Mechanical characteristics of heterogeneous structures obtained by high-temperature brazing of corrosion-resistant steels with rapidly quenched non-boron nickel-based alloys

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Abstract. Recently, the use rapidly quenched boron-containing nickel filler metals for high temperature brazing corrosion resistance steels different classes is perspective. The use of these alloys leads to the formation of a complex heterogeneous structure in the diffusion zone that contains separations of intermediate phases such as silicides and borides. This structure negatively affects the strength characteristics of the joint, especially under dynamic loads and in corrosive environment. The use of non-boron filler metals based on the Ni-Si-Be system is proposed to eliminate this structure in the brazed seam. Widely used austenitic 12Cr18Ni10Ti and ferrite-martensitic 16Cr12MoSiWNiVNb reactor steels were selected for research and brazing was carried out. The mechanical characteristics of brazed joints were determined using uniaxial tensile and impact toughness tests, and fractography was investigated by electron microscopy.

1. Introduction

Recently, the use rapidly quenched boron-containing nickel filler metals for high temperature brazing corrosion resistance steels different classes is perspective. The use of these alloys leads to the formation of a complex heterogeneous structure in the diffusion zone that contains separations of intermediate phases such as silicides and borides [1]. This structure negatively affects the strength characteristics of the joint, especially under dynamic loads and in corrosive environment. Figure 1 shows images in back-scattered electrons (BSE) of brazed joints containing heterogeneities in the diffusion zone.

The work [2] described the development of filler metal based on the Ni-Si-Be system and the method for obtaining a connection by high-temperature brazing.

Nanocrystalline filler metals based on Ni-Cr-Si-Be system were obtained by method of rapidly quenching of a melt [3]. Vacuum high-temperature brazing of austenitic (12Cr18Ni10Ti) and ferritic-martensitic (16Cr12MoSiWNiVNb) steels was carried out with these alloys. The main regularities of the structural-phase state formation of brazed joints and the features of the molten filler metal interaction with brazed materials were revealed, optimum temperature and time parameters of the brazing process were determined.
Figure 1. Brazed joints obtained with the filler metal Ni-7.5Cr-3.5Fe-4.5Si-2.6B wt. %: a) ferritic-martensitic steel 16Cr12MoSiWNiVNb (EP-823), b), c) austenitic steel 12Cr18Ni10Ti (different magnifications).

In the connection obtained with the filler metals containing beryllium, there are no heterogeneities in the diffusion zone because of its significant solubility in steel. It is necessary to compare strength properties to study the operating characteristics of brazed joint obtained with boron and developed non-boron filler metals.

2. Experiment and methods
SSHVE-1.2.5 resistance furnace with tungsten heaters, which allows heating in a vacuum of $10^{-2}$ Pa, is used for brazing samples.

The method of indentation is used to study the degree of brazed joint heterogeneity. Determination of the microhardness values by Vickers was performed on the installation HVS-1000. The measurement is carried out by pressing a diamond pyramid into the surface of the test sample under the action of a load of 50-100 g, which is applied for 10-15 seconds. Microhardness is measured directly in the seam and at a certain distance from the seam in steps of 50-100 μm. Several measurements are made for each characteristic point.

The strength properties of the samples under uniaxial tension were determined using a universal two-column QUASAR 50 testing machine, which has the maximum force of which is 50 kN. The seams obtained by three filler metals: Ni-7Cr-5Si-3Be, Ni-6Si-5Be and standard boron Ni-7.5Cr-3.5Fe-4.5Si-2.6B (table 1) are tested. They were obtained with the same parameters of cylindrical samples manufacturing in accordance with GOST 28830-90 (working part with a diameter of 6 mm) [4].

Table 1. Brazed specimens for uniaxial tension tests.

| Steel          | Filler metal       | Brazing mode |
|----------------|--------------------|--------------|
| 12Cr18Ni10Ti   | Ni-7.5Cr-3.5Fe-4.5Si-2.6B | 1150 °C 40 min |
| 12Cr18Ni10Ti   | Ni-7Cr-5Si-3Be     | 1150 °C 40 min |
| 12Cr18Ni10Ti   | Ni-6Si-5Be         | 1150 °C 40 min |
| 16Cr12MoSiWNiVNb | Ni-7.5Cr-3.5Fe-4.5Si-2.6B | 1150 °C 15 min |
| 16Cr12MoSiWNiVNb | Ni-7Cr-5Si-3Be     | 1150 °C 15 min |
| 16Cr12MoSiWNiVNb | Ni-6Si-5Be         | 1150 °C 15 min |
The chemical composition of the using steels is shown in table 2. Brazing of the samples was carried out at the temperature 1150 °C [5]. The holding time for ferritic-martensitic steel is reduced to 15 minutes, compared to austenitic steel to reduce the effect of structural-phase state changes at the brazing temperature that occurs due to the partial dissolution of Nb, V, W and Mo carbides.

The developed filler metal with 50 μm thickness and the boron filler metal with 35 μm thickness were used in one layer and placed directly in the brazing gap. Brazing was carried out in a special conductor.

| Material                  | Alloying elements, % wt |
|---------------------------|-------------------------|
|                           | C  | Cr | Si | Mn | Ni | Mo | V | Nb | W | Ti |
| 12Cr18Ni10Ti              | 0.12 | 18  | <0.8 | <2 | 10 | - | - | - | - | <1 |
| 16Cr12MoSiWNiVNb          | 0.15 | 11.2 | 1.1 | 0.7 | 0.5 | 0.6 | 0.2 | 0.3 | 0.7 |     |

The fracture zones of the tested samples were analyzed by scanning electron microscopy (SEM) after uniaxial tensile tests. The fractures are investigated in secondary electrons (SE) and back-scattered electrons (BSE) for a more detailed analysis. The profiles of the destroyed samples fractographies after test are also analyzed additionally.

Rectangular samples with dimensions of 10 × 10 × 55 mm without stress concentrators (notches) were made in accordance with the State Standard 23046-78 to determine the impact toughness of brazed joints [6]. The tests were carried out using special apparatus with pendulum. A study of the seam structure before mechanical tests using optical microscopy was conducted to control the quality of the test samples.

3. Results and discussion
The effect of the structural components microhardness on the brazed joints strength [7]. The results are shown in figure 2. The metallographic studies of the brazed joint showed the different structure of the diffusion zone after brazing with boron and beryllium filler metals. The presence of a wide diffusion zone (about 100 μm) with a structure different from steel and seam structure is characteristic for brazed compounds 16Cr12MoSiWNiVNb steel obtained with the Ni-7.5Cr-3.5Fe-4.5Si-2.6B. This zone is formed due to the active diffusion of boron, which leads to recrystallization in steel. The microhardness in this zone is 400±20 HV, which is on 200 HV more than in the joint (figure 2a). The diffusion zone with a size of 100-120 μm is also characteristic for 12Cr18Ni10Ti steel, brazed boron filler metal. However, recrystallization does not occur (figure 2c). Boron forms intermediate phases with chromium along the grain boundaries [8]. Microhardness in this zone falls from 220±10 HV, characteristic of the seam, to 160±10 HV. The difference in the values of microhardness in these regions will lead to the appearance of microstrains.

An eutectic structure is formed in some places in the center of the seam in the case of using the Ni-7Cr-5Si-3Be filler metal. However, its microhardness is close to the microhardness of the nickel matrix in the seam for ferritic-martensitic steel (figure 2b). The microhardness values for austenitic steel from 240±10 HV in the seam fall to 160±10 HV in the diffusion zone and steel (figure 2d).

The structural difference for these two filler metals, as will be seen below, will lead to different results of tests on strength and impact toughness.
Figure 2. Brazed joint steel 16Cr12MoSiWVNiNb, obtained with filler metal: a) Ni-7Cr-3.5Fe-4.5Si-2.6B; b) Ni-7Cr-5Si-3Be; and steel 12Cr18Ni10Ti: c) Ni-7Cr-3.5Fe-4.5Si-2.6B; d) Ni-7Cr-5Si-3Be.

Figure 3 shows the results of the tests. As a result, recrystallization (in the case of the use of boron filler metal) leads to decrease of the mechanical properties. Therefore, the brazed joint 16Cr12MoSiWVNiNb/Ni-7Cr-3.5Fe-4.5Si-2.6B showed low values of the tensile strength (figure 3a).

The destruction occurred over the steel during the tests of 12Cr18Ni10Ti samples brazed with filler metal Ni-6Si-5Be. Therefore, the joint withstands comparable loads with the base material. The joint obtained with the filler metal Ni-7Cr-5Si-3Be showed the best strength properties. It was also taken into account that steel after processing by the brazing mode changes its properties. It is strengthened and has microhardness higher than in the initial state. This is due to changes in the structural-phase state at the brazing temperature.

The study of the brazed joint fractography showed the following: in the case of boron-containing filler metal, the destruction occurs mainly along the boundary of the seam-base material interface with elements of destruction along the seam body. This indicates its low cohesive strength (figure 4a). Destruction over the body of the seam is predominantly brittle with numerous secondary cracks [9]. In the case of a beryllium-containing filler metal, the destruction of the joint occurs along the seam, which indicates a significantly higher cohesive strength of the seam-base material interface (figure 4b). The nature of the fracture is mainly viscous.

The viscous type of fracture of the sample brazed with beryllium-containing filler metal indicates a high plastic deformation and a significantly higher energy of fracture of this sample as compared to the sample, brazed with boron-containing filler metal and brittle destroyed. The results of fractographic studies are confirmed by the results of the sections investigations (figure 5).
Figure 3. The results of tests on a) uniaxial tensile; b) impact toughness for steel 12Cr18Ni10Ti.

Figure 4. Fractography (SE) of destroyed joint steel 16Cr12MoSiWNiVNb, obtained with the filler metal: a) Ni-7Cr-3.5Fe-4.5Si-2.6B; b) Ni-6Si-5Be.

Figure 5. Microstructures of destroyed joint steel 16Cr12MoSiWNiVNb, obtained with the filler metal: a) Ni-7Cr-3.5Fe-4.5Si-2.6B; b) Ni-6Si-5Be.

It can be seen from the figure that the grain is growing strongly due to recrystallization during brazing with boron filler metal. Moreover, intermediate phases (Cr,Fe)\textsubscript{3}B are formed along the boundaries, which weaken these boundaries, therefore, destruction occurs subsequently on them. Diffusion of beryllium, unlike boron, does not lead to recrystallization in steel. It, significantly dissolving, is found both along the boundaries and in the body of grain.

Unlike the results of uniaxial tensile tests, the results on the impact toughness obtained for joint of 12Cr18Ni10Ti steel brazed with Ni-7Cr-5Si-3Be filler metal are higher than for Ni-6Si-5Be and Ni-
7Cr-3.5Fe-4.5Si-2.6B. The worst results were shown by the filler metal Ni-6Si-5Be because of the large content of beryllium, which reduces the ductility of the joint (figure 3b).

It can be concluded that the optimal composition for the developed alloy is Ni-7Cr-5Si-3Be, which demonstrates high values of strength and plasticity.

4. Conclusions

High-temperature brazing of austenitic (12Cr18Ni10Ti) and ferritic-martensitic (16Cr12MoSiWNiVNb) steels with classical boron filler metal Ni-7Cr-3.5Fe-4.5Si-2.6B and developed filler metal based on the system Ni-(Cr)-Si-Be was conducted. Joints were tested for uniaxial tensile strength and impact toughness. Analyzing the obtained data, it can be concluded that the developed filler metal based on the Ni-(Cr)-Si-Be system demonstrate high strength characteristics of brazed joints. The most promising was the composition Ni-7Cr-5Si-3Be. The characteristics obtained for it: tensile strength for 12Cr18Ni10Ti 530±30 MPa, for 16Cr12MoSiWNiVNb 710±30 MPa; impact toughness for 12Cr18Ni10Ti 110±10 J/cm². The problem of the negative influence of the heterogeneous structure in the near-seam zone (the "boride grid") is solved by replacing the boron with beryllium in the composition of the filler metal. However, a large content of beryllium in the alloy (as in the case of Ni-6Si-5Be) is also undesirable, since the plasticity of the joint decreases. The microhardness of the compound was investigated to determine the influence of the structural components of the joint on the strength properties. The possibility of using the developed filler metal Ni-7Cr-5Si-3Be for connecting energy-stressed elements from steels of various classes is shown.

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