The use of platinum metals to increase the corrosion and strength characteristics of industrial titanium casting

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Abstract. The materials used for technological equipment manufacture should have high mechanical strength, chemical and thermal resistance. Technical titanium is widely used for these purposes. The article studies the effect of small palladium additives on titanium chemical and mechanical properties. It was revealed that the introduction of 0.23% palladium during titanium smelting has little effect on the mechanical properties of doped titanium, but it increases its resistance to sulfuric and hydrochloric acids.

1. Introduction

The materials used for technological equipment manufacture should have high mechanical strength, chemical and thermal resistance. Alloy steel or industrial titanium are used for these purposes.

Titanium and its alloys are characterized by high mechanical properties, good resistance to corrosion, and resistance to corrosion cracking. In an oxidizing atmosphere in the presence of oxidizing ions (Cu$^{2+}$, Fe$^{3+}$, Pt$^{4+}$), its deep passivation takes place: titanium is covered with an oxide film (10-20 μm), which protects it from further corrosion. These properties allow the use of titanium and its alloys in oxidizing conditions at temperatures above 470-520°K [1-2].

In the solid state and at moderately high temperatures (up to about 100° C), due to the presence of a strong oxide film, titanium has high corrosion resistance in most aggressive environments: it is stable in nitric acid of any concentration (except for red fuming, which causes corrosion cracking) and in weak sulfuric acid solutions (up to 5% by weight). High corrosion resistance of titanium in sea water and atmosphere, as well as in wet chlorine and some aqueous solutions of acids and salts is of particular importance for its industrial use [3-6].

At the same time, titanium is extensively destroyed, for example, in 10% HCl and 15% H$_2$SO$_4$, especially at a temperature of 100 ° C. Hydrochloric, hydrofluoric, concentrated sulfuric, as well as hot organic acids: oxalic, formic and trichloroacetic react with titanium. Titanium is less resistant in anoxic acids and alkaline media [7].

The corrosion resistance of titanium can be increased by many times by alloying with small palladium additives (up to 0.30%), expanding the possibility of its use as a corrosion-resistant material [8]. The main raw material sources of platinum metals are sulfide ores and placers, as well as chromites and industrial waste [9-13].

By casting qualities, such as the ability to fill the mold, the tendency to form hot cracks, the nature of crystallization, technically pure titanium is a completely satisfactory material and is close in this respect to ordinary carbon steel. Titanium boils well. Titanium-based alloys have good casting
properties. The small value of the temperature range of crystallization provides them with good fluidity and a sufficiently high density of castings. Titanium alloys have a slight tendency to form hot cracks and small linear shrinkage (2-3%) [14].

The disadvantages of titanium cast alloys are: the tendency of molten titanium to rapidly absorb gases contained in the atmosphere, which reduces the ductility of the metal; high activity when interacting with all known molding and refractory materials at temperatures of 1000° C and above. Therefore, titanium cannot be melted in open furnaces and in crucibles made from conventional refractory materials. This explains the difficulty of obtaining castings from titanium [14].

Due to the high chemical activity of titanium, alloys are melted and cast in a vacuum or in a protective atmosphere, and casting molds are made of chemically resistant materials that interact minimally with molten metal - graphite, corundum, magnesite, zirconium dioxide. Foundry technology includes a method for melting and casting metal, manufacturing consumable electrodes, molds, methods for monitoring castings, identifying defects and correcting them [15].

2. Methods of research
When performing this work, a vacuum skull-mounted electric arc furnace with a graphite melting crucible with a capacity of 150 kg of liquid metal was used for melting and casting metal. In a graphite water-cooled crucible, a skull was preliminarily induced, which protects the liquid metal during melting from contact with graphite and prevents its contamination with carbon. Consumable electrodes were made by electric arc melting in a copper water-cooled mould pressed from titanium sponge TG-102 according to GOST 17746 briquettes with a diameter of 160 mm. During pressing, powdered palladium was introduced into briquettes, placed in aluminium foil sachets. Briquettes were melted in a mould with an arc current of 8000-10000 A and voltage of 28-30 V. Two ingots with a diameter of 284 mm with a total weight of 373 kg were made.

The chemical composition of the metal ingots (consumable electrodes) are given in table 1.

| Metal ingot number | C, %   | Fe, % | Si, % | Pd, % | N₂, % | O₂, % | H₂, % |
|-------------------|--------|-------|-------|-------|-------|-------|-------|
| 1                 | <0.1   | <0.2  | <0.15 | 0.23  | <0.03 | 0.08  | 0.005 |
| 2                 | <0.1   | <0.21 | <0.15 | 0.23  | <0.03 | 0.09  | 0.007 |

The body of the direct-flow housing DU40 was taken as an experimental casting selected for the manufacture of titanium-palladium alloy. The length of the housing is 200 mm, there are two flanges with a diameter of 150 mm in the housing, the preferred wall thickness of the housing is 5.5 mm. The selected casting allows making a preliminary assessment of the alloy ability to fill casting molds and its resistance to cracking during cramped metal shrinkage.

The mould for casting was made of magnesium oxide with liquid glass as a binder. The primary hardening of the mould was achieved by blowing it with carbon dioxide, the final hardening of the mold and the complete removal of moisture occurred when it was calcined in an electric resistance furnace at a temperature of 950-10000 °C.

The consumable electrode was melted at a rarefaction of 5-10 Pa, arc current of 9000-10000 A, voltage of 27-29 V. Stabilization of the electric arc and mixing of liquid metal in order to evenly distribute palladium was carried out using centrifugal forces, which provides an increased density of castings.

The surface quality of the castings after bead-blasting was satisfactory, there was no stick observed. Foundry metal shrinkage, measured on the flanges, amounted to 1.2-1.4%, cramped shrinkage on the body, measured near the flange was about 0.5%.

In addition to reinforcement bodies, ingots with a diameter of 100 mm and a height of 300-400 mm were made. The metal ingots together with the metal poured onto the bodies of the slats were used in
the manufacture of samples to determine the mechanical properties, study the corrosion resistance, weldability and other properties of the titanium-palladium alloy.

The effect of palladium on the corrosion resistance of titanium was determined in comparison with the corrosion resistance of unalloyed metal. The studies were carried out on samples with an area of about 12 cm$^2$, weighing 5.0-5.6 kg. The number of samples for each test was 3-6 pieces. The mass of samples was determined before and after the test. The corrosion rate was determined by the weight loss during the test.

Solutions of hydrochloric and sulfuric acids of various concentrations and temperatures were chosen as aggressive media for assessing the effect of palladium. These acids are widely used in various industries and in the performance of scientific research. The concentration of hydrochloric acid was 1, 10 and 25%, sulfuric acid - 3 and 10%, the duration of the test was 20 and 300 hours.

3. Results and their discussion

Table 2 presents the test results of undoped titanium.

| Material | Medium    | Temperature, °C | Duration, hours | Corrosion rate, y/m$^2$ year |
|----------|-----------|-----------------|-----------------|------------------------------|
| titanium | 25% HCl   | 100             | 20              | 75                           |
|          | 25% HCl   | 50              | 20              | 6.7                          |
|          | 25% HCl   | 20-25           | 67              | 0.86                         |
|          | 10% HCl   | 100             | 48              | 14.3                         |
|          | 10% HCl   | 20-25           | 300             | 0.001                        |
|          | 1% HCl    | 100             | 300             | 0.016                        |
|          | 1% HCl    | 50              | 300             | 0.0023                       |
|          | 10% H$_2$SO$_4$ | 20-25      | 300             | 0.001                        |
|          | 3% H$_2$SO$_4$ | Boiling         | 20              | 6.36                         |

The test results of titanium alloyed with 0.23% palladium under the same conditions as unalloyed metal are shown in table 3, figures 1 and 2.

| Material | Medium    | Temperature, °C | Duration, hours | Corrosion rate, y/m$^2$ year |
|----------|-----------|-----------------|-----------------|------------------------------|
| titanium + 0.23% palladium | 25% HCl   | 100             | 20              | 11.14                        |
|          | 25% HCl   | 50              | 20              | 2.5                          |
|          | 25% HCl   | 20-25           | 67              | 0.0028                       |
|          | 10% HCl   | 100             | 48              | 2.75                         |
|          | 10% HCl   | 20-25           | 300             | 0.001                        |
|          | 1% HCl    | 100             | 300             | 0.0035                       |
|          | 1% HCl    | 50              | 300             | 0.0023                       |
|          | 10% H$_2$SO$_4$ | 20-25      | 300             | 0.0015                       |
|          | 3% H$_2$SO$_4$ | Boiling         | 300             | 0.053                        |
Thus, alloying titanium with 0.23% palladium reduces the corrosion rate in hydrochloric acid of various concentrations from 2.3 to 30 times; a sharp decrease in the corrosion rate in boiling 3% sulfuric acid should be noted.

In the manufacture of complex thin-walled castings per 1 ton, about 3 tons of metal are consumed, of the remaining 2 tons of return, about 1.5 tons are suitable for reuse. These wastes in an amount of up to 20-25% by weight of the heat can be used in the manufacture of castings, providing about 0.05% of palladium in them. In the framework of this study, a batch of castings with a content of 0.05% palladium was made, the metal of the castings was investigated in the same environments as above. In some environments, there was no positive effect of such small amounts of palladium, but in some environments the corrosion rate decreased markedly (table 4, figure 2).

**Table 4. Test results for titanium alloyed with 0.05% palladium in acid solutions.**

| Material           | Medium     | Temperature, °C | Duration, hours | Corrosion rate, y/m²·year |
|--------------------|------------|-----------------|-----------------|---------------------------|
| titanium + 0.05% Pd| 25% HCl    | 100             | 20              | 41.50                     |
| titanium + 0.05% Pd| 25% HCl    | 20-25           | 300             | 0.0026                    |
|                    | 10% HCl    | 100             | 20              | 9.02                      |
|                    | 3% H₂SO₄   | 100             | 20              | 0.90                      |

The data in table 4 allow us to recommend the use of our own waste containing palladium in the production of castings for industrial equipment. Depending on the characteristics of the environment in which the equipment operates, it is recommended that the effect of small amounts of palladium on the corrosion resistance of castings be investigated.

Equipment made using castings from titanium alloys, including alloys containing palladium, is operated, as a rule, under conditions of high mechanical loads. To assess the reliability of the equipment, the mechanical properties of the cast titanium-palladium alloy are investigated. Samples for determining the strength of the metal, its ductility and toughness were cut from specially made templates and trial bars, cast in conjunction with valve bodies D40.

The results of studies of the mechanical properties of the cast titanium-palladium alloy are presented in table 5.

The strength and plastic characteristics of undoped titanium and palladium-doped titanium are close. The high values of ductility and toughness of the metal are particularly noteworthy.
Table 5. The results of studies of the titanium-palladium alloy mechanical properties.

| Material                  | Tensile strength, MPa | Yield strength, MPa | Relative extension, % | Relative narrowing, % | Impact strength, kJ/m² |
|---------------------------|-----------------------|---------------------|-----------------------|-----------------------|------------------------|
| titanium + 0.23% palladium | 404                   | 311                 | 37.9                  | 65.1                  | 1881                   |
|                           | 376                   | 300                 | 15                    | 39.1                  | 1980                   |
|                           | 400                   | 309                 | 35.3                  | 67.8                  | 1911                   |

4. Conclusion
Additives of platinum group metals increase the corrosion resistance of titanium and expand the possibilities of its use as a corrosion-resistant material. Alloying titanium with 0.23% palladium reduces the corrosion rate in hydrochloric acid of various concentrations up to 30 times.

Equipment made using castings from titanium alloys, including alloys containing palladium, can be operated under high mechanical loads. One of the promising areas is the manufacture of high-speed wheels from them, which are used in turbo-expander units used on gas pipelines to drain and cool gas.

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