Comparison of the corrosion behavior of the TiNi alloy in the coarse-grained and ultrafine-grained state

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Abstract. This article studies the corrosion behavior of the TiNi alloy in the coarse-grained and ultrafine-grained states. The study of the influence of the initial microstructure on the corrosion behavior of the TiNi alloy was carried out by the gravimetric method in the NaCl and H2SO4 solution for a month. Studies was shown that as a result of the action of a corrosive medium from a sample in a coarse-grained state, it undergoes greater destruction, pitting corrosion was observed, at the same time, in an ultrafine-grained sample only traces of corrosion products are observed on the surface of the samples. Investigations with an inverted light microscope in a dark field made it possible to observe corrosion products and determine their volume fraction. Evaluation of the corrosion rate showed that in the coarse-grained state it is 126 times higher than the corrosion rate in the ultrafine-grained state. Analysis of X-ray phase analysis showed that in the coarse-grained state after corrosion tests, a significant proportion of the TiNiH1.4 phase is observed, while in the ultrafine-grained state all phases correspond only to the TiNi phases. The TiNi alloy contains an Ti2Ni phase enriched Ti both in the coarse-grained state and in the ultrafine-grained state. Moreover, in a coarse-grained state, its share is 2 times higher.

1. Introduction
The TiNi alloys belong to the class of functional materials with shape memory effects (SME), caused by thermoelastic martensitic transformations «B2-B19'» occurring in the temperature range close to room temperature [1-5]. Shape memory alloys have the unique ability to recover significant inelastic deformation. Corrosion resistance is largely determined by the degree of defectiveness of the material. Therefore, it is important to know the features of corrosion behavior that affect the operation of the material. The use of titanium nickelide-based alloys in medicine and technology has stimulated extensive studies of the electrochemical behavior and corrosion resistance of these materials in various corrosive environments.

In works [6-18], the corrosion and electrochemical properties of titanium-nickel alloys are considered. For example, in [9], the results of the corrosion-electrochemical behavior of TiNi alloys in acidic solutions (1 N HCl, 1 N H2SO4) are presented. With the aim of the possible use of titanium-nickel alloys as catalysts that reduce the overvoltage of hydrogen evolution at the titanium cathode, the results of the electrochemical and corrosion behavior of titanium-nickel alloys are presented in [19]. In [20-21], the corrosion-electrochemical behavior of titanium-nickel alloys in various acidic chloride solu-
tions at elevated temperatures was studied, bearing in mind their possible recommendation for use in seawater desalination units. In [22], the corrosion properties of TiNi in a coarse-grained state were described and it was shown that this alloy, in environments similar to human environment, is well passivated. It was also found that a passive oxide layer is formed on the alloy in the presence of a biological medium, on which coatings of calcium phosphate and TiO$_2$ are formed in the future. In this regard, it is interesting to study the corrosion properties of the alloy in various structural states, due to the unique physical and mechanical properties of the material in the coarse-grained and ultrafine-grained states.

2. Materials and methods
The stoichiometric Ti$_{49.0}$Ni$_{51.0}$ alloy was chosen as the research material. This alloy has a bcc lattice, ordered by the B2 type and a Ti$_2$Ni$_3$ phase enriched with nickel. The studies were carried out in two states: coarse-grained (CG), obtained by quenching in water, and ultrafine-grained (UFG), formed by the ECAP method at a temperature of 450 °C $n = 6$.

The study of corrosion behaviour was carried out by the gravimetric method, the samples were kept in an aqueous solution of NaCl and H$_2$SO$_4$ for a month. The main structural parameters were determined using scanning electron microscopy (SEM). For the qualitative and quantitative analysis of the macrostructure of the TiNi alloy, an OLYMPUS GX51 metallographic microscope with software and an AXIO OBSERVER Z1M inverted microscope in the dark field mode were used. The surface study was carried out using scanning probe microscope NT-MDT Integra Prima at the Joint Research Center, 'Nanotech', Ufa State Aviation Technical University. The phase composition was studied using a Rigaku Ultima IV X-ray diffractometer.

In this work, the assessment of the corrosion rate in various structural states was carried out according to the formula:

$$V = \frac{m_0 - m}{S \cdot t},$$

where $m_0$ - sample mass before corrosion tests, $m$ - sample mass after corrosion tests, $S$ - sample area, $t$ - corrosion test time.

3. Results and discussions
The Figure 1 shows the structure of TiNi alloy samples after contact with a corrosive medium - a solution of NaCl and H$_2$SO$_4$ obtained with an optical microscope. A significant degree of corrosion of the samples in the coarse-grained state is observed (Figure 1, a).

![Figure 1. Photographs of the surface of Ti$_{49.0}$Ni$_{51.0}$ alloy samples after corrosion tests: (a) coarse-grained state (b) ultrafine-grained state.](image-url)
The survey of samples on an inverted microscope (Figure 2) made it possible to determine the nature of corrosion damage more clearly. In the case of the coarse-grained state, deep pits are observed, occupying more than 50% of the sample surface, while in the ultrafine-grained state, corrosion products are observed evenly distributed over the surface without damaging the sample.

![Figure 2](image1.png)

**Figure 2.** The structure of samples of the Ti$_{49.0}$Ni$_{51.0}$ alloy on an inverted microscope: (a) coarse-grained state (b) ultrafine-grained state; dark field.

Studies using scanning electron microscopy also made it possible to estimate the average size and depth of pitting corrosion pits in a coarse-grained state (Figure 3, a). The average size of the pits is about 400 µm, the depth is 500 µm on average. In the ultrafine-grained state, it is possible to estimate the average size and volume fraction of corrosion products on the sample surface ($d = 5\pm 2$ µm, $V = 60\pm 5\%$) (Figure 3, b).

![Figure 3](image2.png)

**Figure 3.** Surface structure of Ti$_{49.0}$Ni$_{51.0}$ alloy samples in coarse-grained (a) and ultrafine-grained (b) states after corrosion tests on the scanning electron microscopy.

Table 1 shows the results of evaluating the corrosion rate of alloy specimens in the coarse-grained and ultrafine-grained states, carried out according to eq. 1. According to the calculations, the corrosion rate of specimens in the coarse-grained state is more than 120 times higher than the corrosion rate of specimens in the ultrafine-grained state in NaCl + H$_2$SO$_4$ solution.
Table 1. Corrosion rate data for TiNi alloy in various structural states.

| State | Corrosion rate, g/m²·h |
|-------|------------------------|
| CG    | 3.006                  |
| UFG   | 0.023                  |

X-ray phase analysis made it possible to determine the presence of a high-volume fraction (more than 50%) of hydride of TiNi in the coarse-grained state after corrosion tests, while in the ultrafine-grained state only the TiNi phase. Figure 4 shows the data of X-ray phase analysis of samples after corrosion tests. The TiNi alloy contains an Ti₂Ni phase enriched Ti both in the coarse-grained state and in the ultrafine-grained state. Moreover, in a coarse-grained state, its share is 2 times higher (Table 2).

Figure 4. X-ray diffraction patterns of Ti_{49.0}Ni_{51.0} alloy samples after corrosion.

In the coarse-grained and ultrafine-grained state, the TiNi alloy was an austenitic and an insignificant proportion of the martensitic state (in the case of CG, of UFG), as well as the Ti₂Ni phase before corrosion tests. After corrosion tests in a coarse-grained state 3 phases are observed: austenitic, martensitic and R phase. In the ultrafine-grained state 3 phases are also observed, all of them correspond to the TiNi matrix, the volume fraction of the austenite phase increased, with a slight decrease in martensitic B19' phase, and the formation of R – martensite (Table 2). The formation of the hydride TiNi - TiNiH₁₋₄ is probably associated with a large fraction of the Ti₂Ni phase in the initial coarse-grained state, which is most inclined towards the formation of hydrides of TiNi. At that time, the lower content of this phase in the ultrafine-grained state promotes the formation of R - martensite and corrosion products on the base Ti.
Table 2. X-ray phase analysis data of the Ti<sub>49.0</sub>Ni<sub>51.0</sub> alloy before and after corrosion tests.

| State             | Phases                  | Volume fraction, % | Space group            |
|-------------------|-------------------------|--------------------|------------------------|
| CG before corrosion tests | TiNi B2 austenite 80.8 | Pm-3m, BCC        |
|                   | TiNi B19’ martensite 10.03 | P2/1/m, monoclinic |
|                   | Ti<sub>2</sub>Ni 9.15   | Fd-3m, FCC         |
| CG after corrosion tests | TiNi B2 austenite 43.45 | Pm-3m, BCC        |
|                   | TiNi B19’ martensite 1.74 | P2/1/m, monoclinic |
|                   | TiNiH<sub>1.4</sub> 54.80 | I<sub>4</sub>/mmm, tetragonal |
| UFG before corrosion tests | TiNi B2 austenite 89.16 | Pm-3m, BCC        |
|                   | TiNi B19’ martensite 4.85 | P2/1/m, monoclinic |
|                   | Ti<sub>2</sub>Ni 5.95   | Fd-3m, FCC         |
| UFG after corrosion tests | TiNi B2 austenite 93.35 | Pm-3m, BCC        |
|                   | TiNi B19’ martensite 1.19 | P2/1/m, monoclinic |
|                   | TiNi R martensite 5.45  | P-3, trigonal      |

Studies on a scanning atomic force microscope have shown that in the case of a coarse-grained state, the parameters of roughness and changes in height are significantly higher than in the case of an ultrafine-grained state. The results of examining samples after corrosion tests are presented in Figures 5-6. The height difference in the case of the coarse-grained state is from 0.1 to 9.4, while in the ultrafine-grained state from 2.0 to 5.0, which also confirms the deeper corrosion of the samples in the CG state. In addition, if in the coarse-grained state, a uniform distribution of heights over the surface is observed, while in the ultrafine-grained state, only single peaks are observed, probably corresponding to corrosion products on the surface of the samples.
Figure 5. Results of Ti$_{49.0}$Ni$_{51.0}$ alloy of scanning force microscopy in a coarse-grained state.

Figure 6. Results of Ti$_{49.0}$Ni$_{51.0}$ alloy of scanning force microscopy in ultrafine-grained state

4. Summary
Studies have shown that in the coarse-grained state, corrosion dissolution occurs much more intensively than in the ultrafine-grained state. According to the results obtained, the corrosion rate in the coarse-grained state is more than 120 times higher than the corrosion rate of the samples in the ultrafine-grained state. Analysis of X-ray phase analysis showed that in the coarse-grained state after corrosion tests, a significant proportion of the TiNiH$_{1.4}$ phase is observed, while in the ultrafine-grained state all phases correspond only to the TiNi phases. The traces of pitting corrosion are clearly visible on the surface of the sample, while in the ultrafine-grained state, only minor traces of corrosion products are observed.

5. References
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