite of this, a good overview of various aspects of the production of centrifugally cast steel tubes and properties of cast steel of the 3rd generation is given in the results of research works recently completed in Poland [17, 18].

Summing up the achievements recently obtained in studies of the cast steel of the 3rd generation, it should be mentioned that the trend equally important is that which assumes that various parts of installations made from wrought alloys can be successfully replaced with alloys cast (Tab. 4).

Cast steel of the 4th generation is the latest trend in the research of materials used for tubes. These are alloys dispersion-strengthened with oxides (ODS, "mechanical alloying"), both wrought and cast. The example of the latter group is Paragon A cast steel made by Paralloy [21].

4. Instead of summary

On the European market of the centrifugally cast tube manufacturers, the competitors are mainly the following companies: Manoir Petrochem from France, Schmidt + Clemens Group from Germany and Paralloy UK. Progress in technology used by the chemical, petrochemical and power industry compels the tube manufacturers to constant upgrading of the product quality to meet the new challenges arising from improvements introduced to the production process, including changes in the design and operating conditions of installations. As a result of these activities, the chemical composition of the creep resistant austenitic cast steel undergoes continuous modifications (Fig. 10).

As already noted, the improved utilisation properties of tubes are not only the effect of improved chemical composition of castings. Also technologies used in their production are subject to important innovative changes [1–5].

The recently developed novel solution assumes the replacement of centrifugally cast tubes with wrought bimetallic tubes [4], which consist of two concentrically oriented elements. The inner tube is made of ferritic Incoloy[®] MA956 stainless steel, while outer clad material is austenitic ODS Alloy 803 steel. Both tubes are produced by mechanical alloying technology. This combination ensures a very high creep resistance, while the commercial ferritic Fe-Cr-Al alloy offers a 50% reduction in coke buildup combined with improved carburisation resistance.

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