CORROSION PROPERTIES OF COMMERCIALLY PURE TITANIUM DEPENDING ON THE MICROSTRUCTURE AND SURFACE TREATMENT METHOD

КОРРОЗИОННЫЕ СВОЙСТВА ТЕХНИЧЕСКИ ЧИСТОГО ТИТАНА В ЗАВИСИМОСТИ ОТ МИКРОСТРУКТУРЫ И ВИДА ОБРАБОТКИ ПОВЕРХНОСТИ

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Abstract. *This paper presents the results of preliminary corrosion tests of samples from commercially pure titanium Grade 4 with a coarse-grained (annealed) and ultrafine-grained structure after severe plastic deformation, as well as of samples processed by microarc oxidation and with an ion-plasma coating. The effect of microstructure on the corrosion of the material under study is shown. A comparative evaluation of the corrosion rate is performed.*

KEY WORDS: *CORROSION; COMMERCIALLY PURE TITANIUM; COARSE-GRAINED AND ULTRAFINE-GRAINED STRUCTURE; SEVERE PLASTIC DEFORMATION; MICROARC OXIDATION; ION-PLASMA COATING.*

1. Introduction

Owing to a great interest in the production of high-strength implants for medical applications from commercially pure (CP) titanium, one turns, more and more often, to the technologies based on severe plastic deformation. These technologies enable producing a high-strength state due to the the formation of an ultrafine-grained (UFG) structure that contributes to a significant enhancement of mechanical and functional properties [1, 2].

Promising is the use of high-strength long-length materials with a UFG structure [3], in particular, from CP Ti [4] which can be used for the production of medical implants that are, in particular, in frictional contact in saline medium.

Relatively recently, studies focused on a comparative evaluation of the corrosion resistance of materials with a coarse-grained and UFG structure were initiated [5]. For instance, it was demostrated in [6] that in the investigated materials (low- and medium-carbon steels), having a UFG structure after severe plastic deformation (SPD) processing by equal-channel angular pressing (ECAP), an increase in corrosion resistance is observed. It may be assumed that a similar effect should be expected for CP Ti as well.

There are known works on the fabrication of semi-products from CP Ti for medical applications, having a UFG structure, processed by SPD [7-9] followed by deposition of coatings from titanium nitride [7, 8] and diamond-like carbon with zirconium [9].

At the current stage of research, an express evaluation has been performed, of the corrosion properties of CP Ti, depending on the structural state and the presence of a coating on the surface of the investigated material in the coarse-grained (CG) and UFG states.

2. Material and Research Procedure

As the material for the study, CP Ti Grade 4 was used, with a CG structure in the annealed condition, and with a UFG structure in the SPD-processed condition. Fig. 1 shows the principle of the SPD technique employed to process the material.

The SPD processing of the material was conducted at a temperature of 400^{o}C in 6 processing cycles, with rotation of the billet by 90^{o} around its axis after each cycle. Fig. 2 shows the produced long-length samples from CP Ti Grade 4.

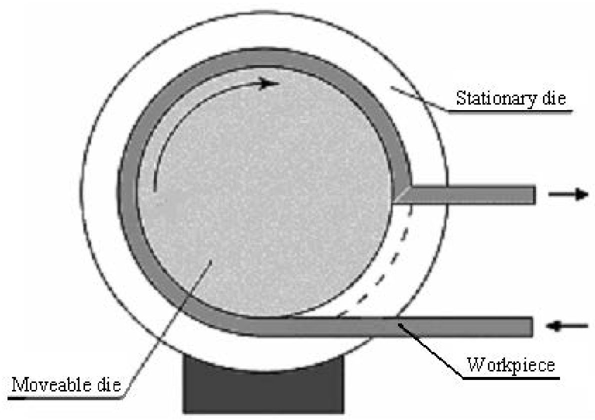

Fig. 1 *Principle of the ECAP-Conform technique for the fabrication of long-length semi-products*

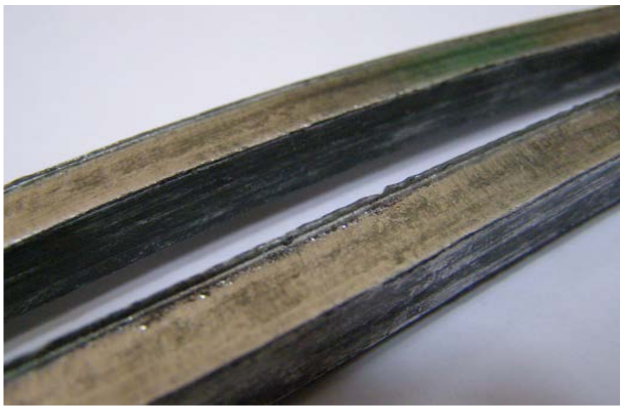

Fig. 2. *CP Ti samples after SPD processing*

After SPD processing, specimens with a length of 25 mm were cut out from the produced rods, for the deposition of ion-plasma coating and surface treatment by microarc oxidation. One specimen was left uncoated. In a similar manner, specimens were prepared from the annealed samples having a CG structure.

Corrosion tests were performed by immersion in 3.5% sodium chloride aqueous saline solution. Fig. 3 shows the diagram of the unit used to perform the corrosion tests.

The immersion tests were carried out in a waterproof thermostat during 28 hours at a temperature of 40±0.2^{o}C.

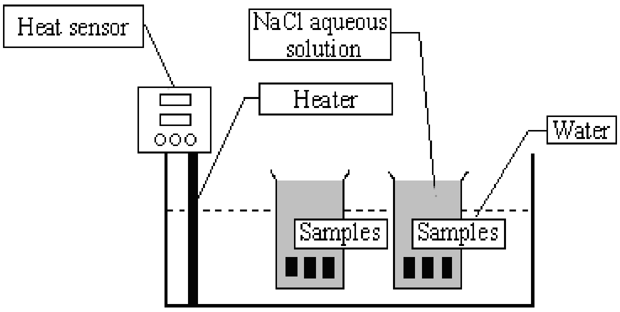

Fig.3. *Principle of the immersion tests*

Metallographic studies were performed, using optical and transmission microscopes.

3. Research Results

Given below are the results of the metallographic studies. Fig. 4 shows an example of microstructure transformation as a result of SPD processing.

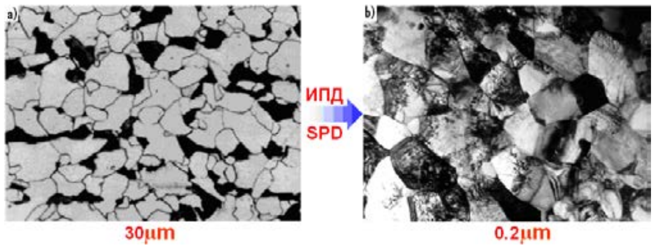

Fig. 4. *Transformation of the material's microstructure as a result of SPD processing: a) coarse-grained structure of the material in the inital state; b) ultrafine-grained structure of the material after SPD processing*

As a result of metallographic studies, it has been established that in the initial state the microstructure of CP Ti represents an equiaxed structure with a mean grain size of 30 µm. The deformation processing by ECAP leads to an efficient grain structure refinement, with the mean grain size equal to 0.2 µm.

As was already noted above, before conducting the corrosion tests, an ion-plasma coating of TiC composition was deposited on the surface of some specimens, and some specimens were processed by microarc oxidation. As a result of the processing by microarc oxidation of specimens with different microstructures, an oxide film of TiO composition was formed on the surface of CP Ti. When studying the film formed through the use of either technology, it was established that its thickness was 3±0.3 µm.

The results of the corrosion tests are given in table 1.

Table 1

Results of corrosion tests

Specimens / Mass, g	Coarse-grained structure (CG)			Ultrafine-grained structure (UFG)		
	Uncoated	Ion-plasma coating	Microarc oxidation	Uncoated	Ion-plasma coating	Microarc oxidation
Initial mass	9.003	8.960	8.436	9.185	9.133	8.787
28 hours	8.993	8.958	8.435	9.182	9.132	8.786
Mass loss, %	0.11104%	0.02232%	0.01185%	0.03266%	0.01095%	0.01138%

For the sake of visualization, the results of the corrosion tests are presented in the form of a bar chart in fig. 5.

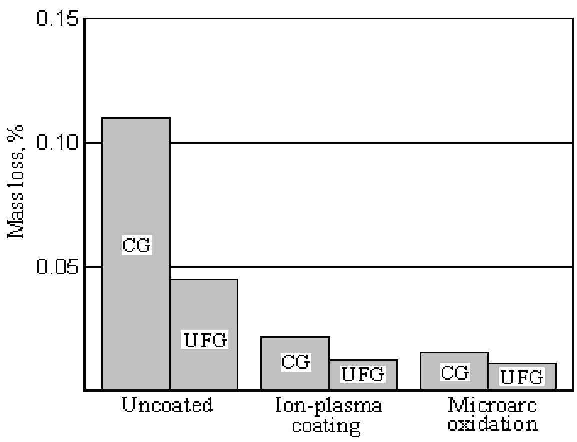

Fig.5. *The results of comparative corrosion tests: CG denotes the coarse-grained material after annealing; UFG denotes the ultrafine-grained material after SPD processing*

As can be seen from the preliminary results of the corrosion tests (fig. 5), the type of the applied coating (ion-plasma deposition and microarc oxidation) has practically no effect on the extent of corrosion damage. The differences between them fall within the statistical error. This may indicate a rather high protective capability of both coating types. At the same time, it is noted that the uncoated material after SPD processing in the UFG state has a considerably lesser degree of corrosion damage, as compared with the initial (annealed) state with a coarse-grained structure. The corrosion rate of the uncoated specimens from CP Ti Grade 4 in two structural states was evaluated. Fig. 6 shows the variation of mass loss depending on the time that the specimens were held in the 3.5% NaCl saline solution.

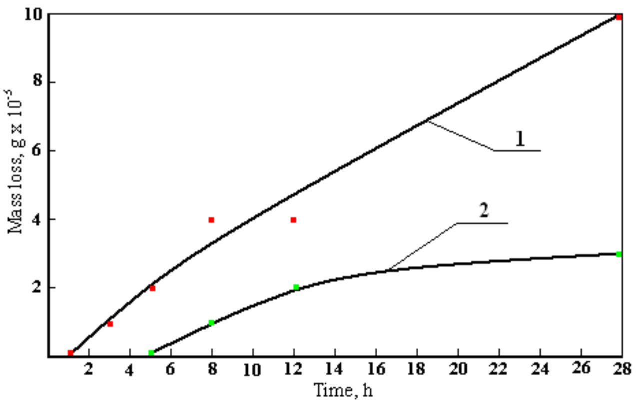

***Fig. 6** Corrosion rate of CP Ti Grade 4: 1 denotes the CG structure after annealing; 2 denotes the UFG structure after SPD processing*

As can be seen from this graph the specimens with a CG structure (curve 1) exhibit a much higher corrosion rate, as compared to the specimens with a UFG structure (curve 2) in the accepted time interval. The variation of mass loss for the CG material in the selected time range has a practically linear character. In contrast, for the specimens with a UFG structure there is observed an area with a small slope of the curve, which indicates a decrease in the corrosion rate. In addition, it is noted that for the specimens with a CG structure, the start of the corrosion process is recorded after the first hour of testing, whereas for the specimens with a UFG structure, the first signs of the starting mass loss are observed only after five hours of testing.

Presumably on the material with UFG structure in connection with more advanced and extended total grain boundary these layers form a dense, almost impermeable barrier, due to which corrosion is strongly inhibited or completely stopped. Passivation is carried out chemically or electrochemically. In the latter case, conditions are created when metal ions under the influence of current pass into a solution containing ions, the ability to form very slightly soluble compounds. This assumption requires further study of the corrosion behavior of commercially pure titanium with different microstructure in an aqueous solution of sodium chloride using electrochemical methods with the formation of anodic and cathodic curves.

These observations require more detailed investigations to study the mechanism of corrosion damage of CP Ti with different microstructures.

4. Conclusions

1. The type of the applied coating (ion-plasma deposition and microarc oxidation) has practically no effect on the extent of corrosion damage of the CP Ti specimens.
2. It has been established that the UFG structure of CP Ti produced as a result of SPD processing contributes to a decrease in the corrosion rate and an enhancement in the corrosion resistance.
3. The material under study (CP Ti) without any coating after SPD processing in the ultrafine-grained state has a considerably lesser degree of corrosion damage (approximately three-fold) as compared to the initial (annealed) state with a coarse-grained structure.

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