Materials Characterization 138 (2018) 38–47

Contents lists available at ScienceDirect

Materials Characterization

journal homepage: www.elsevier.com/locate/matchar

Simultaneously improving mechanical properties and corrosion resistance of pure Ti by continuous ECAP plus short-duration annealing

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ARTICLE INFO

Keywords:
Titanium
Equal channel angular pressing
Short-duration annealing
Mechanical properties
Corrosion
Texture

ABSTRACT

This work investigated the effect of short-duration annealing on mechanical properties and corrosion behavior of bulk ultrafine-grained (UFG) pure Ti (grade 2) produced by high-efficiency equal-channel angular pressing (ECAP), serving the fast developing of marine industries. The initial coarse-grained (CG) Ti achieved higher strength after continuous ECAP at 420 °C for 4 passes, while additional short-duration annealing at 300 °C for 15 min of UFG Ti further led to extraordinary improvement of strength, which was associated with texture strengthening. The yield strength was increased from 362 MPa in as-received state to 561 MPa in post-ECAP annealed condition, and ultimate tensile strength from 450 MPa to 663 MPa. The ECAP-processed UFG Ti had better corrosion resistance in artificial seawater than the initial CG Ti. Short-duration annealing further improved the corrosion resistance of UFG Ti, which was related to stronger basal texture. The corrosion current density decreased from 68.37 nA cm^{-2} for CG Ti in as-received condition to 41.77 nA cm^{-2} for UFG Ti processed by ECAP plus short-duration annealing. The fraction of TiO_2 within the surface oxide film for the post-ECAP annealed sample was increased. The bulk UFG Ti after post-ECAP short-duration annealing revealed an excellent combination of high strength, good ductility and superior corrosion resistance for marine applications.

1. Introduction

Ti and several Ti alloys have demonstrated its superiority in harsh ocean environments and are used as engineering materials in marine and navy industry [1]. In addition to high strength and good ductility, corrosion resistance of Ti need to be controlled for serving the fast developing of marine engineering.

Severe plastic deformation (SPD) techniques are extensively utilized to produce ultrafine-grained (UFG) metallic materials with superior performance [2]. Among these SPD techniques, Equal channel angular pressing (ECAP) has been well developed and attracted a lot of interests [3]. It has been considered as one of the most effective techniques for fabricating bulk UFG materials. During ECAP processing, grain refinement of metallic materials occurs by continuous dynamic recrystallization (CDRX) [4]. Many UFG metallic materials including titanium produced by ECAP exhibit improved mechanical properties [5]. At the same time, the internal stored energy increases in the metallic materials caused by severe plastic deformation during processing, which may give rise to subsequent microstructure change and instability. Appropriate annealing treatment has shown to be able to further enhance thermal stability and mechanical properties of UFG materials. Although many investigations have been conducted on the deformation and properties of materials processed by SPD, few studies have been focused on the annealing behavior of the UFG materials. Valiev et al. [6] and Semenova et al. [7] demonstrated that controlled annealing of UFG Ti could obtain both enhancement of strength and ductility. They attributed the promotion to the recovery of non-equilibium grain boundaries. Mousavi et al. [8] reported that post annealing at 190 °C for 10 min enhanced the ultimate strength of pure copper processed by twist extrusion for about 45 MPa, which was due to the new formed small grains after annealing. Huang et al. [9] and Kamikawa et al. [10] reported that annealing treatment improved the strength and reduced the ductility of pure aluminium processed by accumulative roll-bonding. This phenomenon was attributed to dislocation source-limited hardening. Zhao et al. [11] observed that annealing treatment at 60 °C for 30 min resulted in higher strength and lower elongation of UFG Al, which was concerned with the nucleation and motion of dislocations. Volkov and Kliukin [12] indicated that low-temperature annealing at 150 °C increased the strength and plasticity of pre-deformed magnesium by the self-blocking of dislocations. Though

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https://doi.org/10.1016/j.matchar.2018.01.050
Received 24 August 2017; Received in revised form 3 January 2018; Accepted 31 January 2018
Available online 02 February 2018
1044-5803/

the reasons for the above results have been explained, the effect of annealing on microstructures, textures, and mechanical properties of UFG Ti has not been investigated systematically.

Besides strength and ductility, the corrosion behavior is also to be considered for the application of UFG materials. Brunner et al. [13] found that the corrosion mode of aluminium alloy in 0.5 M NaCl transitioned from intergranular corrosion to pitting by ECAP processing. Kim and Kim [14] demonstrated that the grain size reduction improved the corrosion resistance of magnesium alloy in 0.1 M NaCl solution. Maleki-Ghaleh et al. [15] and Hajizadeh et al. [16] reported that the corrosion rate of nanostructured stainless steel in Ringer's solution decreased substantially compared with the coarse-grained sample. Imantalab et al. [17] suggested that the electrochemical behavior of pure copper was improved by SPD process. As for titanium, Balyanov et al. [18] and Kim et al. [19] demonstrated that UFG Ti achieved enhanced corrosion resistance in HCl and H_2SO_4 solutions compared with coarse-grained (CG) Ti. Also, it has been reported by Maleki-Ghaleh et al. [20] and Gurao et al. [21] that UFG Ti showed improved corrosion resistance in simulated body fluid. In contrast, there have been different opinions in terms of the corrosion behavior of UFG Ti in 0.9% NaCl solution. Garbacz et al. [22] believed that UFG Ti revealed a slight lower corrosion resistance in comparison with the CG Ti in 0.9% NaCl solution. On the contrary, Hoseini et al. [23] put forwarded that UFG Ti was more corrosion resistant in 0.16 M NaCl solution and the texture was dominating in controlling the corrosion behavior of Ti compared with the grain size. Afterwards, Filho et al. [24] suggested that the corrosion behavior of UFG Ti produced by SPD was not changed in 0.9% NaCl solution. The above studies demonstrated that the corrosion response of UFG Ti varies among corrosion solutions. Kim et al. [25] also suggested that post-rolling annealing treatment of UFG Ti resulted in an increase of the corrosion resistance in H_2SO_4 solution. It is worth noting that little research has been done on the corrosion behavior of UFG Ti in marine environments.

Thus, the main aim of the present work is to investigate a practical procedure of enhancing both mechanical properties and corrosion resistance in marine environment of bulk UFG Ti. Herein, bulk UFG Ti was successfully produced by a high-efficiency rotary-die ECAP (RD-ECAP) and subsequently annealed for a short duration. We would discuss the effect of post-ECAP annealing on microstructure, textures, as well as mechanical properties at room temperature and corrosion behavior of UFG Ti in artificial seawater. In this paper, a bulk UFG Ti with high strength, good ductility and enhanced corrosion resistance was achieved by continuous RD-ECAP plus short-duration annealing, thus meeting the fast-rising demand of marine exploitation.

2. Materials and Experiments

Commercially pure Ti (grade 2) was used in the study. The chemical composition (wt%) of the as-received samples was 0.015%C, 0.059%Fe, 0.062%O, 0.013%N, 0.002%H and balance Ti. The as-received raw material was hot-forged and in cylinder form. The diameter of the Ti rod was 120 mm and the mean grain size of the initial state was ~10 μm, as shown in Fig. 1.

ECAP billets with 40 mm in length and 19.5 × 19.5 mm^2 in cross-section were machined from the initial CG material. The billets were continuously pressed for 4 ECAP passes in a rotary die, as described in detail elsewhere [26,27]. Both the billets and die were preheated to 420 °C before the processing. The processing speed was 0.1 mm s^{-1}. The temperature dropped gradually to about 410 °C after each pass. Then the billet and die were heated to 420 °C during the consecutive passes for 5 min. Molybdenum disulphide and graphite was used as lubricant. The effective strain (ε) per pass was about 1.15. The 4-passed samples had an ultrafine grain size of ~500 nm. After 4 passes of ECAP, the samples were cooled in air, and then some of the UFG Ti samples processed by ECAP were annealed at 300 °C for 15 min, 30 min, 60 min, respectively, and air cooled.

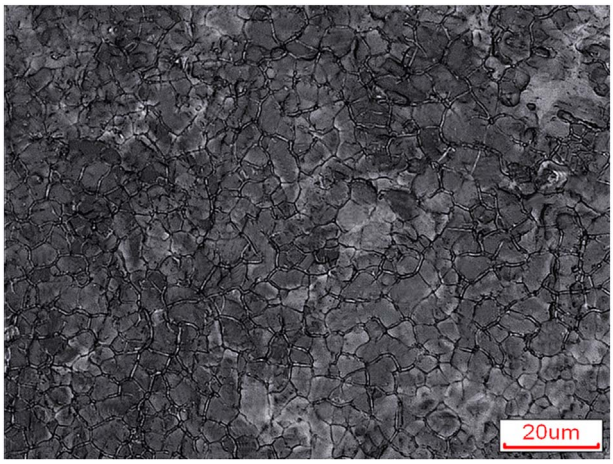

Fig. 1. Optical micrograph of the as-received pure Ti.

The observation of microstructure was performed by optical microcopy and transmission electron microcopy (TEM). The ECAP-processed Ti samples were machined along the longitudinal axis. For optical examination, samples were prepared by metallographic polishing and etching. The etching solution was a mixture of HF, nitric acid, and distilled water. Samples for TEM were mechanically thinned to ~60 μm and twin jet polished. The twin-jet polishing solution was a mixture of 6% perchloric acid and 94% ethanol. TEM images and selected area electron diffraction patterns (SAED) were obtained by using a FEI Tecnai G2 electron microscope. The operating voltage was 200 kV.

Tensile tests were performed at room temperature. Tensile samples were machined from the regions near the center of the processed billets parallel to the pressing direction. The gauge length of the samples was 6 mm. The gauge width and thickness were 2 mm and 2 mm, respectively. The displacement rate of tensile tests was 1 mm min^{-1}. Ultimate tensile strength, yield strength and elongation were measured. At least three samples for each state were tested and the final tensile curve for each state was the closest one to the average of the tests.

Corrosion tests were performed at room temperature in artificial seawater with the composition of 26.7 g/l NaCl, 2.3 g/l $MgCl_2$, 0.72 g/l KCl, 3.3 g/l $MgSO_4$, 0.2 g/l $NaHCO_3$, and 1.2 g/l $CaCl_2$, according to ASTM D1141. Samples for electrochemical tests were cut from the central part of the processed billets parallel to the pressing direction, and molded in epoxy with exposed surface of 1 cm^2. All the samples were polished and cleaned with ethanol solution. The electrochemical impendence spectroscopy tests (EIS) were conducted at open circuit potential (OCP) using a voltage signal amplitude of 10 mV, over frequency from 100 KHz to 10 mHz. Tests of potentiodynamic polarization were carried out at a scan rate of 1 mV. The reference electrode was a saturated calomel electrode. The electrochemical impedance spectra were analyzed using equivalent circuits (R(RQ)(RQ)). At least five replicate samples for each state were tested to evaluate the electrochemical behavior.

The chemical composition of the passive film formed on the samples was analyzed by X-ray photoelectron spectroscopy (XPS). All the specimens were polished and exposed to artificial seawater for 1 h and then cleaned and dried prior to XPS analysis. The PHI 5000 VersaProbe instrument was used. Vacuum of the chamber was kept at 5 × 10^{-10} Torr and a monochromatic Al-Kα (1486.6 eV) source illuminated the sample with 90° incident angle. The sampling depth was approximately 10 nm. The calibration of the XPS spectra was done by C1s peak position (284.5 eV). Shirley method was used for the back ground correction and the mixture of the Gaussian and Lorentzian peaks (GL = 20%) was used for the curve fitting.

Samples were prepared along the pressing axis for X-ray diffraction, with Cu Kα radiation at room temperature. The data were recorded at a