Physics of the Solid State, 2022, Vol. 64, No. 13

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Influence of the structural state and oxide coating on the mechanical stability of VT1-0 titanium under its cyclic loading

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Received May 12, 2021
Revised May 12, 2021
Accepted May 13, 2021

It was found that the fatigue properties of submicrocrystalline titanium are significantly higher than those for its coarse-grained state. The application of the oxide coating leads to a slight increase in these properties for titanium with a submicrocrystalline and coarse-grained structure. Some features of fatigue fracture of submicrocrystalline and coarse-grained titanium are analyzed.

Keywords: submicrocrystalline and coarse-grained titanium, VT1-0, fatigue, microarc oxidation.

DOI: 10.21883/PSS.2022.13.52319.109

1. Introduction

Titanium, due to its specific properties (low density, corrosion resistance, good biocompatibility), is the main structural material in the medical field [1,2]. Considering this the manufacturing of high-strength titanium, and studying the effect on the evolution and stability of its strength characteristics under conditions of long-term cyclic loading is very important. Equally important is the assessment of the oxide coating effect on the titanium strength, which improves the biocompatibility of titanium implants with the human body [1]. Currently, for manufacturing the high-strength titanium with submicrocrystalline (SMC) structure, the methods of severe plastic deformation (SPD) are usually used [3–5]. However, the structure formed during SPD is unstable [5,6], and its evolution during long-term loading can lead to the strength properties decreasing [7,8]. It is also important to evaluate the surface coating contribution to these properties.

Considering all of the above, the main goal of this paper was to study the effect of complex cyclic loading by the magnitude and mechanical stability of the strength properties of titanium with SMC and coarse-grained (CG) structure, and to assess the contribution of the oxide coating to the evolution of these properties. When analyzing the features of fatigue failure, the previously obtained results were considered [9–13].

2. Materials and methods

The object of studies in this paper is technical purity titanium (VT1-0 alloy) in the SMC and CG states. The SMC state was obtained according to the mode of mechanical-heat treatment developed by the authors [2] with use of longitudinal and helical rolling, which makes it possible to obtain SMC titanium rods with a diameter of 4−10 mm. In this paper we used titanium rods of VT1-0 alloy with diameter of 8 mm, which were subjected to final annealing at a temperature of 623 K for 3 hours to relieve internal stresses of the first kind. After said treatment the alloy is characterized by a homogeneous grain-subgrain structure with an average size of structural elements of the order of 190 nm. The homogeneous recrystallized structure VT1-0 (CG state) was obtained from the SMC structure by holding at $T = 823$ K for one h. The average grain size for the CG state is $2.35\,\mu$m.

To study the fatigue properties the samples were made from rods with working area thickness of 1 mm and a width of 3 mm. A coating with a thickness of $8-10\,\mu$m was applied to the surface of the samples both in the SMC, and in the CG state by the method of microarc oxidation (MAO). The coating composition includes silicon oxides (min. 30 mol.%), calcium oxides (min. 2.5 mol.%), phosphorus oxides (max. 6 mol.%), sodium oxides (from 0.5 to 3.0 mol.%), as well as titanium oxides (min. 20 mol.%).

Such coatings having high macroporosity and good wear resistance, are successfully used in these days in prosthetic care and dentistry [1]. Titanium dentures with biocompatible coating can stay in the human body for many years. Throughout this period, they experience cyclic loads. Therefore, the fatigue life study of titanium, including with applied coating, is one of the urgent tasks in biomedicine.

To study the fatigue characteristics under a tensile load for samples of titanium alloy VT1-0, Instron Electropulse

E3000 testing machine equipped with an electromagnetic drive was used in a loading mode with a frequency of 50 Hz at room temperature. The tests were carried out according to the tensile loading scheme in a symmetric sawtooth cycle in the loading region $0.9\sigma_{\max}-0.2\sigma_{\max}$. The limiting number of cycles for the samples studied was $2 \cdot 10^6$, and the load value, at which no failure occurred at this number of cycles, was used as a characteristic of the conditional endurance limit.

One of the reasons of SMC titanium instability, which contributes to a its strength properties decreasing under prolonged loading, can be associated with the nanoporosity formation during SPD. Indeed, it is shown in [9–16] that, under different SPD methods pores with sizes $\sim 10-100$ nm are formed in metals and alloys. The presence of such nanopores practically does not affect the strength characteristics under „short-term" loading (ultimate strength, yield strength, microhardness), but under conditions of long-term loading in the creep and fatigue mode these nanopores can be „centers" of the microfracture development reducing high mechanical properties and mechanical stability of titanium [7].

Considering this circumstance, the parameters of nanopores were determined, and their amount was estimated by the method of small-angle X-ray scattering modernized by the authors [9,10,17]. Besides, the titanium density before and after SPD was measured using the method of precision triple hydrostatic weighing (the error did not exceed 10^{-4}). Density and its change (density defect) made it possible to estimate the total amount of damage introduced by SPD. Comparison of the density defect and the amount of nanopores revealed by the method of small-angle X-ray scattering allows the contribution calculation of the latter to the total damage due to SPD.

Using the method of scanning electron microscopy, we obtained and analyzed data on the fracture surface of SMC and CG titanium samples after fatigue testing at $2 \cdot 10^6$ cycles and break.

3. Results and discussion

First of all, let us consider and analyze the results of cyclic tests for samples of SMC and CG titanium. Fig. 1 shows for these samples the applied loads value (in the region $0.9\sigma_{max}-0.2\sigma_{\max}$) vs. the number of cycles (Weller curves). The conventional endurance limit (CEL) was determined by the curve, the equation of which was selected according to the experimental points by the least squares method. As a result, it was found that the value of the conventional endurance limit for titanium with SMC-structure is 611 ± 8 MPa, and for titanium with CG-structure — 450 ± 8 MPa. Thus, for $2 \cdot 10^6$ loading cycles, the CEL of titanium with SMC structure by ~ 1.4 times exceeds the same for the CG analog. It is revealing that the fatigue curves for SMC titanium are much higher than for the CG state in the entire range of the studied loads.

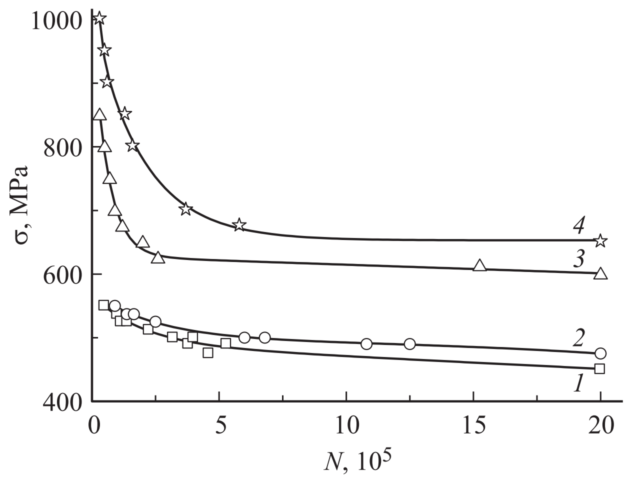

Figure 1. Weller curves of VT1-0 titanium in various states: *1* — CG state, *2* — CG state + MAO-coating, *3* — SMC state, *4* — SMC state + MAO coating.

However, as can be seen from Fig. 1, for SMC titanium the fatigue curve decreases more sharply with increased number of cycles than for CG titanium. This leads to the fact that in the process of cyclic loading „the efficiency" of SMC state decreases: at $2 \cdot 10^5$ cycles, the CEL of SMC titanium was by 1.6 times higher than for CG titanium, and at $2 \cdot 10^6$ cycles, this ratio decreased to 1.4.

The drop of „efficiency" of SMC structure can be associated with the development of damage (mainly nanoporosity) in SMC titanium after SPD.

Indeed, the results of the investigated MRD of the samples of SMC and CG titanium subjected to small-angle X-ray scattering before their fatigue tests showed that nanopores ~ 20 nm in size are formed in SMC titanium after SPD.

Fig. 2 shows the second invariant of X-ray scattering before and after sample exposure to hydrostatic pressure 1 GPa. As shown in [9,10,17], this pressure tends to heal the discontinuities.

This makes it possible to reveal the fraction of small-angle scattering caused by the presence of discontinuities. Assuming a spherical shape of the nanopores according to [17,18] their average sizes and concentrations, as well as the volume fraction were estimated. It was found that for SMC titanium the volume fraction is $\sim 4 \cdot 10^{-4}$.

Similar studies carried out for titanium in the CG state practically did not reveal the nanoporosity presence. Obviously, high-temperature annealing, which was used to obtain CG titanium, led to significant healing of nanopores.

We also measured the density of CG- and SMC-titanium before testing them under cyclic loading. It was identified that the density of CG titanium is 4.4983, and that of SMC titanium — is 4.4963 g/cm^3, i.e. much less. The density defect when comparing SMC titanium containing nanopores and nonporous CG titanium was $4.4 \cdot 10^{-4}$. This value is in good agreement with the number of nanopores

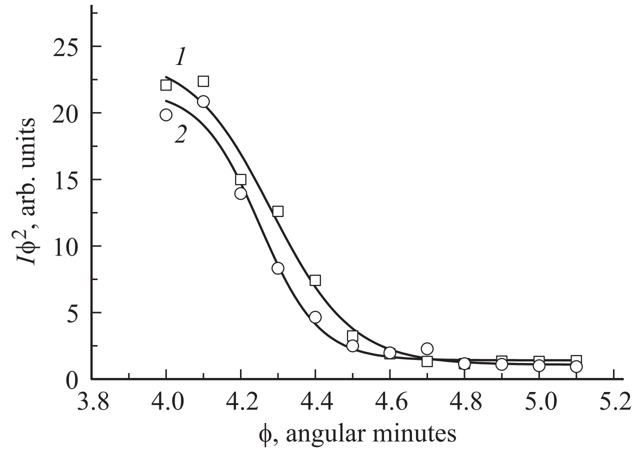

Figure 2. Curves of second invariants of X-ray scattering for VT1-0: *1* — SMC state, *2* — SMC state after application of hydrostatic pressure 1 GPa.

revealed in SMC titanium by the method of small-angle X-ray scattering. The latter indicates that the softening formed in SMC titanium during its production by the SPD method is mainly due to the formation of nanoporosity.

Thus, a slight decreasing of the conventional endurance limit during fatigue loading is obviously due to the evolution of the nanoporosity, which was formed during the preparation of high-strength SMC structure. Nevertheless, the mechanical stability of SMC titanium remains rather high, and its conventional endurance limit after $2 \cdot 10^6$ cycles, as it was already noted, is much higher than for the CG state.

The effect of the nanoporosity formed in SMC titanium during SPD on the conventional endurance limit is also confirmed by the data obtained by the authors earlier [12]. In the range of 10^4-10^7 cycles Weller curves were obtained for two batches („A" and „B") of SMC titanium manufactured in the same mode as in the present paper. Structural studies shown that the grain size (~ 190 nm) and their misorientation in batches „A" and „B" are the same. However, the conventional endurance limit of the samples in the batch „A" turned out to be 252, and in the batch „B" — 212 MPa. In this case, the level of nanoporosity formed after SPD in the batch „B" turned out to be higher than in the batch „A".

Note that the higher nanoporosity of SMC titanium of the batch „B" is obviously due to the higher (than in the batch „A") content of non-metallic inclusions such as carbides. In the process of high SPD these inclusions contribute to the formation of increased concentration of vacancies, the coagulation of which leads to the formation [10] and decreasing of CEL and durability under cyclic loading.

In this regard, it is important to note that under long-term loading and under conditions of high-temperature creep of a number of SMC metals and alloys prepared by different SPD methods, it is the evolution „of the initial" nanopores that leads to their decreased durability (mechanical stability). Thermobaric healing of nanopores formed during SPD process makes it possible to increase the durability (service life) of high-strength SMC-metals and alloys [7,8].

The totality of the data obtained and considered above assumes that the mechanical stability of implants made of SMC titanium can also be increased due to the development of optimal modes of healing the discharge-type damage formed in them during SPD.

Let us now consider and analyze the data obtained in this paper on the fatigue characteristics of SMC and CG titanium with oxide coatings applied on their surface (Fig. 1). These coatings have a branched porous surface (Fig. 3), which, as noted earlier, enhances the biocompatibility of implants with the human body. Besides, as it follows from the data obtained (Fig. 1), the oxide coatings also lead to a slight increasing of fatigue properties (Weller curves) within the entire studied range of cyclic loads. This hardening effect of coatings occurs for both SMC and CG titanium. However, the fatigue curve decreasing with increased number of cycles for SMC samples with coatings occurs more sharply than for CG samples with coatings. A similar effect is observed for SMC and CG titanium without coatings, but in the case of coatings it is even stronger. For example, for coated SMC titanium at $2 \cdot 10^5$ cycles, the CEL is by 1.8 times higher than for CG titanium. For $2 \cdot 10^6$ cycles this ratio is 1.4. In other words, in cyclic tests of SMC titanium with coatings the tendency for the conventional endurance limit decreasing with number of loading cycles increasing is even slightly higher than for SMC titanium without coatings.

It seems that the main reason for the „efficiency" decreasing of SMC titanium with and without coatings is the evolution under cyclic loading „of the initial" nanoporosity. In the case of coated SMC titanium there is obviously one more factor effecting the Weller curve change. This factor can be the surface morphology of SMC and CG titanium, on which the oxide coating is applied. It is known that under

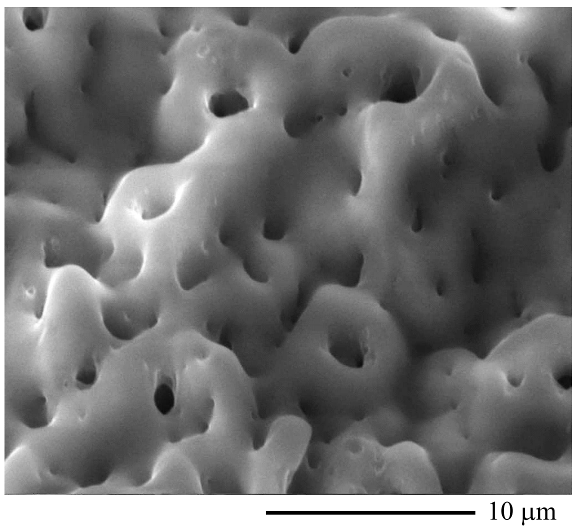

Figure 3. Image of the surface morphology of MAO coatings on VT1-0 alloy. Scanning electron microscopy at a magnification of 100 000 at an angle of 45°.

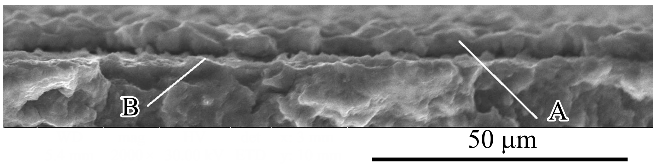

Figure 4. Image of fracture surface of the VT1-0 sample with MAO coating in the fatigue fracture area; A — MAO-coating, B — metal–coating interface.

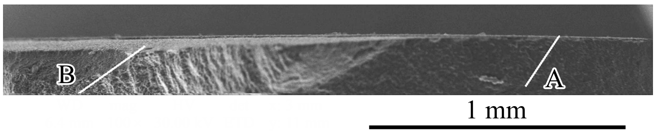

Figure 5. Image of fracture surface of VT1-0 sample with MAO coating in the fatigue fracture area after break; A — peeled MAO-coating, B — area of MAO coating peeling.

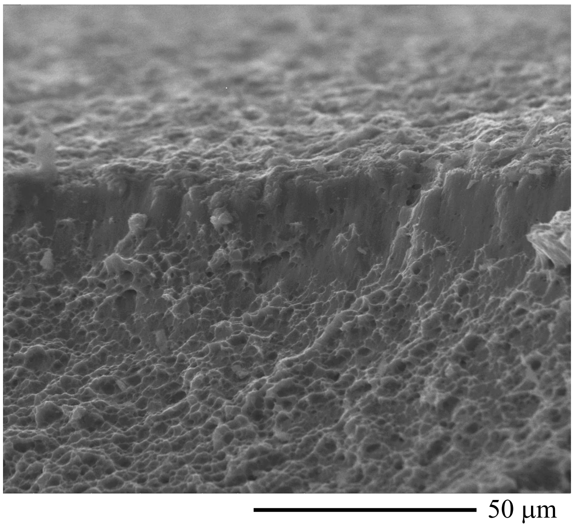

Figure 6. Image of fracture surface in the near-surface region of the coated VT1-0 sample after fatigue tests in the break region.

cyclic loading the role increases of surface defects [19–21] and features of the dislocation-disclination structure of thin ($\sim 10-30\,\mu$m) near-surface layers [22–24]. It is possible that annealing at a rather high temperature, which was carried out to transfer the SMC structure to the CG state, led to a less defective surface structure of CG titanium as compared to the SMC analog. This circumstance increases the ratio of the conventional endurance limit at 10^5 loading cycles of SMC and CG titanium with coatings as compared with these samples without coatings.

Let us now consider some of the results of electron microscopic studies, which were carried out when studying the rupture surface of samples after cyclic loading and bringing them to rupture under active loading.

The main focus of these studies was on the effect of coatings and their relationship to fatigue failure. First of all, note that the data obtained on the fracture surface indicate the absence of coating peeling during the samples destruction (Fig. 4). Peeling is observed only in the area of destruction due to large local deformation of the samples during their breakage (Fig. 5). This indicates a good adhesion of the coatings to the surface of the titanium samples. In surface titanium samples coatings have a hardening effect and resist to plastic deformation. This is confirmed by the change in the direction of the pits shape during fatigue failure in the near-surface layers: the pits are not elongated along the direction of the load, but are perpendicular to the surface of the coating (Fig. 6). (As you know, the pits stretch along the maximum load).

It is likely that the higher value of fatigue strength for specimens with coatings is associated with their effect on the healing of surface and near-surface defects, which are „centers“ for the fracture development under cyclic loading. It also cannot be excluded that oxide coatings can have higher mechanical characteristics than SMC and CG titanium, and their application contributes to increased fatigue characteristics.

4. Conclusion

It was established that the conventional endurance limit (CEL) at $2 \cdot 10^6$ loading cycles for SMC titanium with and without coatings is by 1.4 times higher than that of similar CG titanium. Oxide coatings lead to a small ($\sim 8\%$) increasing of the fatigue characteristics of SMC and CG titanium over the entire range of study of cyclic loading.

A tendency of CEL decreasing in SMC titanium with increased number of loading cycles is found. For example, for SMC titanium without coatings CEL at $\sim 2 \cdot 10^5$ cycles was by 1.6 times higher than for CG titanium. Structural studies shown that the observed effect (CEL ratio decreased from 1.6 to 1.4) may be due to the evolution of damages (especially nanoporosity) formed during SPD upon the formation of the SMC state.

For coated SMC titanium this effect at $2 \cdot 10^5$ loading cycles turns out to be 1.8, i.e. much more. The nature of the hardening effect of oxide coatings on durability and CEL under cyclic loading of SMC and CG titanium is analyzed.

Acknowledgements

Acknowledge to Cand. in Physics and Mathematics I.V. Nelasov (Belgorod State National Research University, Russia) for his valuable contribution to microscopic studies.

Work funding

The study was carried out with the financial support of the Russian Foundation for Basic Research (the project No. 19-58-26005) and the Czech Science Foundation (the project No. 20.14450 J).

Conflict of interest

The authors declare that they have no conflict of interest.

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