Materials science in the field of heat-resistant austenitic alloys

S V Afanasiev¹, O Z Ismaylov², A V Pyrkin², Yu N Shevchenko¹ and T P Guschina¹,³

¹ Togliatti State University, Togliatti, 445020, Russia
² LLC “Reaction Pipes”, Togliatti, 445045, Russia
³ E-mail: TPGuschina@yandex.ru

Abstract. Centrifugally cast pipes from heat-resistant steels and alloys are widely used in many branches of engineering. These are radiation pipes in thermal furnaces with a protective atmosphere, bottom rollers in continuous thermal and heating furnaces of metallurgical plants, rollers in continuous annealing units, etc.

The question of the possibility of increasing the operating parameters of the process of high-temperature conversion of natural gas in ammonia and methanol units is very important, because increasing the temperature and pressure not only improves the performance of the plants, but also reduces the cost of the product and allows obtaining higher purity hydrogen. In connection with the above, specialists are making efforts to improve the compositions used in steels of the type H25N35C2 by means of their additional doping.

Depending on the temperature of the catalytic process, the service life of centrifugally cast pipes of known alloys varies over rather wide intervals. After the development of the resource they must be replaced, because strength under operating conditions (temperature, pressure) decreases sharply, which can lead to depressurization of the pipe and emergency shutdown of the reforming furnace.

The situation is complicated by the fact that during the pyrolysis of petroleum fractions and lower hydrocarbons, not only the processes of destruction and isomerization occur, but also the formation of significant amounts of coke deposited on the inner surface of the reaction pipes. Diffusing into the alloy, it is able to react with iron to form cementites, on contact of which methane is released with hydrogen, which causes the appearance of numerous cracks. As a result of hydrogen corrosion, the physical and mechanical properties of the metal are significantly reduced.

So the decomposition of butane occurs in accordance with the following scheme:

\[
\begin{align*}
\text{C}_4\text{H}_{10} & \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 & (1) \\
\text{C}_2\text{H}_4 & \rightarrow \text{CH}_4 + \text{C} & (2)
\end{align*}
\]

To suppress coke formation, various technological methods are used, in particular, the joint supply of water vapor and hydrocarbon. Along with this practiced annealing of deposited coke. For this purpose, the principle of the reactor - regenerator is used, which consists in the periodic disconnection of the reaction pipes from the process and the supply of water vapor to the heated tube.

When this occurs, the local ignition of coke and the movement of the flame front along the reaction tube up to the complete burning of carbon. This is accompanied by an increase in the surface temperature of the pipes and contributes to the accumulation of stresses in the alloy.
It is generally accepted that damage to the reaction pipes in tube furnaces for the production of olefins occurs due to the simultaneous effects of thermal loads and deformations caused by the high pressure of the reaction gas inside the tube. Total stresses with a carburizing effect cause creep, which mainly affects the inner surface of the pipes.

In turn, the creep of the alloy near the boundaries of austenitic grains leads to the appearance of voids, which later line up and lead to the appearance of microcracks.

This process proceeds in three stages.

At the initial stage of operation of the reaction pipes, in the process of metal hardening, the strain rate decreases. When this occurs, the movement of microelements in the alloy structure is slowed down; however, the formation of micropores is observed at the interface between grains and phases.

The secondary creep stage is caused by the aging of the high-temperature alloy and manifests itself as an increase in the diameter of the pipes with a constant but slow speed. At this stage, growth and association of micropores occurs.

Tertiary creep is characterized by a high rate of deformation and the integration of microcracks into deep cracks larger than austenitic grain.

The increasing rate of deformation ultimately leads to the destruction of the reaction tube from a heat-resistant alloy.

To increase the efficiency of the reaction pipes, it is extremely important to determine the moment of the end of secondary creep, as well as to postpone the process of the onset of tertiary creep, at which the voids at the grain boundaries expand to the formation of cracks in the metal structure.

One of the possible reasons for the insufficiently high heat resistance of pipes made of the known high-temperature chromium-nickel alloys is the increased relative particle size of secondary carbides, their low uniformity and uneven distribution in the metal. Many researchers rightly believe that the alloy hardening mechanism is quite complex and cannot be explained from the standpoint of the carbide theory [1].

At the same time, it cannot be denied that the formation of carbides in the microstructure of the metal leads to a certain inhibition of its creep.

It is known that, by their structure, carbides are divided into two types: primary carbides, which are formed during solidification in the form of a fine mesh on the boundaries of austenite grains and secondary carbides, which are formed during high-temperature loading of the reaction pipes. During the operation of pipes, they are deposited in the form of finely dispersed particles, not at the boundaries, but in the austenitic grains of the heat-resistant alloy themselves (the aging process). Each finely dispersed particle of secondary carbide at the level of the microstructure acts as a peculiar obstacle preventing deformation shear.

Depending on the composition of the heat-resistant alloy and the conditions for its production, along with carbides, various intermetallic compounds are formed in it, which not only impede the process of creep and carburizing the inner surface of the reaction pipes, but significantly increase their service life.

Only from the standpoint of the formation of carbides and intermetallic compounds it is possible to carry out the formulation of austenitic alloys.

In particular, for high-carbon austenitic alloy consisting of 25 % wt. chromium, 35 % wt. Ni and having a high value of tensile strength, the addition of 1% wt. Nb significantly improves creep resistance. Entering a minimum amount of titanium and zirconium contributes to an additional improvement in long-term strength. In the presence of these additives, especially in the presence of rare earth metals, such characteristics of steels as oxidation and carburization resistance at elevated temperatures improve, and the high chromium content provides the necessary corrosion resistance.

In order to improve the reliability of the reaction pipes, which are one of the most responsible and most metal-consuming elements in hydrocarbon conversion plants, a new base alloy based on iron-nickel type HN33BS doped with microadditives has been proposed [2, 3]. It includes chromium, nickel, niobium, cerium, silicon, manganese, vanadium, titanium, aluminum, tungsten and iron, subject to two additional conditions:
%Ni + 32 %C + 0,6 %Mn + %Cu = 40,08 – 46,870%  (3)
%Cr + 3 %Ti + %V + %Mo + 1,6 %Si + 0,6 %Nb = 21,322 - 26,39%  (4)

The inventive alloy is purely austenitic, since its structure is retained when heated. It is not hardened by heat treatment, that is, it is not prone to dispersion hardening, it is smelted only in induction furnaces with a basic lining and using mostly pure charge materials. The specificity of metal melting in induction furnaces through the use of a high-frequency heating method ensures good dispersion of the alloy components in the smelting process, and also allows to obtain an alloy with a low gas content and avoid carburization, as happens in an electric arc furnace [4].

Extended tests of products from a new heat-resistant alloy were carried out in the Federal State Unitary Enterprise Central Research Institute for Ferrous Metallurgy named. IP Bardin in comparison with the known alloy 45H25N35BC (prototype).

The average grain size was determined in an eyepiece of a metallographic microscope on frosted glass (GOST 5639 “Steel. Methods for detecting and determining grain size”). It was established experimentally that due to the optimization of the metal composition, the grain size of the primary carbides is about 250 microns (instead of 215 microns for the prototype). In parallel with this, an improvement in the structure of the alloy, estimated by the inhomogeneity coefficient

$$A = \frac{R_{\text{max}}}{R_{\text{min}}}$$

where R_{\text{max}} и R_{\text{min}} are the maximum and minimum linear dimensions of the grains in the steel structure, respectively. In the prototype, it varies in the range of 1.13 - 1.17, and for the inventive alloy 1.08 - 1.12, which indicates a higher homogeneity of the crystalline formations.

A metallographic study of the HN33BS alloy showed the presence of equiaxed grains of an austenitic solution Fe-Cr-Ni. In a sufficiently large quantity, there is a eutectic phase containing carbide of the type Cr_7C_3 and having a lamellar structure.

An equally important strengthening factor is the presence of two intermetallic inclusions in the austenitic matrix, described by the following formulas — Cr_{39}Fe_{4}Ni и Nb_{28}Cr_{3}FeNiTi. Their presence was confirmed by micro X-ray diffraction analysis of the alloy sample using a Sigma scanning electron microscope from Karl Zeiss, equipped with an EDAX analytical system (USA) with an Apollo detector and a Hikari backscattered electron detector.

From the above formulas it follows that the first intermetallic compound is enriched in chromium, and the second - in niobium. By adjusting the content of individual elements in the alloy, it is possible to reduce or increase the content of reinforcing phases, as well as to change their composition.

The temperature of the phase transformations of the alloy - solidus and liquidus, found by the DTA method on samples weighing 1.8 grams using the molybdenum reference sample are shown in table 1.

| The name of the temperature characterizing the change in phase state | The temperature of the phase transformation of the alloy mode: |
|---|---|
| Solidus temperature T_S, °C | 1313 |
| Liquidus temperature T_L, °C | 1343 |
| Eutectic crystallization temperature, °C | - |
| Dissolution temperature of niobium carbides, °C | 1250 |

The data on long-term strength obtained at a temperature of 960 °C on samples of DP-5 type with a working part of Ø5, 25 mm long with direct loading of samples in accordance with GOST 10145 are in good agreement with the obtained results.

It is established that the tested samples after rupture are weakly oxidized, the elongation and reduction of the cross-sectional area are zero. The value of the long-term strength σ_w alloy HN33BS at a temperature of 960 °C per 100,000 h, obtained by the extrapolation method, is 17.4 N/mm², which is
26% higher than the data on the heat resistance of the 45H25N35VS alloy. At 810 and 1110 °C, the value of this indicator is 66 and 4.9 MPa, respectively, which is 1.5 and 2 times higher than the allowable stresses $\sigma$.

The high level of mechanical properties of the alloy was confirmed in the course of its testing at temperatures of 20 and 960 °C on samples with a working part of $\varnothing 5, 25$ mm long according to GOST 9651, which is illustrated by the data in table 2.

Table 2. Mechanical properties of alloy HN33BS.

| Test temperature, °C | $\sigma_\text{в}$, H/MM$^2$ | Yield strength $(\sigma_{0.2})$, N/mm$^2$ | Relative lengthening $(\delta_\text{5})$, % | Relative narrowing of the cross section $(\psi)$, % |
|----------------------|-----------------|-----------------|-----------------|-----------------|
| 20                   | 480-580         | 240-300         | 9.9-14.3        | 8.5-13.8        |
| 960                  | 110-128         | 105-119         | 18.0-21.5       | 29.0-39.0       |

Along with the considered base alloy, low-carbon and high-carbon chromonic-nickel alloys of austenite structure were created and introduced, which made it possible to manufacture a full range of components for reforming furnaces (table 3).

Table 3. Assortment of heat-resistant alloys of austenitic structure.

| Alloy grade | Patent for invention |
|-------------|---------------------|
| Austenite -1 | RU №2393260 [4] |
| Austenite -2 | RU №2446223 [5] |
| Austenite -3 | RU №2485200 [6] |
| Austenite -4 | RU №2533072 [7] |

Due to the development carried out at the site of LLC “Reaction Pipes”, Togliatti, industrial production of reaction pipes with a reduced wall thickness was organized [8, 9].

Their introduction on ammonia units of the AM-76 type and Kemiko PJSC “Togliattiazot” increased the productivity of reforming furnaces by more than 30 % and significantly reduced the consumption rates for natural gas. At the same time, the service life of the reaction pipes increased to 125,000 hours at a temperature of operation of 800-850 °C and a pressure of about 4 MPa.

References
[1] Gruzdev B L 2014 Weldability of austenitic heat-resistant steels and alloys. (Ufa: Ufa State Aviation Technical University) p 77
[2] Afanasyev S V, Sergeev S P 2015 New innovative developments in the field of reaction pipes for reforming furnaces Chemical technology 8 8-9
[3] Patent RU No 85844 2009 Installation of centrifugal casting of heat-resistant pipes (Moscow: Rospatent)
[4] Sergeev S P, Roshchenko O S and Afanasyev S V 2016 Technology for producing synthesis gas by steam reforming of hydrocarbons Chemical technology 6 30-2
[5] Patent RU No 2446223 2012 Heat-resistant nickel-chromium alloy with austenitic structure (Moscow: Rospatent)
[6] Patent RU No 2485200 2012 Heat-resistant nickel-chromium alloy with austenitic structure (Moscow: Rospatent)
[7] Patent RU No 2533072 2014 Heat resistant alloy (Moscow: Rospatent)
[8] Afanasyev S V, Sergeev S P, Pyrkin A V, Afanasyev A S 2016 Reaction pipes for petrochemical plants with increased service life Oil. Gas. Exposition 1(47) 56-8
[9] Afanasyev S V 2018 Industrial catalysis in gas chemistry (Samara: Publishing House of the Samara Scientific Center of the Russian Academy of Sciences) p 160