Original article

Institution of MECHANICAL ENGINEERS

Journal of PROCESS MECHANICAL ENGINEERING

Corrosion-fatigue resistance of ultrafine grain commercially pure titanium in simulated body fluid

Proc IMechE Part E:
J Process Mechanical Engineering
1–11

DOI: 10.1177/09544089221140682
journals.sagepub.com/home/pie
SAGE

Reza Naseri[1], Hamed Hiradfar[2], Mahmoud Shariati[2] and Mehran Kadkhodayan[2]

Abstract

Commercially pure titanium (CP-Ti) due to excellent biocompatibility and high specific strength is known as a metallic biomaterial and is widely utilized in medical applications as implant material. Because of low strength of CP-Ti as compared to other bio-metals, it has been proved in literatures that applying equal channel angular pressing (ECAP) process can be useful to enhancement of mechanical and metallurgical properties of CP-Ti by improvement of initial microstructure to ultrafine grained (UFG). Implant in human body is attacked from cyclic fatigue loads and corrosion, simultaneous. Hence, aim of this study is examination of corrosion-fatigue resistance of CP-Ti before and after introducing ECAP in simulated body fluid (SBF) as a saline solution close to blood plasma. In this study, multi-pass ECAP is conducted on CP-Ti at room temperature and then the axial fatigue test is performed in SBF environment with temperature 37 °C. The comparison of stress-cycle curves demonstrated that corrosion-fatigue resistance of ECAPed CP-Ti is extremely higher than initial annealed one. Moreover, it was observed that by increasing the pass number of ECAP, corrosion-fatigue resistance improves significantly. Furthermore, these results are compared to fatigue behavior of CP-Ti in air environment. The results show that corrosion-fatigue resistance of unECAPed and ECAPed CP-Ti in SBF is slightly lower than fatigue ones in air. According to the results of this experimental research, it is concluded that UFG CP-Ti has an awesome corrosion-fatigue resistance in human body and it is very suitable for utilizing as material of implants.

Keywords

Commercially pure titanium, equal channel angular pressing, ultrafine grains, corrosion-fatigue resistance, simulated body fluid

Date received: 26 November 2021; accepted: 26 September 2022

Introduction

Metallic biomaterials as one of the most usable materials for medical or implant application must satisfy conditions such as long-term biocompatibility, specific mechanical properties and corrosion resistance.[1–3] Stainless steels, Ti-alloys and Co–Cr alloys are known as three major categories of orthopedic implants.[4,5] Generally, in these alloys since toxic ions release due to corrosion and wear debris, disease and tissue damage occur. Therefore, there is a tendency to use pure metals with biocompatibility properties.[3,4] Among the metallic biomaterials, commercially pure titanium (CP-Ti) can be an appropriate alternative instead of other biomaterials. The reasons of this choice are high specific strength, biocompatibility and elastic modulus close to modulus of bone hard tissue. However, critical weakness of CP-Ti is its low strength.[6–8] There are general parameters such as mechanical-metallurgical properties, biological compatibility, erosion/corrosion behavior, wear, osseo-integration, biological responses of hierarchical and the other important parameters for selection a material in medical applications and implants.[5,9,10] Literature review shows that most of these parameters have been investigated and reported on CP-Ti.

Since static and dynamic strengths of CP-Ti are lower than other medical alloys, introducing processes without any changes in chemical composition such as severe plastic deformation (SPD) techniques[11] such as equal channel angular pressing (ECAP),[12] can be an effective method for improvement of its mechanical properties. ECAP process is known as one of the most effective and

[1]Department of Mechanical Engineering, Technical and Vocational University (TVU), Tehran, Iran
[2]Department of Mechanical Engineering, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

Corresponding author:
Reza Naseri, Department of Mechanical Engineering, Technical and Vocational University (TVU), Tehran, Iran.
Email: rnaseri@tvu.ac.ir

useable SPD procedures to produce the ultrafine grained (UFG) or nanocrystalline (NC) bulk metals with improving microstructural evolution and mechanical properties.[5,8,13] Average grain size in UFG metals is between 100 nm and 1 μm and in NC metals it is less than 100 nm.[14] Formerly, it was demonstrated that a decrease in size of grains leads to the enhancement of strength of metals.[12] Previous studies have been shown that strength of this pure material can be promoted close to the common medical Ti alloy (Ti–6Al–4V) by imposing ECAP.[8,13,15]

Human body fluid can attack and damage to implant material due to its salt and protein content.[3] Actually, saline environment of human body is a corrosive environment for implants materials.[16] Combination of alternating loading and corrosion can be more effective in destruction of material rather than influence of each of these. Therefore, corrosion, fatigue and fatigue-corrosion resistances are three main properties that must be evaluated before utilizing a material in medical implant applications. The previous researches shown that combination of SCC (stress corrosion cracking) and CF (corrosion fatigue) can be one of the most effective agents of implant destruction in human body.[3] Moreover, it has been proved that pitting corrosion is known as an active mechanism in fatigue crack growth.[16] Surface finishing and grain size in microstructural aspect and thermo-mechanical properties like hardness have a significant effect on fatigue strength, corrosion and combination of these.[16–18] One of the most popular methods for improving dynamic strength like fatigue in biomaterials is imposing residual compressive stress and hard coating. Recently, converting the coarse grained (CG) to UFG or even nanocrystalline (NC) microstructures by SPD processes has been create a reliable evolution in improving static–dynamic mechanical properties[11,16] and even in erosion/corrosion properties of metals.[19–21] Observations indicate that it is possible to apply SPD process on CG CP-Ti to enhance its mechanical properties.[7,8,13]

Fatigue behavior analysis as one of the most important criteria for utilizing materials in structural applications has been significantly accomplished on UFG/NC metals such as copper, Al and Ti.[22–26] Research results on fatigue behavior of CG/UFG/NC metals have been shown that generally with increasing static strength and flowing stress due to reduction of grain size, fatigue strength and fatigue endurance limit are increased remarkably.[23,24,27,28] Too limited investigations have been conducted on fatigue behavior of UFG/NC CP-Ti produced by cold/warm/hot ECAP and most studies have been focused on CP-Ti imposed by warm/hot ECAP.[13,27,29–33] The research's results have demonstrated however pressing at high temperatures is easier, but optimum UFG microstructures it will be obtained when cold-working was performed at lowest possible temperature (like room temperature, RT) from this aspect that there are not any appreciable cracks on work-piece. By keeping pressing temperature low, it will be assured that all effective factors for improving properties of metals like "minimum of average grain size", "increasing density of dislocations" and "the highest percentage of high angle grain boundaries (HAGBs)" are obtained.[12]

By focusing on fatigue performance of CP-Ti produced by ECAP at RT, two studies, by Figueiredo et al.[15] and Naseri et al.[13] can be found. In first study, the fatigue test was carried out according to ISO 14801 standard to evaluate fatigue behavior of dental implant.[15] In second research, cold ECAP at RT were introduced to bi-material work-piece (including the CP-Ti as a core and Al-7075 as a casing) and then axial fatigue strength of UFG CP-Ti in air environment was evaluated.[13] Similar results of these studies were that by decreasing grain size of metals, fatigue properties can be improved in addition to static strength.[13,15]

The literature's review indicated that few studies have been performed on investigation of corrosion-fatigue behavior of UFG metals especially on SBF environment. Abdulstaar et al. in 2014, by imposing rotary-swaging process on aluminum alloy AA5083 and then evaluation of corrosion-fatigue properties of this material in air and NaCl, found that the performance of this UFG metal was remarkably improved in both environments.[34] In a similar research, corrosion-fatigue performance of steel AISI 316L in two conditions as-received and worked by rotary-swaging was compared to that in the Ringer's solution. Results of Ahmed et al. in 2014, proved that fatigue life of this metal increased in air and solution after applying the SPD process.[35]

Due to saline environment of human body, simulated body fluid (SBF) or Hank's solution can be an appropriate laboratory solution for variety of corrosion and biocompatibility tests.[36] Only case that has been investigated the corrosion and corrosion-fatigue behavior of UFG metals at SBF is related to the UFG niobium–zirconium alloy[3] and also its strength properties such as tensile strength and low cycle fatigue (LCF) have also been reported.[37] In this research, the NbZr alloy processed using ECAP at RT and so grain refinement from CG to UFG structure was carried out. Then, achieved UFG NbZr was imposed under corrosion, high cycle corrosion-fatigue and fatigue crack growth tests at SBF. Electrochemical evaluations demonstrated that this material has passive and stable behavior at SBF. By analyzing the HCF (high cycle fatigue) test in SBF observed that there was no any alteration in crack initiation behavior due to presence of corrosive environment. In addition, no corrosion products in solution and the pitting on material have not been observed. Investigating on crack initiation behavior also showed that crack growth rate increases slightly in saline SBF. Finally, it is concluded according to corrosion and corrosion-fatigue performance of UFG NbZr, this material is awesome for using an medical implant material.[3]

As it is clear, a few studies have been conducted on corrosion-fatigue behavior of UFG CP-Ti in a corrosive solution especially in SBF. Hence, evaluating of UFG CP-Ti corrosion-fatigue properties satisfy this research from the point of view of innovation. In addition, investigation of corrosion-fatigue behavior of UFG CP-Ti in

SBF solution guaranties the safety utilizing of this material as medical implants.

In this study, bimetal work-piece (CP-Ti as a core and Al-7075 as a casing) was pressed up to three passes in cold ECAP process and grain size of CP-Ti was improved from coarse to ultrafine. Then, the axial fatigue test was performed on CG/UFG CP-Ti in SBF environment. The aim of this research was the comparison of the corrosion-fatigue behavior of CG and UFG CP-Ti in a solution like a human body and based on this results possibility of using UFG CP-Ti in medical applications like implants was evaluated. Finally, observations of this study were compared to the results of the previous research[13] on the fatigue behavior of UFG Ti at air environment that had been accomplished before by authors of this article.

Material and experimental procedures

Materials

In this study, a bimetallic rod (core: CP-Ti-grade 2 and casing: 7075 aluminum alloy) was used as work-piece. The chemical compositions (wt.%) of the CP-Ti and Al-7075 obtained by the emission spectrometry method were base Ti–0.02 Fe–0.02 C–0.03 N–0.001 H–0.06 O and base Al–5.78 Zn–2.73 Mg–1.47 Cu–0.36 Fe–0.34 Si–0.21 C–0.05 Mn, respectively. The aims of using of bimetallic billet are reducing the forming load, improvement of mechanical properties and uniformity in the strain distribution and consequently deformation in the core material (CP-Ti) and finally obtaining the homogenous structures.[38–41] According to the geometry of used ECAP die, the work-piece length, core diameter and the outer diameter of the casing were considered 100 mm, 10 mm and 15 mm, respectively. In addition, it should be noted that the core material (billet) was inserted into the casing with an interference fit. As it is clear, the target material is CP-Ti in core (was named as billet) and the casing is sacrificed material. The CP-Ti was annealed at 800 °C for 1 hour and air-cooled inside the shut-off furnace.[30] Furthermore, the annealing of Al-7075 was carried out at 415 °C for an hour and cooled outside the furnace.[40] Hence, in target material (Grade 2 CP-Ti), a homogenous, equiaxed, stable and coarse grain microstructures were achieved without any residual stresses. The results of optical observations have shown that the average grain size of this microstructure was about 55 μm.[13]

ECAP process

The mentioned bimetallic billet was ECAPed up to three passes in route Bc with 135° channel angle and 20° corner angle at environment temperature. According to the geometry of ECAP die, it can be proved that a strain equal to 0.46 was applied on work-piece per each pass.[12,42] For pressing, a hydraulic press with nominal capacity of 60 tons and ram speed of 9 mm/s was used. In addition, to reduce the undesirable effect of friction between the work-piece and the inner side of the die, MOLYKOTE 1000 PASTE lubricant was utilized. It should be noticed that after forth pass and based on macroscopic observations, the cracks were seen on the upper surface of the core material (CP-Ti); so the forth pass was not considered as a successful pass, and all studies were conducted on passes 1 to 3. Real illustrations of ECAP die and appearance of work-pieces before and after introducing ECAP are shown in Figure 1.

Experimental tests

Tensile test, hardness test and microstructural evaluations. The tensile and Vickers hardness tests were performed on unECAPed and 3 passes ECAPed samples according to ASTM E 8M-00 and ASTM E 92 standards, respectively. In addition, to prove the microstructural changes of material from primary coarse grains to ultrafine grains after introducing the third pass, the microstructural evaluation was carried out on the cross-section of CP-Ti work-piece. The samples were etched via immersing in a solution containing 2 mL HF, 5 mL H_2O_2 (35%) and 100 mL water up to 70 seconds to reveal the grain boundaries and then the microstructural observations were performed by OM (optical microscope) and SEM (scanning electron microscope). The conditions and details of conducting these experimental tests have been explained comprehensively in part 1 of this research that presented previously. Therefore in the "Results and discussion" section, the results of these tests are presented.[8,13] The purpose of this subsection is to provide the methodology of axial fatigue test is SBF environment, which will be discussed in the next subsections.

Preparation of simulated body fluid. The SBF or Hank's solution is commonly used to evaluate of the properties

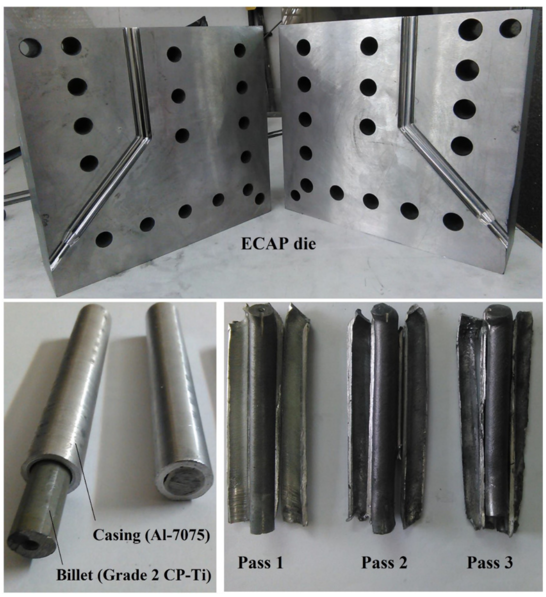

Figure 1. Real views of ECAP die and bimetallic work-pieces before and after 1 to 3 passes in route Bc.

of a biomaterial in environment similar to the human body. This fluid is prepared using KOKUBO method in laboratory with an ionic concentration close to and similar to the human blood plasma. In this study, the reagents presented by Chavan et al.[36] were dissolved in the double distilled water and the SBF solution with pH 7.4 was achieved. Then, this liquid was used to investigate the corrosion-fatigue behavior of CG/UFG CP-Ti under periodic loading at 37 °C similar to the normal temperature of human body. Therefore, the specimens were placed in a chamber containing SBF and at the same time, the axial fatigue test was introduced to them while the temperature was constant at 37 °C.

Axial fatigue test in SBF environment. In this study, all fatigue tests were performed on CP-Ti Grade 2 samples before and after imposing 1 to 3 passes of ECAP at 1 to 3 passes. In order to compare the dynamic mechanical properties of this material before and after applying ECAP, the axial fatigue test was carried out according to the ASTM E 466-96 standard in air (at ambient temperature) and in SBF environment (at 37 °C, similar to human body temperature). Literatures review has demonstrated that some organs such as hip,[5] tibia[43] and dental[44,45] are subjected to compression and tension axial loads. Therefore, the axial fatigue test was chosen to evaluate the effect of the periodic axial loading on the corrosion-fatigue life of CG/UFG CP-Ti material for utilizing as implant material.

For axial fatigue test in the air environment as described in the first part of this research,[13] the dog-bone shaped specimens were machined from annealed un-ECAPed and ECAPed samples and their surfaces were polished to prevent from surface effects in results of fatigue tests. The axial fatigue specimen has the effective diameter of 5 mm, effective length of 15 mm, fillet radius of 10 mm and dumbbell diameter of 8 mm.

The periodic axial loading in the form of sine-wave and with stress/load control were applied on the specimens by using Zwick/Roell-Amsler HB100 servo-hydraulic fatigue machine. The specimens were subjected to fatigue test in the tension-tension condition with the frequency of 10 Hz ($f = 10$ Hz) and cycle asymmetry factor of 0.05 ($R = 0.05$). In other words, in each cycle, the minimum stress level is equal to 5% of the maximum stress. The specimens were loaded up to approximately 10^6 cycle under fatigue loading. The LEO 1450VP SEM with the voltage of 20 kV was utilized for observing the fracture surface of specimen after performing the fatigue test. It should be noted that, in this study, the stress–number of cycle diagram (S–N) behavior of unECAPed and 3 passes ECAPed samples were compared in HCF test. In addition to evaluate the effect of each pass on the fatigue life value for each four samples, the initial annealed and 1 to 3 passes ECAPed samples were subjected to axial fatigue test at a constant stress for obtaining the fatigue life value of each samples.

For performing the corrosion-fatigue (CF) test in SBF corrosive environment, all conditions of the fatigue test in air[13] that were described in the previous section, were also considered in this test except that all samples were placed in the chamber containing the SBF with temperature 37 ± 1 °C and then were subjected under the axial fatigue loading until failure. Since some standards for fatigue strength calculations and for detail category determination prescribe at least three tests at each particular level, in this research four or five tests have been conducted at each stress level.[46]

A liquid chamber with special clamp (including the fixed and movable jaws) was utilized instead of lower clamp of the fatigue machine for placing the specimens inside the SBF and loading the axial stress. This designed clamp with V shape groove was machined using the cold worked SPK 2080 steel and then hardened up to 60 RC. For placing the chamber with the designed clamp on the lower clamp of fatigue device, fixed jaw of the clamp was pasted on the chamber made of steel plate and sealed with aquarium glue. In addition, a sealed tubular heater element and a temperature controller were used to adjust the SBF temperature and stabilize it at approximate temperature of 37 °C during the fatigue test. Real view of the chamber, designed clamp, embedded tubular heater element and general setup of corrosion-fatigue test that was used in this study were illustrated in Figure 2. In addition, a zoom-in view of the chamber with clamp embedded in the lower and upper clamps of fatigue device was displayed. It should be noticed that the axis of the fatigue sample is aligned with the axis of the clamps.

In this corrosion-fatigue test, similar to the fatigue test in air ambient,[13] HCF test was conducted on the unECAPed and ECAPed samples (after the third pass), based on the mentioned condition, and the S–N diagram was extracted. The aim of this study was to investigate the effect of SBF corrosive environment on the fatigue behavior of Grade 2 UFG CP-Ti and the feasibility of using it as an implant material. Moreover, to compare the effect of the number of ECAP pass on the fatigue life of material in SBF, the annealed material and ECAPed samples from 1 to 3 passes were subjected to fatigue test in a constant stress and the obtained lifetime was compared with the lifetime of these specimens in air. Moreover, fracture surfaces of fatigue samples were observed and evaluated using SEM model LEO 1450VP with a voltage of 20 kV.

Results and discussion

Mechanical properties and microstructural evolution

Based on the results of previous study,[8,13] the mechanical properties including tensile strength (yield and ultimate strength, σ_Y, σ_U), elongation (δ), hardness and average grain size of the target material (Grade 2 CP-Ti) before and after applying 3 passes of ECAP, were presented in Table 1. The results clearly show that by introducing the cold ECAP process at RT on this material, the SPD led to reduction in magnitude of the average grain size from 55 μm in the initial annealing material to 650 nm after 3 passes, and consequently led to improve mechanical properties. So that, mechanical strength was enhanced from 174 MPa to 273 MPa after final pass.[13] By considering that the mechanical strength can be directly related to hardness, the hardness increased from 153 Vickers to 274 Vickers and this has been predictable after ECAP process.[8] Similar to the behavior of the other metals after SPD processes, the improvement of the static and dynamic mechanical properties in this material can be related to various factors.[8] These factors show significant reduction in grain size to UFG, high fraction of homogeneous equiaxed microstructures, developing the grain

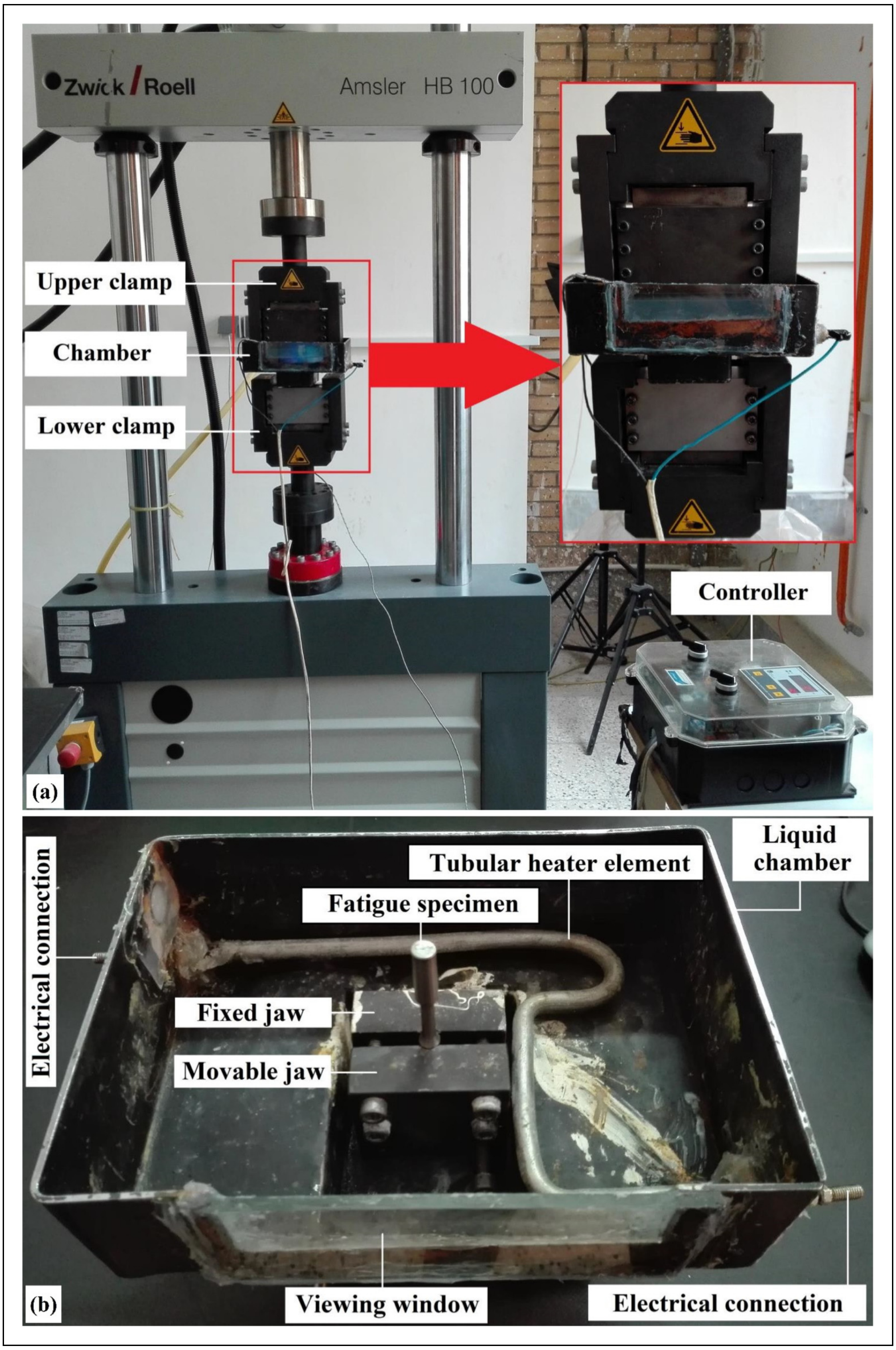

Figure 2. (a) General setup of corrosion-fatigue test and (b) real illustration of liquid chamber with fixed and movable jaws and tubular heater element.

boundaries with high angles of misorientation, increasing the densities of dislocation and twins after RT SPD and raising strain-hardening rate.[8,47,48]

Fatigue and corrosion-fatigue properties

Fatigue in simulated body fluid. The S–N curve obtained from axial fatigue test in the corrosive SBF has been shown in Figure 3. This diagram has two S–N curves for unECAPed (CG) and ECAPed after 3 passes (UFG) samples of Grade 2 CP-Ti. As it is known by analyzing the results of performed corrosion-fatigue or stress corrosion test, it can be seen that corrosion-fatigue properties of this material have been remarkably improved after ECAP due to development of its coarse-grained microstructure to UFG microstructure. Improvement of corrosion-fatigue behavior in the UFG compared to CG metals is related to decreasing the grain size, microstructure evolution to high angle boundaries and increasing the density of dislocations and twins.[30,49]

Table 1. Mechanical properties of Grade 2 CP-Ti before and after introducing by ECAP at room temperature.[8,13]

Passes (N)	δ (%)	σ_Y (MPa)	σ_U (MPa)	Hardness (HV)	Average grain size (μm)
0	38.7	174	396	153	55
1	20	183	531	193	11
2	18.9	216	613	215	3
3	19.5	273	715	247	0.65 | 650 nm

By fitting the power function of Basquin ($S_{max} = A\ N^B$)[30] on the data resulting from this corrosion-fatigue test (see Figure 3), the equations of S_{max} (MPa) = 654.43 $N^{-0.081}$ and S_{max} (MPa) = 1656.6 $N^{-0.11}$ for Grade 2 CP-Ti in CG and UFG state of microstructure were obtained, respectively. R-squared (R^2) value[50] is known as a parameter to prove the accuracy of curve. The results demonstrated that the reliable amounts of $R^2 = 0.9478$ and 0.8887 were calculated from the curve superimposing on CG and UFG CP-Ti experimental data. In addition, fatigue limit of maximum stress (MPa) at 10^6 cycles was obtained equal to 214 MPa and 362 MPa for CG and UFG state of material, respectively.

The parameters of Basquin fitting (A and B) for describing of the corrosion-fatigue life distribution, R^2 value as a parameter to prove the accuracy of fitting and fatigue endurance limit of maximum stress (MPa) at 1 million cycles, were summarized in Table 2.

In order to investigate the effect of ECAP pass on the axial fatigue life of Grade 2 CP-Ti in SBF solution, the maximum stress of 484 MPa or constant load 9.5 kN was used. In this test, the fatigue samples that machined from 0 to 3 ECAPed billets were imposed under axial fatigue test at a constant stress in the SBF environment and number of cycle to failure was reported as a measure of fatigue life. Figure 4 shows the values of fatigue life in a constant tension of 484 MPa for 0 to 3 passes of ECAPed specimens in SBF corrosive environment. As it is known, with the increase in ECAP pass, the fatigue life is increased, and it depends to enhancement of

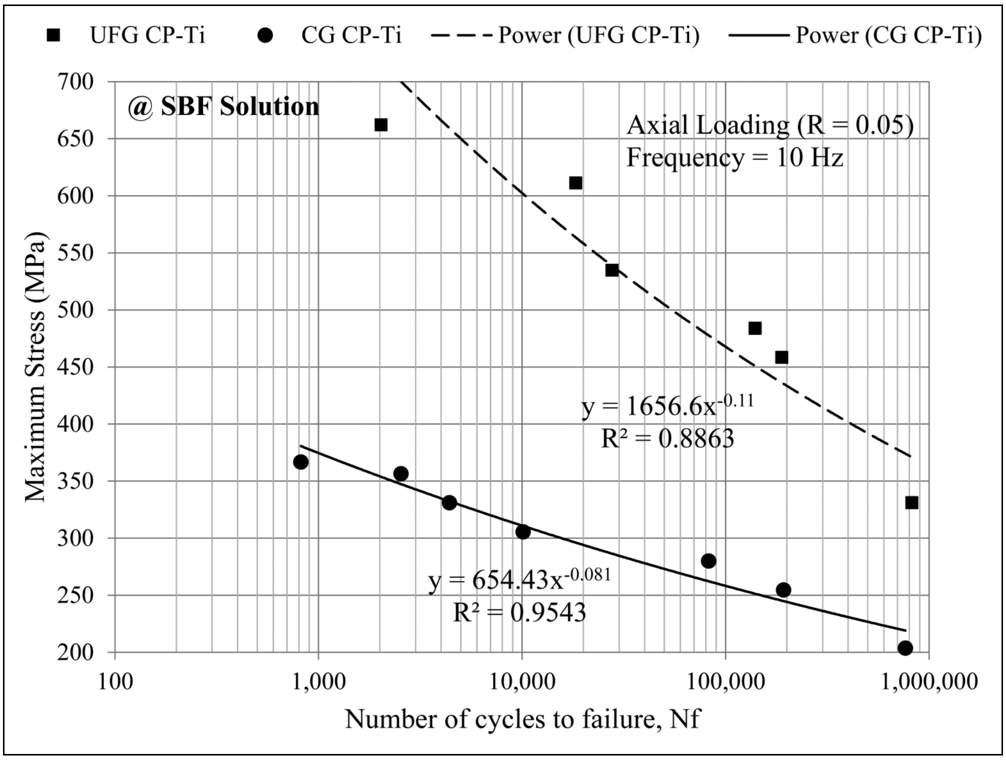

Figure 3. S–N curves obtained from corrosion-fatigue test in SBF solution for the CG/UFG Grade 2 CP-Ti processed by ECAP at room temperature.

the static strength due to microstructural evolution (such as forming the HAGBs and increasing the density of dislocations and twins) and decreasing the average grain size from CG to UFG.[30,49]

Comparing fatigue behavior in air and SBF environment

S–N curves. Fatigue behavior of unECAPed (CG) and 3 passes ECAPed in air and SBF environment were presented in Figure 5. The aim of this comparison was to analyze the influence of SBF corrosive solution on the fatigue properties of CG/UFG CP-Ti. Complete results of fatigue behavior of this material in the air and under present condition have been described in detail in previous research of these authors.[13]

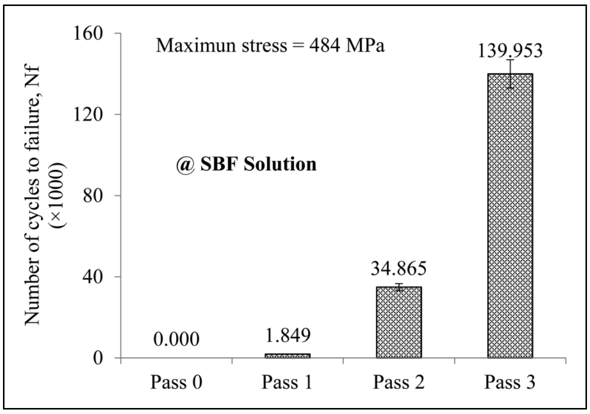

Figure 4. Corrosion-fatigue life in SBF solution of Grade 2 CP-Ti before and after ECAP process up to 3 passes subjected to a constant maximum stress of 484 MPa.

As it can be observed, the fitting curve of Basquin in the corrosion-fatigue test in SBF is slightly lower than the Basquin curve in fatigue test in the air for both CG and UFG state. In fact, at the same stress, in this material the fatigue life or number of cycle to failure (Nf) in SBF solution is slightly lower than air environment. In the other words, by considering the diagram it can be seen at a constant Nf the maximum stress can be applied to the specimen is greater in air in comparison with SBF. This can be due to saline properties of the SBF solution and its effect on the nucleation and initiation of cracks and consequently rapid growth caused by fatigue during the test at 37 °C.[3]

In addition by comparing two curves in the CG or UFG states in both air and SBF conditions, it can be easily seen that by decreasing the maximum stress or increasing the fatigue life, the separation or the vertical distance between two curves increases on the right side of S–N curve. Actually in a constant maximum stress, the number of cycle to failure or fatigue life in SBF is

Table 2. Corrosion-fatigue (in SBF) properties of Grade 2 CP-Ti in CG and UFG states due to RT ECAP process.

Grade 2 CP-Ti	*A* (MPa)	*B*	R^2	Limit of maximum fatigue stress (MPa)
Pass 0 (CG)	654.43	−0.081	0.9478	214
Pass 3 (UFG)	1656.6	−0.11	0.8887	362

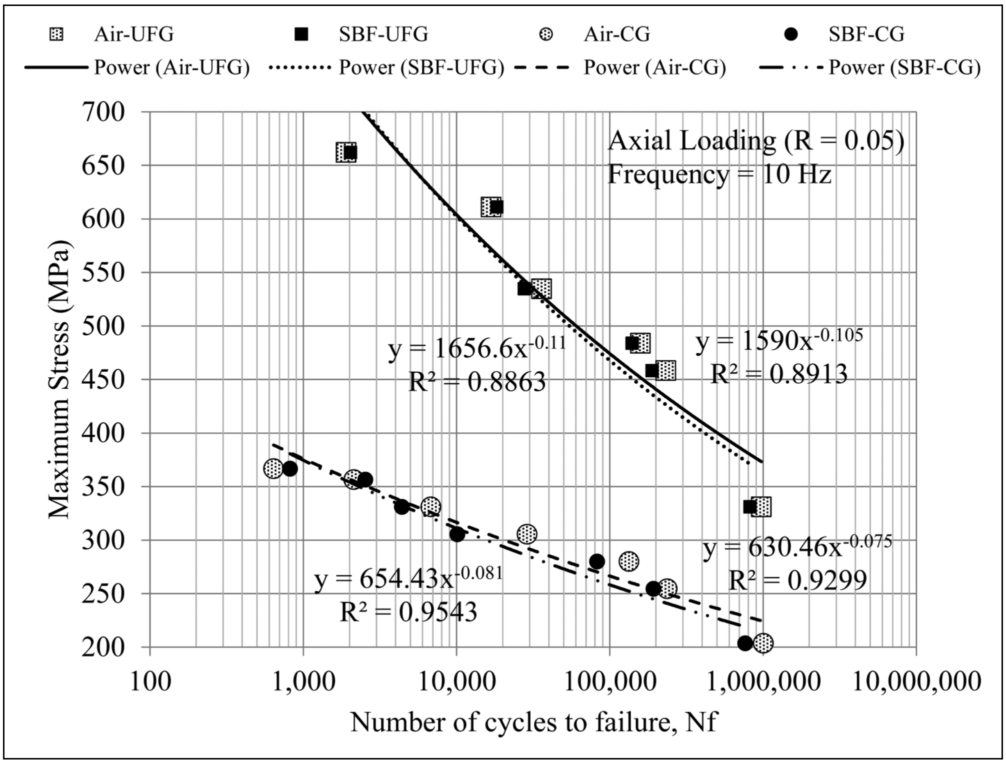

Figure 5. Comparison of S–N curves for CG/UFG CP-Ti after axial fatigue test in air[13] and SBF solution at 37 °C.

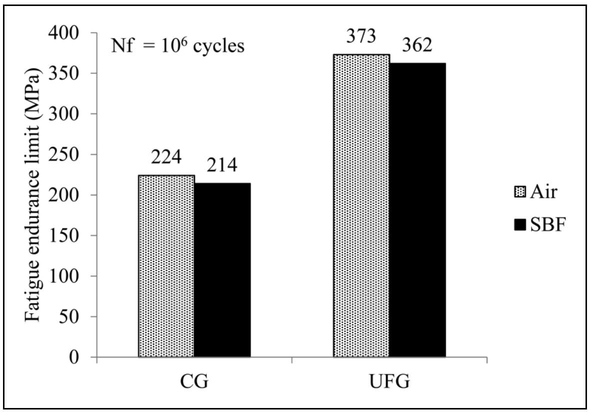

Figure 6. Comparison of fatigue endurance limit in 10^6 cycles for CG/UFG CP-Ti in both air[13] and SBF environment based on Basquin equation.

lower than in air in both states of CG and UFG. This shows that the SBF corrosive environment in higher cycle, or in other words in lower maximum stress, has longer time to affect on the initiation, growth and development of fatigue cracks and reduce the lifetime further more in lower stresses. Actually, at lower stress, because more time is needed for initiation of cracks in the material and finally failure, Hank corrosive environment has more opportunity and time that affect on the cracks and ultimately accelerates the growth of cracks.[3] Furthermore, the results demonstrate that the separation at the end of curves in UFG state is less in comparison with CG state. It is can be related that the higher resistance of UFG CP-Ti against the corrosion and corrosion-fatigue in SBF, proportion that CG CP-Ti, due to improvement in microstructural evolution.[3,19]

Therefore, it can be concluded that applying ECAP process on CP-Ti and converting its CG structure to UFG structure, not only lead to improve the fatigue and corrosion-fatigue properties of CP-Ti but it makes closer the corrosion-fatigue behavior of this material in SBF to fatigue behavior in air. Of course, it should be noticed that the slight difference between the Basquin curves on the S–N diagrams in each CG or UFG states generally depends on low corrosive effect of SBF solution and also high stability and high corrosion resistance of CP-Ti.[13,19] According to the results of this research, it can be concluded that the SBF has no significant effect on fatigue behavior of unECAPEd (CG) and ECAPed (UFG) in comparison with air ambient. Therefore, it can be reliably considered that the influence of the corrosive environment of body plasma on implants made by ECAPed CP-Ti that are under periodic loading can be ignored.

Fatigue endurance limit. In Figure 6, the comparison of fatigue endurance limit in 1 million cycles for CG and UFG CP-Ti has been shown in both air and SBF environment. The presented fatigue endurance limits are the result of inserting the lifetime (N) of 10^6 cycles in Basquin equation available in Table 2 and Figure 3. As it is clear, by

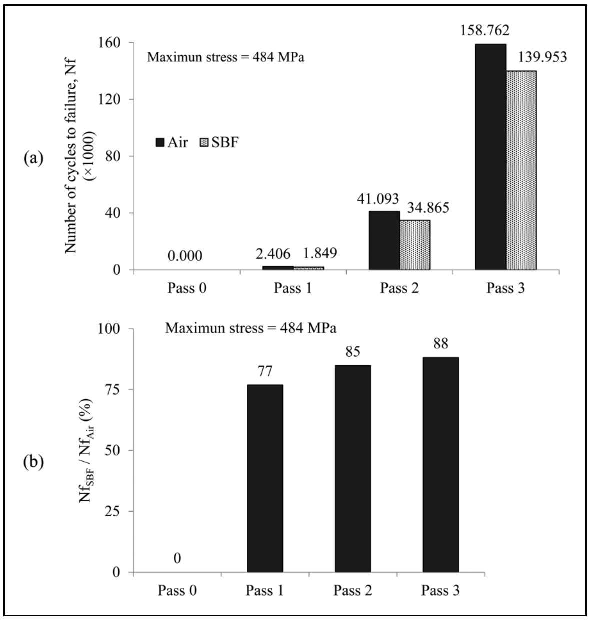

Figure 7. Comparison of fatigue properties in air[13] and SBF for Grade 2 CP-Ti before and after applying 1 to 3 passes of ECAP, under constant maximum stress of 484 MPa: (a) fatigue life and (b) fatigue life ratio in SBF to air.

evolution of the microstructure from CG in annealed state to UFG after 3 passes of ECAP, the amount of fatigue endurance limit is increased. Hence, this demonstrates that the positive effect of ECAP process enhances the fatigue properties of CP-Ti. In addition, it can be obtained from the result that fatigue endurance limit in corrosion-fatigue in SBF is slightly lower than fatigue in air and it is due to the effect of SBF corrosive environment on increasing the rate of initiation and growth of fatigue cracks.[3] However, it should be noted that due to the negligible difference in fatigue endurance limit in these two environments, it could be concluded that CP-Ti has stability and resistance under fatigue loading in presence of SBF. In addition, consequently, it was proved that CP-Ti is reliable biomaterial for manufacturing the metallic implants for utilizing in human body from point of view of static–dynamic mechanical strength.

Fatigue life in constant maximum stress. The fatigue life in air and the corrosion-fatigue life in SBF at maximum stress of 484 MPa applied on the unECAPed and ECAPed CP-Ti from 1 to 3 passes were presented in Figure 7(a). The obtained results show that in both air and SBF environment, by increasing the number of ECAP pass, the fatigue life enhances. This is because of enhancement of static strength due to increasing in dislocation density, enhancement of volume fraction of HAGBs to low angle grain boundaries (LAGBs), increasing the density of twins and decreasing in average grain size by increasing the number of ECAP passes. All these items have direct effect on the improvement of the dynamic strength (or fatigue) of metals.[30,49] It is also found that the SBF corrosive environment has negative effect on the fatigue life and it is seen a slight reduction

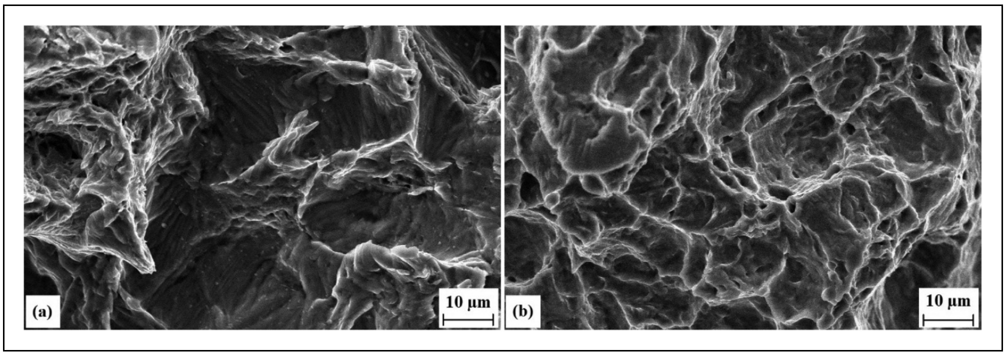

Figure 8. Fracture surface of CG/UFG Grade 2 CP-Ti after applying the corrosion-fatigue in SBF solution: (a) CG, 204 MPa, 764,761 cycles and (b) UFG, 331 MPa, 823,496 cycles.

in fatigue life in SBF in comparison with in air in all of ECAP passes.

In Figure 7(b), fatigue life ratio in SBF to air was shown in term of percentage (%) at 1 to 3 passes of ECAP. As it can be seen, the amount of Nf_{SBF}/Nf_{air} in maximum stress of 484 MPa in passes 1, 2 and 3 is 77%, 85% and 88%, respectively. According to these results, it is clear that by increasing the number of passes, the ratio of fatigue life gradually increases to 100%. This shows that with decreasing the average grain size in higher passes of ECAP, the corrosion resistance of CP-Ti increase and the negative effect of corrosive SBF and consequently the human body environment can be neglected on UFG CP-Ti. These results have a good agreement with the other previous researches.[3,19]

Fracture surfaces. Figure 8 shows fracture surface of CP-Ti after corrosion-fatigue in SBF environment in both CG and UFG states. Since the effect of corrosive environment is more in high number of cycles to failure, the fatigue specimens under the low maximum stresses equal to 204 MPa and 331 MPa were selected for CG and UFG condition, respectively, to investigate the fracture surface. The pitting or cavity due to the corrosion is often considered as the most active mechanism for initiating of fatigue crack in corrosion-fatigue of metals.[16] As it can be observed in fracture surface images, there is no significant cavity or pitting as the main vestige of corrosion-fatigue. This issue confirms the numerical result of the tests that SBF effect on reduction of the fatigue life can be ignored, and practically SBF does not have much effect on the corrosion-fatigue behavior of CG and UFG CP-Ti. The reason of this claim is the high stability and excellent resistance of CP-Ti against corrosive environment.[3,19]

Conclusions

The achieved results of this research lead to the following conclusions, so that these results are in good agreement generally with the findings of similar researches:

- CP-Ti was processed by ECAP at room temperature up to 3 passes and the average grain size of material changed from 55 μm for annealing state to 11, 3 and 0.65 μm for 1 to 3 passes, respectively. In addition, yield and ultimate strength of CP-Ti remarkably increased by imposing ECAP. Amounts of 174 MPa, 183 MPa, 216 MPa and 273 MPa and also 396 MPa, 531 MPa, 613 MPa and 715 MPa are related to the yield and ultimate stresses for passes 0 to 3, respectively. In addition, Vickers hardness enhances from 153 Hv for CG to 193 Hv, 215 Hv and 247 Hv for ECAPed state after 1 to 3 passes, respectively.
- Corrosion-fatigue behavior of CG/UFG CP-Ti was investigated under the axial fatigue loading in SBF at 37 °C. Comparison of S–N diagram demonstrated that corrosion-fatigue life of ECAPed CP-Ti is higher than initial annealed CG.
- Fatigue endurance limit of CG CP-Ti in air and SBF are 224 and 214 MPa, respectively. Furthermore, these amounts for UFG CP-Ti (3 pass ECAPed) in air and SBF are, 373 MPa and 362 MPa, respectively. This demonstrates that fatigue properties of CP-Ti in air are better than SBF in both CG and UFG state. This depends on saline corrosive properties of SBF on CP-Ti.
- Number of cycles to failure of CP-Ti in constant maximum stress of 484 MPa in SBF environment are obtained equal to 0, 1849, 34,865 and 139,953 cycles for 0 to 3 passes of ECAP, respectively. This shows that by increasing passes of ECAP, fatigue life increases.
- In lower maximum stress or higher failure cycles, corrosion effect of SBF on fatigue life of CG/UFG CP-Ti is more than higher stress.
- By increasing the number of passes, amounts of number of cycles to failure in SBF proportion to air, in the other words, fatigue life ratio in SBF to air enhance from 0% to 77%, 85% and 88% for 0 to 3 passes of ECAP, respectively. This demonstrates that corrosion-fatigue properties of UFG CP-Ti in SBF are close to air.
- Effect of SBF in reduction of fatigue life of UFG is lower than CG CP-Ti. Nevertheless, it can be concluded that influence of SBF in stress-corrosion of CP-Ti in both states of CG and UFG is negligible.

- Analyzing the fracture surface of fatigue samples shows that there isn't any vestige of pitting as most important factor of stress-corrosion on the surface. This indicates that influence of SBF on CG/UFG CP-Ti can be ignored.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

ORCID iDs

Reza Naseri https://orcid.org/0000-0002-6656-7785
Mahmoud Shariati https://orcid.org/0000-0003-0878-7998
Mehran Kadkhodayan https://orcid.org/0000-0001-9880-8558

References

1. Long M and Rack HJ. Titanium alloys in total joint replacement – a materials science perspective. *Biol Mater* 1998; 19: 1621–1639.
2. Wang K. The use of titanium for medical applications in the USA. *Mater Sci Eng A* 1996; 213: 134–137.
3. Rubitschek F, Niendorf T, Karaman I, et al. Corrosion fatigue behavior of a biocompatible ultrafine-grained niobium alloy in simulated body fluid. *J Mech Behav Biomed Mater* 2012; 5: 181–192.
4. Niinomi M, Nakai M and Hieda J. Development of new metallic alloys for biomedical applications. *Acta Biomater* 2012; 8: 3888–3903.
5. Geetha M, Singh AK, Asokamani R, et al. Ti based biomaterials, the ultimate choice for orthopaedic implants – a review. *Prog Mater Sci* 2009; 54: 397–425.
6. Roodposhti PS, Farahbakhsh N, Sarkar A, et al. Microstructural approach to equal channel angular processing of commercially pure titanium – a review. *Trans Nonferrous Met Soc China* 2015; 25: 1353–1366.
7. Chen YJ, Li YJ, Walmsley JC, et al. Microstructure evolution of commercial pure titanium during equal channel angular pressing. *Mater Sci Eng A* 2010; 527: 789–796.
8. Naseri R, Kadkhodayan M and Shariati M. Static mechanical properties and ductility of biomedical ultrafine-grained commercially pure titanium produced by ECAP process. *Trans Nonferrous Met Soc China* 2017; 27: 1964–1975.
9. Attarilar S, Djavanroodi F, Irfan OM, et al. Strain uniformity footprint on mechanical performance and erosion-corrosion behavior of equal channel angular pressed pure titanium. *Results Phys* 2020; 17: 103141.
10. Attarilar S, Djavanroodi F, Ebrahimi M, et al. Hierarchical microstructure tailoring of pure titanium for enhancing cellular response at tissue-implant interface. *J Biomed Nanotechnol* 2021; 17: 115–130.
11. Valiev RZ, Islamgaliev RK and Alexandrov IV. Bulk nanostructured materials from severe plastic deformation. *Prog Mater Sci* 2000; 45: 103–189.
12. Valiev RZ and Langdon TG. Principles of equal-channel angular pressing as a processing tool for grain refinement. *Prog Mater Sci* 2006; 51: 881–981.
13. Naseri R, Hiradfar H, Shariati M, et al. A comparison of axial fatigue strength of coarse and ultrafine grain commercially pure titanium produced by ECAP. *Arch Civ Mech Eng* 2018; 18: 755–767.
14. Huang Y and Langdon TG. Advances in ultrafine-grained materials. *Mater Today* 2013; 16: 85–93.
15. Figueiredo RB, Barbosa E, Zhao X, et al. Improving the fatigue behavior of dental implants through processing commercial purity titanium by equal-channel angular pressing. *Mater Sci Eng A* 2014; 619: 312–318.
16. Antunes RA and De Oliveira MCL. Corrosion fatigue of biomedical metallic alloys: mechanisms and mitigation. *Acta Biomater* 2012; 8: 937–962.
17. Leon A and Aghion E. Effect of surface roughness on corrosion fatigue performance of AlSi10Mg alloy produced by selective laser melting (SLM). *Mater Charact* 2017; 131: 188–194.
18. Gurao NP, Manivasagam G, Govindaraj P, et al. Effect of texture and grain size on bio-corrosion response of ultrafine-grained titanium. *Metall Mater Trans A* 2013; 44: 5602–5610.
19. Balakrishnan A, Lee BC, Kim TN, et al. Corrosion behaviour of ultra fine grained titanium in simulated body fluid for implant application. *Trends Biomater Artif Organs* 2008; 22: 58–64.
20. Djavanroodi F, Irfan OM and Al-Mufadi FA. Erosion corrosion behavior of nanostructure commercial pure titanium in simulated body fluid. In: MATEC Web of Conferences 2019, EDP Sciences.
21. Hoseini M, Shahryari A, Omanovic S, et al. Comparative effect of grain size and texture on the corrosion behaviour of commercially pure titanium processed by equal channel angular pressing. *Corros Sci* 2009; 51: 3064–3067.
22. Agnew SR, Vinogradov AY, Hashimoto S, et al. Overview of fatigue performance of Cu processed by severe plastic deformation. *J Electron Mater* 1999; 28: 1038–1044.
23. Vinogradov A and Hashimoto S. Fatigue of severely deformed metals. *Adv Eng Mater* 2003; 5: 351–358.
24. Mughrabi H, Höppel HW and Kautz M. Fatigue and microstructure of ultrafine-grained metals produced by severe plastic deformation. *Scr Mater* 2004; 51: 807–812.
25. Estrin Y and Vinogradov A. Fatigue behaviour of light alloys with ultrafine grain structure produced by severe plastic deformation: an overview. *Int J Fatigue* 2010; 32: 898–907.
26. Ebrahimi M and Shamsborhan M. Monotonic and dynamic mechanical properties of PTCAE aluminum. *J Alloys Compd* 2017; 705: 28–37.
27. Semenova IP, Salimgareeva GK, Latysh VV, et al. Enhanced fatigue strength of commercially pure Ti processed by severe plastic deformation. *Mater Sci Eng A* 2009; 503: 92–95.
28. Ebrahimi M. Fatigue behaviors of materials processed by planar twist extrusion. *Metall Mater Trans A* 2017; 48: 6126–6134.
29. Czerwinski A, Lapovok R, Tomus D, et al. The influence of temporary hydrogenation on ECAP formability and low cycle fatigue life of CP titanium. *J Alloys Compd* 2011; 509: 2709–2715.
30. Kim WJ, Hyun CY and Kim HK. Fatigue strength of ultrafine-grained pure Ti after severe plastic deformation. *Scr Mater* 2006; 54: 1745–1750.
31. Medvedev A, Ng HP, Lapovok R, et al. Comparison of laboratory-scale and industrial-scale equal channel angular

pressing of commercial purity titanium. *Mater Lett* 2015; 145: 308–311.

32. Semenova IP, Salimgareeva GK, Latysh VV, et al. Enhanced fatigue properties of ultrafine-grained titanium rods produced using severe plastic deformation. In: *Solid state phenomena* 2008, Switzerland: Trans Tech Publications. pp.167–172.
33. Terent'ev VF, Dobatkin SV, Nikulin SA, et al. Fatigue strength of submicrocrystalline Ti and Zr-2.5% Nb alloy after equal channel angular pressing. *Kovove Mater Metall Mater* 2011; 49: 65–73.
34. Abdulstaar M, Mhaede M, Wollmann M, et al. Investigating the effects of bulk and surface severe plastic deformation on the fatigue, corrosion behaviour and corrosion fatigue of AA5083. *Surf Coat Technol* 2014; 254: 244–251.
35. Ahmed AA, Mhaede M, Wollmann M, et al. Effect of surface and bulk plastic deformations on the corrosion resistance and corrosion fatigue performance of AISI 316L. *Surf Coat Technol* 2014; 259: 448–455.
36. Chavan PN, Bahir MM, Mene RU, et al. Study of nanobiomaterial hydroxyapatite in simulated body fluid: formation and growth of apatite. *Mater Sci Eng B* 2010; 168: 224–230.
37. Niendorf T, Canadinc D, Maier HJ, et al. Microstructure–mechanical property relationships in ultrafine-grained NbZr. *Acta Mater* 2007; 55: 6596–6605.
38. Naseri R, Kadkhodayan M and Shariati M. An experimental investigation of casing effect on mechanical properties of billet in ECAP process. *Int J Adv Manuf Technol* 2017; 90: 3203–3216.
39. Djavanroodi F, Daneshtalab M and Ebrahimi M. A novel technique to increase strain distribution homogeneity for ECAPed materials. *Mater Sci Eng A* 2012; 535: 115–121.
40. Shaeri MH, Djavanroodi F, Sedighi M, et al. Effect of copper tube casing on strain distribution and mechanical properties of Al-7075 alloy processed by equal channel angular pressing. *J Strain Anal Eng Des* 2013; 48: 512–521.
41. Ebrahimi M, Shaeri MH, Naseri R, et al. Equal channel angular extrusion for tube configuration of Al–Zn–Mg–Cu alloy. *Mater Sci Eng A* 2018; 731: 569–576.
42. Horita Z, Furukawa M, Nemoto M, et al. Development of fine grained structures using severe plastic deformation. *Mater Sci Technol* 2000; 16: 1239–1245.
43. Niinomi M. Biologically and mechanically biocompatible titanium alloys. *Mater Trans* 2008; 49: 2170–2178.
44. Serra G, Morais L, Elias CN, et al. Nanostructured severe plastic deformation processed titanium for orthodontic mini-implants. *Mater Sci Eng C* 2013; 33: 4197–4202.
45. Hanawa T. Biofunctionalization of titanium for dental implant. *Jpn Dent Sci Rev* 2010; 46: 93–101.
46. Siválk P and Ostertagová E. Evaluation of fatigue tests by means of mathematical statistics. *Procedia Eng* 2012; 48: 636–642.
47. Valiev R. Nanostructuring of metals by severe plastic deformation for advanced properties. *Nat Mater* 2004; 3: 511–516.
48. Zhao X, Fu W, Yang X, et al. Microstructure and properties of pure titanium processed by equal-channel angular pressing at room temperature. *Scr Mater* 2008; 59: 542–545.
49. Mohammadhosseini A, Masood SH, Fraser D, et al. Dynamic compressive behaviour of Ti–6Al–4V alloy processed by electron beam melting under high strain rate loading. *Adv Manuf* 2015; 3: 232–243.
50. Homaei E, Farhangdoost K, Tsoi JKH, et al. Static and fatigue mechanical behavior of three dental CAD/CAM ceramics. *J Mech Behav Biomed Mater* 2016; 59: 304–313.