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Short Communication

Comparative effect of grain size and texture on the corrosion behaviour of commercially pure titanium processed by equal channel angular pressing

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ABSTRACT

The effect of grain size and texture on the corrosion properties of commercially pure titanium was investigated. Equal channel angular pressing (ECAP) was used to produce different grain size and various crystallographic orientations. Electrochemical impedance spectroscopy was employed to measure the corresponding surfaces' general corrosion resistance. Samples with the (0 0 0 2) planes parallel to the surface were found to offer the highest corrosion resistance, regardless of their grain size.

1. Introduction

Sever plastic deformation (SPD) techniques have been used to convert coarse-grained (CG) into ultra fine-grained (UFG) commercially pure titanium (CP Ti) in order to increase its mechanical strength [1–4]. It was demonstrated that decreasing the grain size (using SPD) resulted in an improved biocompatibility of the CP Ti [4]. Corrosion resistance is another key property of SPD-processed materials that could be affected by the applied manufacturing process [3,5,6]. However, the related literature reports wide scattering results, spanning from the higher [5,7–9] to the lower corrosion resistance [3], and also reporting that there is no significant difference [6,10] in the corrosion resistance of UFG and CG alloys and pure metals. The corrosion resistance of CP Ti was shown to be slightly improved as a result of applying equal channel angular pressing (ECAP) [5]. This improvement was attributed to the dispersion of impurities in the bulk of CP Ti as the result of ECAP.

It should be noted that the ECAP process produces changes in the grain size and crystallographic orientation (texture) [11]. However, in the related literature on the corrosion of UFG materials, merely the change in the grain size has been studied, with no analysis of the role of texture in corrosion behaviour [3,7,8]. Thus, the present work addresses this problem, and the influence of the ECAP process on the corrosion resistance of CP Ti, in correlation with the changes in the material's grain size and texture.

2. Materials and methods

CP Ti (grade 2) cylindrical samples, 12 mm in diameter and 60 mm in length, were annealed at 800 °C for 4 h prior to the ECAP, yielding an average grain size of 20 μm. Chemical composition of CP Ti samples used in this study was (wt%) 0.16% O, 0.095% Fe, 0.01% N, 0.02% C and Ti (balance). The ECAP process was carried out using a $\Phi = 90^\circ$ die with $\Psi = 20^\circ$ outer arc of curvature, as described elsewhere [11]. The samples were subjected to successive ECAP passes, from 1 to 8 via route B_C at 450 °C. Route B_C refers to 90° rotation of the sample following consecutive passes [12]. Following ECAP process, disc-shape samples (12 × 2 mm) were cut perpendicular to the direction of ECAP die exit channel and were polished successively down to 4000 grit papers. The samples were then rinsed with de-ionized water and degreased with ethanol and prepared for subsequent characterization experiments. All the characterization techniques were performed on this polished surface (perpendicular to the exit channel) with no residue of oxide layers/debris from the ECAP process. These experiments were comparatively conducted on a sample that was not subjected to the ECAP (0 pass), and on samples subjected to 1, 2, 4 and 8 passes.

An Ecochemie Autolab PGSTAT30 Potentiostat/Galvanostat, controlled with GPES/FRA v.4.9.5 software was used for electrochemical impedance spectroscopy (EIS) measurements. EIS was performed at open circuit potential (OCP) over a frequency range of 50 kHz to 10 mHz using an AC voltage amplitude of ±10 mV. Subsequently Tafel polarization was conducted starting from −100 mV toward +100 mV with respect to OCP. A 0.16 mol L^{-1}

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NaCl aqueous solution was used as electrolyte in electrochemical measurements. In order to remove dissolved oxygen and maintain inert atmosphere above the solution, the solution was purged with argon for 30 min prior the electrochemical measurements, and also during the measurements.

Microstructure of samples was investigated using a Philips XL-30 FEG-SEM equipped with TSL orientation imaging microscopy (OIM). The texture of samples was measured using a SIEMENS DX-500 X-ray diffractometer and inverse pole figures were calculated with TextTools software.

3. Results and discussion

It has been demonstrated that the grain refinement during ECAP in route B_C, starts with grain elongation occurring in the initial passes, followed by gradual grain fragmentation [1]. This results in the formation of an equiaxed grain structure after the eighth pass [1]. Fig. 1 shows the microstructure of the initial sample (0 pass), and of samples subjected to 2 and 4 passes. The results demonstrate a change in the grain size following the ECAP. It has been shown that applying 8 passes of ECAP via route B_C, decreases the pure titanium grain size down to ca. 260 nm, which is claimed to be the minimum achievable grain size for titanium using this process [1,2]. In fact, we determined that the microstructure of samples subjected to 4 and 8 passes was almost identical. It was mentioned, in earlier literature, that changing the grain size can affect the corrosion behaviour of pure titanium [3,5]. Thus, it would be interesting to examine the influence of the grain size change following the ECAP on the corrosion behaviour of the investigated specimens.

Electrochemical impedance spectroscopy (EIS) was used to measure the general corrosion resistance of the CP Ti samples at different stages of ECAP processing. Fig. 2 shows the Nyquist and Bode plots of the samples subjected to 0, 2 and 4 passes. In order to obtain information on the corrosion behaviour of the samples, experimental EIS data were modeled by an electrical equivalent circuit (EEC). A two-time constant EEC model (inset to Fig. 2a was found to give the best agreement between the simulated and experimental data. The corresponding fitting (EEC parameters) values along with the calculated corrosion current densities using Tafel polarizations are listed in Table 1. The details of the EIS data analysis have been reported in the literature [13–15] and will not be discussed here. However, it should be noted that the overall resistance of the material to general corrosion is the sum of R_1 and R_2, and it represents the polarization resistance (R_P) (Table 1) [15,16]. The corrosion current density was calculated using Tafel slopes obtained from potentiodynamic polarization curves and the R_P values obtained from EIS measurements.

Fig. 3 presents general corrosion resistance (R_P) values for the investigated samples. The trend shows a maximum at the sample subjected to 2 passes ($p < 0.05$, compared to 0, 1, 4 and 8 passes). However, it should be noted that the R_P value for the 0, 1, 4 and 8-pass samples are not significantly different ($p > 0.05$). However, Balyanov et al. [5] reported higher corrosion resistance for pure titanium after 8 passes of ECAP compared to untreated sample, employing weight loss measurements in an acidic solution. The decrease in the grain size and the subsequent dispersion of impurities were claimed to be responsible for the observed improvement in the corrosion resistance. It is known that in the ECAP process via route B_C, samples attain the smallest grain size and an equiaxed microstructure after 8 passes [1]. Therefore, the 8-pass sample with the smallest grain size is expected to exhibit the highest degree of dispersion of impurities and, therefore, the best corrosion resistance. However, our results show that this is not the case, but the 2-pass sample with larger (and elongated) grains exhibits a higher corrosion resistance (R_P) value than the 8-pass sample.

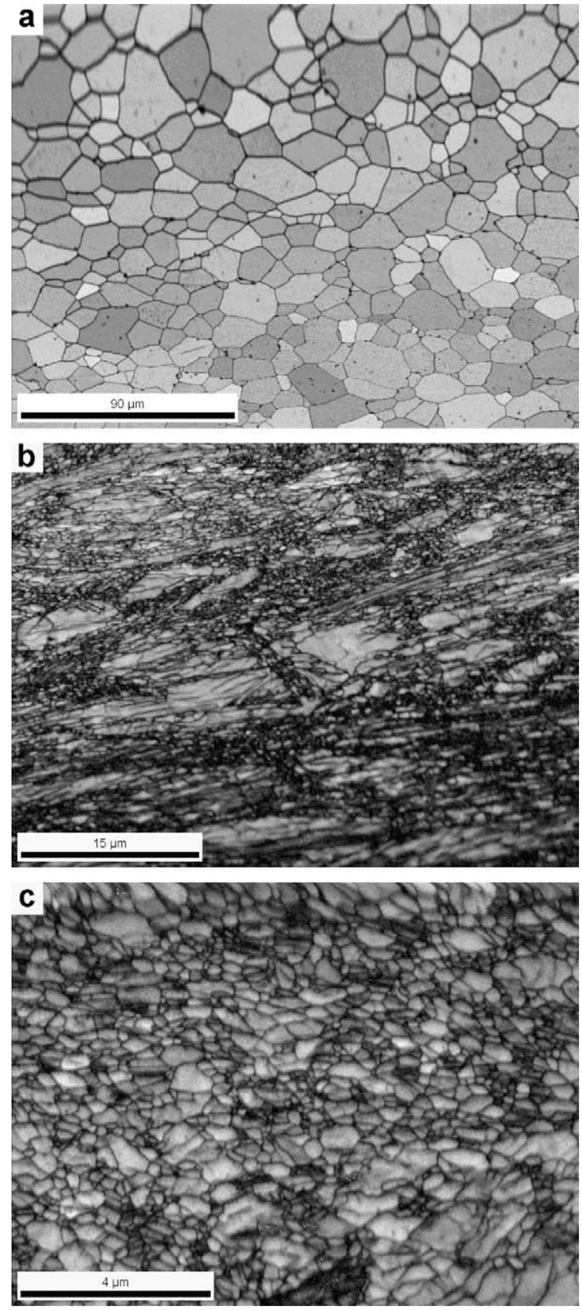

Fig. 1. OIM microstructure of pure titanium: (a) as-received + annealed, (b) following 2 pass and (c) 4 pass of ECAP. The average of grain size decreased from 20 to 0.3 μm for the annealed and ECAPed samples, respectively.

Thus, our opinion is that the change in grain size resulted from this SPD technique is not the major factor controlling the corrosion behaviour.

The SPD techniques, depending on the nature of the process, can greatly influence the material's texture [12]. On the other hand, the texture is shown to significantly affect the corrosion behaviour [17,18]. However, in the literature related to corrosion properties of SPD-treated materials, the effect of texture has been neglected. In the ECAP process conducted in this work, the texture of the samples is expected to change and evolve during the fabrication process. This is due to a large shear strain applied in each pass and the 90° rotation (route B_C) of the sample prior to the next pass. Thus, it is of importance to simultaneously evaluate the effect of ECAP-induced changes in grain size and texture on the corrosion

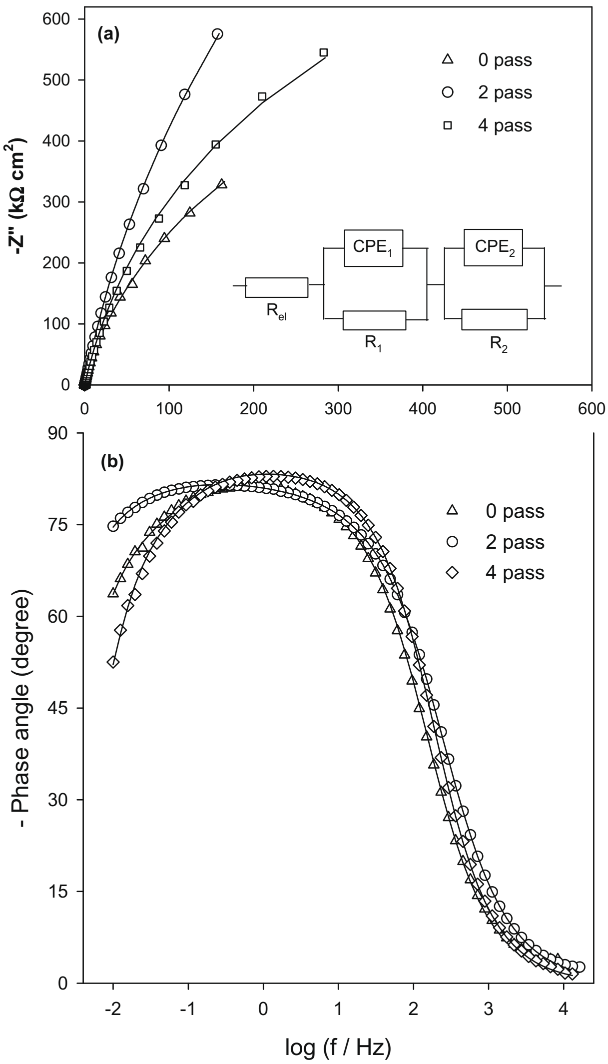

Fig. 2. (a) Nyquist and (b) Bode representations of EIS spectra recorded in 0.16 M NaCl for titanium samples following 0, 2 and 4 passes of ECAP. Inset to figure (a): the equivalent electrical circuit (EEC) used to model experimental data. Experimental data are shown by symbols, while solid lines represent the model.

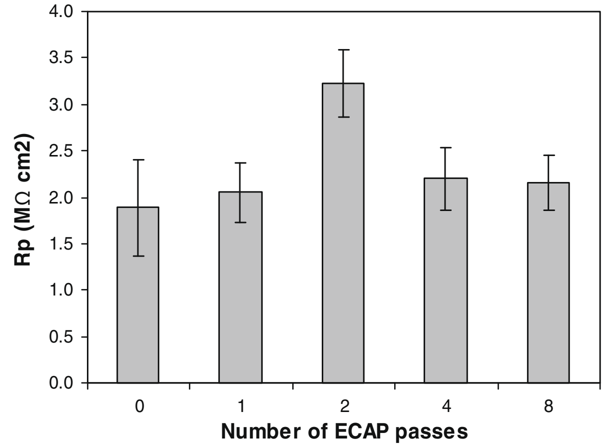

Fig. 3. Polarization resistance (R_P) values obtained from the EIS measurements recorded in 0.16 M NaCl, for titanium samples following 0, 1, 2, 4 and 8 passes of ECAP. Each experiment was repeated three times and the data represent mean values ± SD.

behaviour. For assessment of the corrosion resistance, it is therefore important to determine the orientation of the planes parallel to the corrosion-exposed surface of the samples.

Inverse pole figures represent the statistical distribution of the crystallographic planes parallel to the sample's surface. Fig. 4 shows the inverse pole figure representations of the investigated ECAP samples. The position of the most abundant crystallographic orientation of the 0-pass sample (Fig. 4a) lies between $(11\bar{2}0)$ and $(10\bar{1}0)$ planes. Fig. 4a shows a typical texture for the surfaces perpendicular to the direction of an extrusion process [19], indicating the history of the 0-pass samples. The changes in the inverse pole figures show the evolution of texture during the ECAP process. The texture of the 1-pass sample shows only a slight difference compared to that of the 0-pass sample. However, following the second pass of ECAP (the 2-pass sample), a substantial change in the texture is observed (Fig. 4c). The inverse pole figure of the 2-pass sample demonstrates that the peak is shifted toward the (0 0 0 2) planes, indicating that basal planes in the majority of grains are parallel to the surface. Nonetheless, the inverse pole figures of the 4-pass and 8-pass samples reveal that the texture gradually reversed to its original crystallographic distribution prior to the ECAP.

Thus, the results presented in Fig. 4 demonstrate that the major difference in texture occurs following the second pass of ECAP, where basal planes constitute the most abundant crystallographic plane. The basal plane is the most densely packed crystallographic plane in a *hcp* system. It has been shown that crystallographic planes with higher atomic density exhibit higher resistance to corrosion [17,20,21]. Our investigation of corrosion behaviour of titanium single crystal has also revealed that the (0 0 0 2) plane offers higher corrosion resistance compared to $(11\bar{2}0)$ and $(10\bar{1}0)$ planes [18]. The positive influence of planar atomic density on corrosion resistance in a chloride containing solution has also been reported for 316L stainless steels, with (1 1 1) plane exhibiting the best corrosion behaviour [17]. The observed texture for the 2-pass sample (Fig. 4c), showing (0 0 0 2) as the major crystallographic plane parallel to the surface, is thus responsible for its superior corrosion behaviour (Fig. 3).

It should be noted that the grain size for the samples in Fig. 1 decreases in the following order: 0-pass > 2-pass > 4-pass. This, combined with the texture analysis (Fig. 4), indicates that the effect of texture outweighs the effect of grain size on the corrosion behaviour. This outcome pertains to the ECAP processing of titanium with the minimum achievable grain size of 260 nm [1,2,12]. Decreasing the grain size of pure titanium further down to 90 nm using hydrostatic extrusion (HE), did not result in any

Table 1
EEC component values obtained by modelling experimental EIS data using the EEC presented in inset to Fig. 2.

	R_{el} (Ω cm^2)	CPE$_1$ ($\times10^6$ Ω^{-1} s^n cm^{-2})	n_1	R_1 (kΩ cm^2)	CPE$_2$ ($\times10^5$ Ω^{-1} s^n cm^{-2})	n_2	R_2 (MΩ cm^2)	R_P (MΩ cm^2)	i_{corr} (nA cm^{-2})
0-pass	68 ± 1	2.9 ± 0.7	0.89 ± 0.03	0.7 ± 0.2	1.9 ± 0.3	1.00 ± 0.00	1.9 ± 0.5	1.9 ± 0.5	18 ± 4
1-pass	65 ± 1	5 ± 1	0.80 ± 0.00	0.3 ± 0.1	1.0 ± 0.1	0.96 ± 0.02	2.1 ± 0.3	2.1 ± 0.3	14 ± 2
2-pass	66 ± 1	2.7 ± 0.3	0.78 ± 0.01	0.6 ± 0.1	1.0 ± 0.0	0.98 ± 0.01	3.2 ± 0.4	3.2 ± 0.4	8 ± 1
4-pass	65 ± 1	6 ± 2	0.7 ± 0.1	0.6 ± 0.1	0.9 ± 0.2	0.95 ± 0.04	2.2 ± 0.3	2.2 ± 0.3	17 ± 3
8-pass	67 ± 1	2.4 ± 0.2	0.79 ± 0.02	0.4 ± 0.1	1.3 ± 0.1	0.99 ± 0.02	2.2 ± 0.3	2.2 ± 0.3	12 ± 2

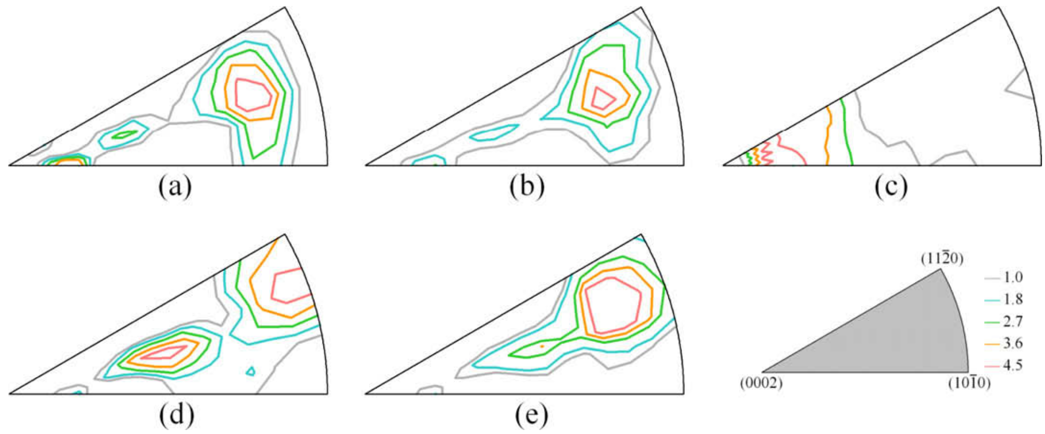

Fig. 4. Inverse pole figures illustrating the texture of titanium samples following: (a) 0, (b) 1, (c) 2, (d) 4 and (e) 8 passes of ECAP. The results show the distribution of crystallographic planes on the surface exposed in corrosion experiments. A reference inverse pole figure showing various crystallographic planes and intensities is also presented (right bottom).

significant change in the corrosion resistance [3]. Corrosion, as a surface-dependent property, is an anisotropic characteristic of materials [22,23]. Although, the grain size has been considered to have an influence on corrosion resistance [3,5,6], the impact of texture should also be evaluated. It was mentioned earlier that grain size has been extensively correlated to changes in corrosion behaviour of SPD-processed materials. Our opinion is that the observed controversial results could be related to lack of information on the texture of the examined specimens.

4. Conclusion

The presented results demonstrate a direct correlation between corrosion behaviour and microstructural features of pure titanium. The material's grain size was shown to be directly influenced by the applied ECAP process. Significant changes in the material's texture were also observed. Although, the sample following 8 passes of ECAP showed the smallest grain size, the highest corrosion resistance was observed for the sample obtained after 2 passes. Combined studies of the deformation-dependent changes in the grain size and texture suggest that the texture is the dominant factor controlling the corrosion properties of commercially pure titanium.

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