Structural heterogeneity of reaction pipes from austenitic high-temperature alloys

S VAfanasiev¹,³, O Z Ismaylov², A V Pyrkin², M V Kravtsova¹ and O P Pisklova¹

¹ Togliatti State University, Togliatti, 445020, Russia
² LLC “Reaction Pipes”, Togliatti, 445045, Russia
³ E-mail: svaf77@mail.ru

Abstract. The article deals with the formulation of austenitic heat-resistant steels and its influence on the structural heterogeneity of reaction pipes based on them for reforming furnaces manufactured by centrifugal casting. Using highly informative methods, the formation of two intermetallide phases in the austenitic matrix, performing the function of metal hardening at high temperatures, is shown. Their composition was determined, the heterogeneity of the distribution along the length of the reaction tube and, as a result, the variation of the values of mechanical parameters were shown.

Austenitic steels include high-alloyed metal composites that form a single-phase austenitic matrix (γ-Fe) with a face-centered lattice during the crystallization process and retain it when cooled down to room temperature. Such steels contain 18–25 % Cr, which provides heat and corrosion resistance, as well as 8–35 % Ni, stabilizing the austenitic structure and increasing the heat resistance, ductility, and processability of steels in a wide temperature range [1, 2]. This allows the use of these steels as corrosion-resistant, heat-resistant structural materials in the chemical, petrochemical and oil refining industries, in installations where the metal is subjected to the joint action of high stresses, temperatures and corrosive media.

Industrial steam reforming is carried out in the presence of a nickel-containing catalyst, which is filled with reactor pipes. In contact apparatuses of the specified type, the heat necessary for the chemical process to flow is transferred from the fuel combustion zone through convective and radiative transfer to the outer surfaces of the reaction pipes [3 - 5].

Technological lines have been created for their production, using the centrifugal casting method. Heat-resistant reaction pipes produced on them are designed for long-term trouble-free operation at temperatures close to 1100 °C and pressure up to 50 atm.

The aggregate plant for the production of castings, including self-propelled carts with buckets and weighing devices for metal dosing, molds, centrifugal casting machines with filling funnels and a cooling system, chutes for coating the inner surface of molds, mechanisms for lifting and tilting the molds, and an ejector [6].

It should be borne in mind that the implementation of this method of production requires higher rotational speeds of the mold, especially in the production of thick-walled castings, the non-observance of which leads to the segregation of alloy components and the occurrence of cracks in the casting. Similar defects can manifest themselves as a result of the rapid cooling of injection molds.
To improve the quality of the reaction pipes, the most suitable is the installation of centrifugal casting of heat-resistant pipes, including an induction melting furnace, a platform with a trolley and a mechanism for its movement, with a tank and a nozzle placed on it to feed the separation slurry into the mold cavity, a centrifugal casting machine and a casting extraction unit, as well as a gas burner unit, providing the necessary temperature gradient on the surface of the chill mold, controlled from a remote control unit that converts the display of pyrometric temperature sensors, which are functionally connected with it, into electrical signals that come to the control valves for the supply of air and fuel gas to the combustion zone [7].

A schematic diagram of a centrifugal casting installation designed for the use of iron-chromium-nickel austenitic alloys of a certain composition is shown in the figure 1.

Figure 1. Centrifugal casting line for heat-resistant pipes.

Its advantages include the presence of a gas burner system that creates a temperature gradient on the surface of the chill mold, whose operation is automatically controlled by a control unit functionally connected to pyrometric sensors and valves for supplying fuel gas and air to the combustion zone.

The work of the centrifugal casting line is illustrated by examples 1 and 2.

Example 1 (alloy HN35B).

In the induction furnace 1 with a capacity of 1050 kg/hour, the necessary charge components are sequentially loaded in order to obtain a heat-resistant alloy of composition, wt. %: Carbon, 0.40 - 0.45, silicon 1.10 - 1.50, manganese 1.10 - 1.40, chromium 24 - 27, nickel 33 - 35, niobium 0.6 - 1.1, vanadium 0.0005 - 0.10, titanium 0.05 - 0.15, aluminum 0.01 - 0.05, zirconium 0.01 - 0.20, cerium 0.005 - 0.10, tungsten 0.005 - 0.10, cobalt 0.01 - 0.10, iron and impurities - the rest.

The separation coating based on a water suspension TERMODUR 1409/20 is preliminarily applied to the inner surface of the chill mold, having a length of 6 m, by moving the carriage 3 with the tank 4 connected to the nozzle 5 on the platform 2. The release of anti-adhesive through the nozzle 5 is achieved by compressed air supplied to the tank. Three zones of the mold are heated to operating temperatures of 330 °C (head), 340 °C (central part) and 350 °C (tail section) by means of a gas burner unit 6 containing 120 nozzles. These temperatures are maintained by the control unit 7, which converts the readings of the pyrometers with infrared sensors 8 into electrical signals to the air and fuel gas control valves.

The casting ladle with a temperature of 600 - 700 °C is installed on the tensor and the necessary amount of an alloy with a temperature of 1640 °C is poured into it. The bucket is moved to the centrifugal casting machine 9, by means of which the rotation of the chill mold is set at a speed of 1510 turns per minute and the molten metal is poured into it in the form of a continuous jet.

The centrifugal casting machine is stopped, and the pipe casting is pulled out at block 10 and guided to the bore.

Heat-resistant pipes based on the alloy used were characterized by a tensile strength and yield strength of at least 600 and 300 MPa, respectively [8, 9].

Example 2 (alloy 25,35NB).
Conditions for obtaining heat-resistant pipes of example 1.

The iron-chromium-nickel alloy had the following composition, wt. %: carbon 0.30 - 0.40; chromium 20 - 23; nickel 30 - 33; niobium 1.0 - 1.7; cerium 0.07 - 0.11; silicon 0.45 - 0.95; manganese 0.8 - 1.45; vanadium 0.0005 - 0.15; titanium 0.0005 - 0.15; aluminum 0.0005 - 0.10; tungsten 0.05 - 0.5; iron and trace impurities - the rest [10].

The resulting alloy is characterized by the ultimate strength $\sigma_B$ at 20 °C (490 - 580) MPa and the yield point $\sigma_{02}$ (250 - 300) MPa.

As in the case of Example 1, no cracks and segregation manifestations were investigated on the castings, which were studied by acoustic and other non-destructive methods of control.

For this reason, the uptime for the operation of reaction pipes based on the above alloys for ammonia units is more than 125,000 hours and methanol units not less than 100,000 hours at temperatures of 850 and 950 °C, respectively.

The chemical composition of the steel austenitic structure is presented in table 1.

### Table 1. The chemical composition of the investigated six-meter pipes, % mass.

| Alloy pipes on the basis of | C    | Si   | Mn   | Cr   | Ni   | Nb   | Fe   |
|---------------------------|------|------|------|------|------|------|------|
| HN35B *)                  | 0.406| 1.363| 1.229| 24.00| 33.11| 0.862| rest |
| 25.35NB **)               | 0.347| 0.773| 1.136| 25.79| 34.36| 1.222| rest |

*) pipes (A); **) pipes (B).

Three coils corresponding to the cold (AH and BH), middle (AS and BS) and hot (AG and BG) sections were cut out from each pipe. The latter is located near the place of pouring metal into the chill mold.

Table 2 shows the values of yield strength, tensile strength and relative elongation of samples made from pipes corresponding to the test and test alloys tested at 20, 800 and 1000 °C.

### Table 2. The homogeneity of the reaction pipes by mechanical parameters.

| Sample     | t, °C | $\sigma_{02}$, MPa | $\sigma_B$, MPa | Relative extension, % |
|------------|-------|-------------------|----------------|----------------------|
| BH/AH      | 20    | 261/260           | 506/470        | 11.2/7.1             |
|            | 800   | 165/157           | 254/250        | 18.3/13.3            |
|            | 1000  | 102/95            | 116/106        | 34.8/23.5            |
| BC/AC      | 20    | 289/271           | 513/498        | 9.6/9.3              |
|            | 800   | 179/169           | 275/257        | 13.0/15.2            |
|            | 1000  | 104/96            | 107/107        | 31.9/30.5            |
| BG/AG      | 20    | 270/254           | 482/479        | 8.7/10.7             |
|            | 800   | 151/150           | 242/242        | 15.8/13.7            |
|            | 1000  | 91/89             | 100/100        | 25.0/30.0            |

From it follows that the value of the working parameters at the investigated temperatures pass through an extremum falling on the middle part of the pipe.

The reason for the spread of mechanical parameters is that the physico-mechanical parameters of the alloys under study depend on the content of strengthening phases - the main austenitic matrix, which includes mainly iron, chromium and nickel and two intermetallic phases enriched in chromium and niobium, respectively.

Their presence is confirmed by X-ray microanalysis. by detecting backscattered electrons.

The percentage of phases in different samples is illustrated by the data of table 3.

In the case of an intermetallic compound with a high chromium content, it is determined by the composition of the austenitic alloy and the distance from the place of pouring the metal into the chill mold.
Table 3. Distribution of hardening phases in the reaction pipes *).

| Pipe fragment | Alloy | Pipe surface | The content of the phases, % of the mass. | austenitic matrix | intermetallic phase enriched in chromium | intermetallic phase enriched with niobium |
|---------------|-------|--------------|-----------------------------------------|------------------|-----------------------------------------|-----------------------------------------|
| Hot part      | HN35B | external     | 93                                      | 5                | 2                                       |                                         |
|               |       | internal     | 91                                      | 7                | 2                                       |                                         |
|               | 25.35NB | external   | 90                                      | 8                | 2                                       |                                         |
|               |       | internal     | 92                                      | 6                | 2                                       |                                         |
| Middle part   | HN35B | external     | 94                                      | 4                | 2                                       |                                         |
|               |       | internal     | 90                                      | 9                | 1                                       |                                         |
|               | 25.35NB | external   | 94                                      | 5                | 1                                       |                                         |
|               |       | internal     | 95                                      | 4                | 1                                       |                                         |
| Cold part     | HN35B | external     | 95                                      | 4                | 1                                       |                                         |
|               |       | internal     | 95                                      | 4                | 1                                       |                                         |
|               | 25.35NB | external   | 91                                      | 8                | 1                                       |                                         |
|               |       | internal     | 96                                      | 3                | 1                                       |                                         |

*) The studies were performed on a Zeiss Sigma scanning raster electron microscope.

For the studied high-temperature alloys, the mass ratio of the austenitic matrix and the intermetallic compounds Cr_{25-60}Fe_{3-7}Ni and Nb_{30\pm4}Cr_{13\pm0.4}(FeNiTi)_{1\pm0.1} is (88 \div 94): (4 \div 10): (1 \div 3). Thus, on the basis of the conducted study, it was shown that the mechanical characteristics of static tensile tests of samples of heat-resistant reaction pipes have high values, but not identical in their length. The difference in the chemical composition of austenitic alloys causes a variation in the content of the metal matrix and the intermetallic phase enriched in chromium in them, which in turn affects the tensile strength and yield strength of the heat-resistant metal compositions.

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