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Microstructures and mechanical properties of ultrafine grained pure Ti produced by severe plastic deformation

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Abstract Microstructure evolution and mechanical behavior of ultrafine grained (UFG) commercially pure Ti produced by equal channel angular pressing (ECAP) were investigated. Repetitive pressings of the same sample were performed to six passes at 683 K, using the procedure designated as route B_c. After the sixth pass was finished, recrystallized grains were observed as similar as the fourth pass. The average size of the recrystallized grains was approximately 0.3 μm. The hardness value (H_v) continuously increases with decreasing grain size. The H_v values are in good agreement with the other experimental data of Ti produced by severe plastic deformation processes. The similar slop k_H suggests that these microstructures have similar density of dislocations in the grains produced by the severe plastic deformation processes such as torsion straining, multiple forging, and ECAP. The grain size dependence of k_y in the present samples is 7.9 $MPa\sqrt{m}$. After six-pass ECAP, the ultimate tensile strength was increased by 60%. This is most likely due to considerable grain refinement through severe deformation by ECAP. The standard Hall–Petch relation for yield strength and hardness in the ECAPed Ti implies that the ECAPed Ti samples have similar texture and that the effect of grain size on strength may prevail over the effect of texture on the strength in Ti.

Keywords Ultrafine grained · Pure titanium · Microstructures · Grain size · Severe plastic deformation

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Introduction

The equal channel angular pressing (ECAP) process is recognized to be quite effective in improving the strength of many metallic alloys through (sub) grain refinement [1, 2]. The ECAP process has been applied mainly to metals and alloys having cubic crystal structure, and the number of severe plastic deformation studies on hexagonal materials is limited. It is well known that deformation behaviors of hexagonal metals are significantly different from those of cubic metals due to the limited number of active slip systems. Pure titanium is important in biomedical applications due to its low weight, excellent corrosion resistance, and high biocompatibility [3]. However, the application of ordinary coarse-grained commercial pure Ti is limited by its relatively low ultimate tensile and fatigue strengths. Utilizing ECAP for pure Ti is great interest for its enhancement in tensile strength through grain refinement. However, the mechanical properties of the pure Ti produced by ECAP have not been systematically studied. The purpose of this study is to develop a better understanding of the microstructure evolution during ECAP and tensile behavior of ultrafine grained (UFG) pure Ti produced by ECAP. Emphasis is placed on investigating TEM microstructures and the Hall–Petch relationship for the ECAPed pure Ti.

Experimental

A commercially pure titanium (grade 2) was cut to the rods with a diameter of 14.5 mm and a length of 90 mm and then annealed at 1,073 K for 1 h in Ar atmosphere, and then quenched into room-temperature water. Its chemical composition was Ti-0.06Fe-0.01N-0.01O-0.01H (wt%). The average grain size was 105 μm after the heat treatment. ECAP was conducted using a die with an internal angle Φ of 110° and an outer curvature angle Ψ of 25°. The present ECAP die was designed to give an approximate strain ε of $\sim$0.76 on each pressing according to the following equation [2];

$$\varepsilon = \frac{2\cot(\frac{\Phi}{2}+\frac{\Psi}{2}) + \Psi \cos ec(\frac{\Phi}{2}+\frac{\Psi}{2})}{\sqrt{3}} \tag{1}$$

Repetitive pressings of the same sample were performed to six passes. During ECAP, all pressings were conducted at 683 K, using the procedure designated as route B_c, in which each sample was rotated 90° around its longitudinal axis between the passages. The details of the ECAP processing have been reported elsewhere [4]. Micro-hardness and tensile tests were carried out to evaluate the strength and ductility of the ECAP processed materials. Vickers micro-hardness (H_v) was measured on the plain perpendicular to the longitudinal axes, by imposing a load of 100 g for 15 s. Tensile properties in the transverse longitudinal directions of the ECAPed and unECAPed Ti rods were measured using the miniature tensile specimens with geometry of 5-mm gauge length, 2-mm width, 1-mm thickness, and 1.5-mm shoulder radius. The tensile samples were extracted from the center portion of the ECAPed and unECAPed materials using electro-discharge machining. A displacement rate of 1 mm/min was used for tensile testing, corresponding to an initial strain rate of 3.3×10^{-3}/s. The microstructure of the ECAPed samples was investigated using a transmission electron microscopy (TEM). The TEM specimens were thinned mechanically to a thickness of around 50 μm. Disks of 3-mm diameter were punched out of the thinned sheet, and followed by a jet polishing technique using a solution of 25% HF+75% HNO_3. TEM observations were conducted using a Philip EM420 operated at 120 kV.

Results and discussion

Prior to the ECAP process, the annealed pure Ti (unECAPed) sample contains a low dislocation density. Figure 1a shows the bright field TEM image of unECAPed pure Ti sample. In the TEM images, the low number of straight or crooked dislocations was observed in the large grains of about 150-um size. Even though typical twin images were not observed, twin-like straight striations of 5 ~ 15-nm interval were observed inside of the grains. The twin-like striations were distinguished with typical twin structures because the boundaries of the striation patterns were not shown clearly, specifically in the region exposed to the electron beam. A possible mechanism of the twin-like striation formation is considered as follows: During polishing procedure for the preparation of TEM specimens, the specific surface oxidation layer of several nanometers in thickness might be formed on Ti. The oxidation layer as the straight striations was produced by the interaction with the Ti matrix. However, the extra spots, i.e., the so-called satellite spots in the selected area diffraction (SAD) pattern image of the striations (Fig. 1b), suggested a low possibility for the oxidation layer because the satellite spots related with the several-nanometers-thick oxidation layer might not be observed in the SAD pattern. Therefore, the oxidation effect was not produced in the current microstructure. It was inferred that twin-like striation structure was made by the short-range displacement induced within one lattice spacing. In other words, the boundaries of the patterns indicated the formation of crookedness by elastic deformation, i.e., tweed.

Tweed is a modulated structure formed in the elastic deformation regime prior to twin structure. With regard to Ti, tweed is a metastable deformation structure of hexagonal close packed (HCP) lattice by strain or supersaturation. In the tweed microstructure, satellite diffraction spots mean that lattice dispersive wave (LDW) related with deformed lattice or charge density wave (CDW) representing the special periodicity of electron density is built in the matrix, which is corresponding to the formation mechanism of metastable pre-martensite.

TEM micrographs of pure Ti observed after the first ECAP pass are shown in Fig. 2a, b, c. Figure 2 indicates the dislocation density increased by ECAP deformation. The dislocations were mainly distributed at the interface between the columnar or polygonal grains. The straight band structures observed in Fig. 2a were analyzed as the slip bands. Firstly, severe plastic deformation induced during ECAP

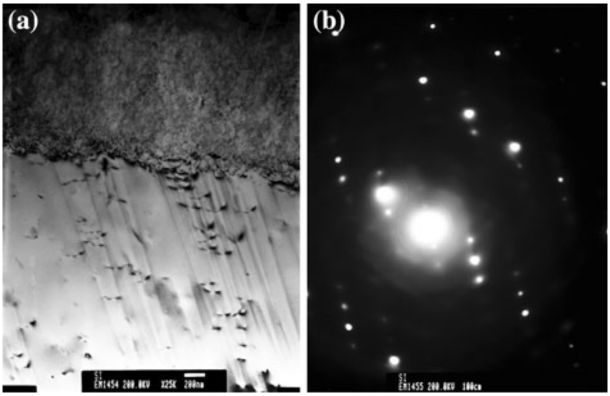

Fig. 1 TEM micrographs of pure Ti observed in unECAPed sample: **a** bright field and **b** SAD pattern image

produced the slip bands. After the first ECAP pass, the microstructures shown in Fig. 2b, c were also observed partially. Depending on the region deformed by ECAP process, relatively larger (Fig. 2b) or smaller polygonal grains (Fig. 2c) were observed. The smaller polygonal grains were formed in the more severely strained regions. Consequently, it was estimated that the columnar slip bands were broken and transformed to the polygonal gains as the induced strain was increased, and the polygonal grains became to the small one and simultaneously rotated during the transformation. As shown in Fig. 2c, new small regions representing the complex pattern were also observed between the polygonal grains. The region was judged as a cluster of low-angle grain boundaries.

After the second pass of ECAP, the observed slip band width was thinner than that of the first pass, and the band interfaces were distinguished more clearly (Fig. 2d). Meanwhile, the straight-shaped bands varied partially to the crooked shape in the severely strained region. Moreover, the discriminable images with average size of about 0.5 um were also observed in the intermittent places of the broken slip bands, indicating the most severely strained region (Fig. 2e). These images represented the clusters of low-angle grain boundaries as mentioned above. Finally, the broken polygonal gains and clusters of low-angle grain boundaries were transformed to the recrystallized grains through the repeated grain rotation and merging (Fig. 2f). The size of the recrystallized grains was approximately 1 um and definitely coarse in comparison with the slip band width in Fig. 2d or the former grains size observed in Fig. 2e.

The recrystallized gains were uniformly distributed throughout the specimen after the fourth ECAP pass was completed (Fig. 2g). Phase transformation into the recrystallized grains was considered to be completed throughout the specimen. The average size of the recrystallized grains was approximately 0.4 um. After the sixth pass was finished, the recrystallized grains were observed as similar as the fourth pass (Fig. 2h). However, the size distribution of the grains was more uniform than that of the fourth pass. The accumulated deformation energy by the additional ECAP process might change the sub-micron grains into the finer ones. However,

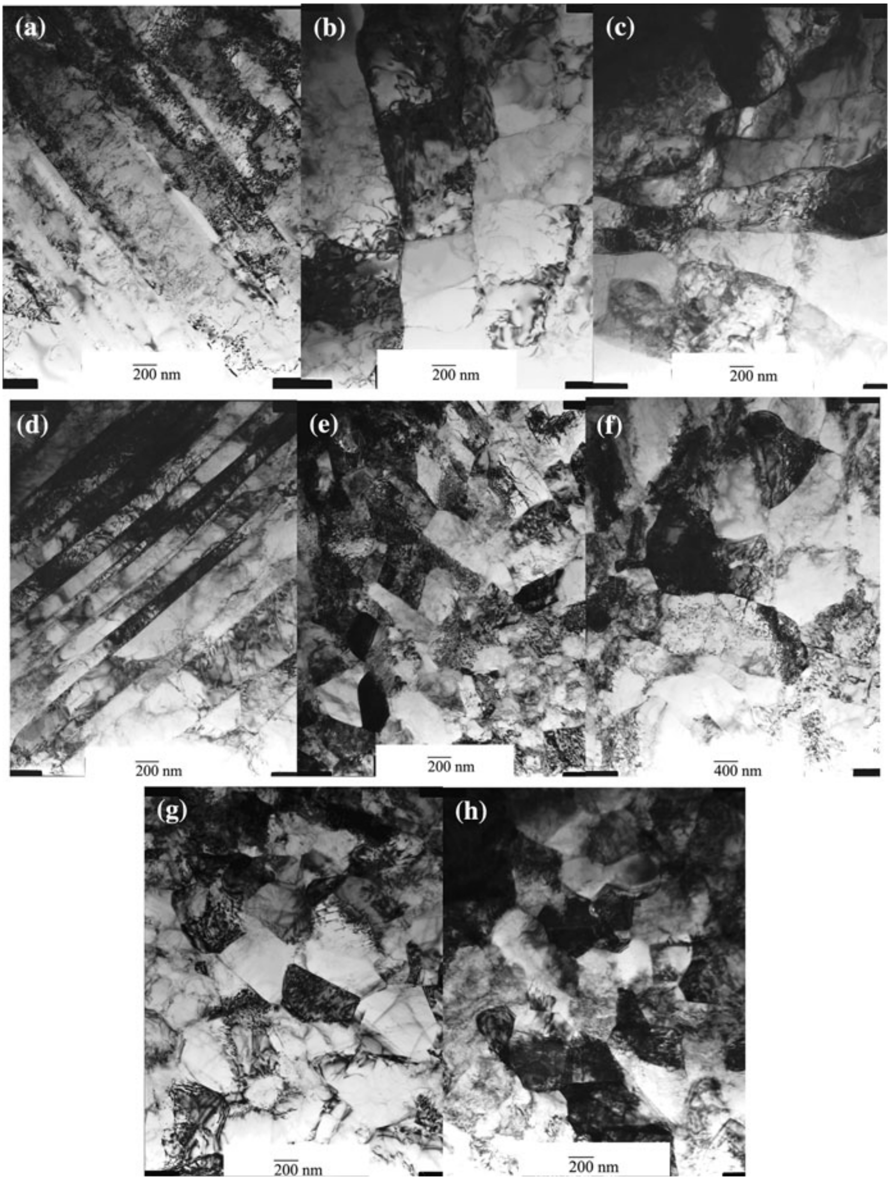

Fig. 2 TEM micrographs of pure Ti observed after ECAP

significant grain size reduction was not observed and the average size of the recrystallized grains was approximately 0.3 um. According to the result by Valiev et al. [5] on eight passed pure Ti with a total strain of 800%, the grain size was 0.3 μm, suggesting that the grain refinement effect with repeated pressing seems to diminish after about 400–500% total strain. Therefore, the grain size reduction following the recrystallization was estimated to be minor by the additional ECAP passes. In summary, the average size of recrystallized grains decreased to 1, 0.4, and 0.3 um with respect to the ECAP pass number of 2, 4, and 6, respectively.

Figure 3 shows the relation of H_v against $d^{-1/2}$ plotted in order to examine the Hall–Petch relationship for the ECAPed Ti.

$$H_V = H_0 + k_H d^{-1/2} \tag{2}$$

where H_0 and k_H are the material constants. The H_v value continuously increases with decreasing grain size. Present experimental data point lie on a single straight line depicted by Eq. (2) with $H_0 = 156.5\ H_v$ and $k_H = 1.04\, H_V\sqrt{mm}$. The present results are in good agreement with the experimental data of Ti produced by high pressure torsion by Sergueeva et al. [6]. However, experimental data of multiple forged Ti by Salishchev et al. [7] have lower H_0 (=123.4 H_v) with similar $k_H\,(= 1.01\, H_V\sqrt{mm})$. The similar slop k_H suggests that these microstructures have similar density of dislocations in the grains produced by the severe plastic deformation processes such as torsion straining, multiple forging, and ECAP. The values of H_0 and k_H can be converted to 1,533.7 MPa and $10.2\, MPa\sqrt{mm}$, respectively. The k_H slope of present pure Ti $(= 10.2\, MPa\sqrt{mm})$ was close to that of UFG Mg alloy $(= 12.7\, MPa\sqrt{mm})$ [8] and much higher than that of UFG pure Al $(= 3.6\, MPa\sqrt{mm})$ [9]. In general, severe plastic deformation processes lead to a larger k_H slope because the ultrafine grains contain a high density of dislocations. This result suggests that the dislocation density of the present ECAPed Ti sample is

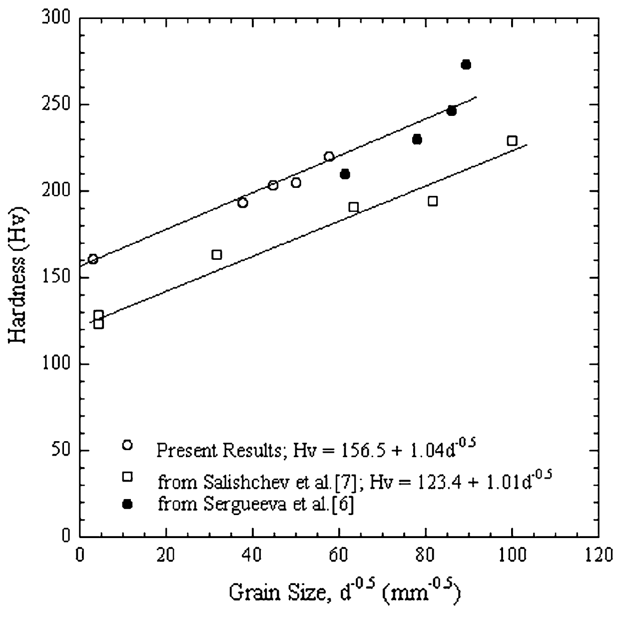

Fig. 3 Room temperature hardness against grain size for CP Ti from Refs. [6, 7] and current investigation

relatively high. The difference of H_0 (156.5 H_v ~123.4 H_v) might be due to a difference in the impurity content in Ti.

The engineering stress-engineering strain curves of the unECAPed and ECAPed Ti samples from one pass to six passes are shown in Fig. 4. Their data for yield stress (YS), ultimate tensile strength (UTS), hardness, elongation to failure, and grain size are summarized in Table 1. Similar to the tensile behavior of UFG materials reported previously [1], the ECAPed sample showed no strain hardening behavior. However, the unECAPed sample exhibited the large strain hardening behavior with large elongation. The relationship between tensile strength (YS, UTS) and number of pressings in the ECAPed Ti is shown in Fig. 5. The UTS and YS increase with an increase in the number of pressings up to six in a similar pattern. The ultimate tensile strength (UTS) and yield strength (YS) of the six-pass ECAPed sample were found to be 669 and 635 MPa, respectively. Especially, UTS and YS increase dramatically due to grain refinement (from 105 to 0.7 μm) after one pass. In contrast, the UTS and YS of the unECAPed sample were 418 and 248 MPa, respectively. After six-pass ECAP, the ultimate tensile strength was increased by 60%. This is most likely due to considerable grain refinement through severe deformation by ECAP. This fact suggests that the UFG structure of pure Ti is very advantageous for improving titanium's strength without alloying, so that it would be suitable for use in medical devices. The tensile elongation was, however, largely decreased by 31%. This is related to the decrease of strain hardening capability after ECAP, which commonly occurs in other alloys after ECAP [1].

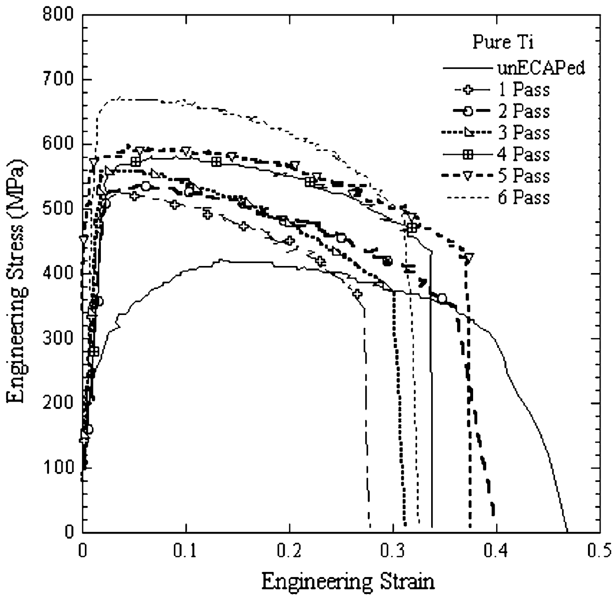

Fig. 4 Tensile stress–strain curves for the unECAPed and ECAPed Ti samples

Table 1 Mechanical properties and grain size of pure Ti

Material (unit)	UTS (MPa)	YS (MPa)	ε_f (%)	H_v -	δ (mm)
unECAPed	418	248.0	47	160.9	105
1 pass	524.1	466.6	27.8	193.4	0.7
2 pass	536.1	481.2	40.0	203.6	0.5
3 pass	558.3	523.7	31.3	–	–
4 pass	583.3	538.7	33.8	205.2	0.4
5 pass	593.7	553.3	37.5	208.3	–
6 pass	668.8	635.1	32.5	220.3	0.3
ECAPed [5]	810	650	15	–	0.3
ECAPed [14]	1,050	970	8	–	0.15
unECAPed [15]	460	380	26	–	15
unECAPed [16]	440	315	–	–	9
unECAPed [16]	380	248	–	–	32
unECAPed [16]	377	190	–	–	100

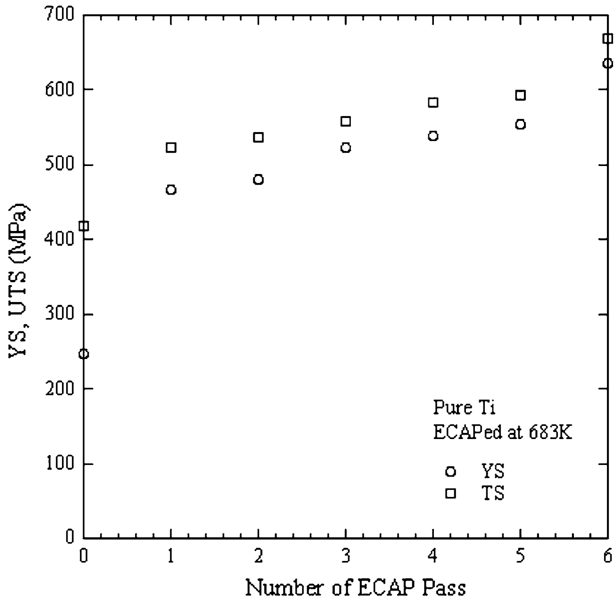

Fig. 5 UTS and YS against grain size of the unECAPed and ECAPed Ti samples

The Hall–Petch relationship correlates the grain size of a material to its yield stress. According the to Hall–Petch relationship, the yield stress σ_y of a material can be expressed as:

$$\sigma_y = \sigma_0 + k_y d^{-1/2} \tag{3}$$

where σ_0 is the lattice friction stress, k_y is the stress intensity for plastic yielding across polycrystalline grain boundaries, and d is the grain size in mm. The values of

σ_0 and k_y were determined to be 206.5 MPa and $7.9\,MPa\,\sqrt{mm}$, respectively, from Fig. 6. The grain size dependence of $k_y$in the present samples ($= 7.9\,MPa\,\sqrt{mm}$) is much lower than that for pure Ti ($= 21.2\,MPa\,\sqrt{mm}$) [10] and almost close to that for a hot extruded AZ31 alloy ($9.6\,MPa\,\sqrt{mm}$) [11]. In the absence of appreciable work hardening, the hardness (H_v) of the material is proportional to the yield stress through the expression $H_v \approx 3\sigma_y$ [12]. The slope $k_y$in the present samples ($= 7.9\,MPa\,\sqrt{mm}$) can be converted to about $2.4\,H_V\sqrt{mm}$, which is twice higher than that of k_H ($= 1.04\,H_V\sqrt{mm}$) obtained from the hardness tests for the present samples. It is not clear why there is inconsistency between YS and H_v. this difference right now.

According to Table 1, YS and hardness results are consistent each other. The yield stresses of the ECAPed Ti are higher than the unECAPed material whereas the hardness of the former is higher than that of the latter. This result is similar to from the report on the ECAPed Al alloys where a good correlation between YS and hardness was observed [13]. Inconsistency between YS and H_v has been also reported in the ECAPed Mg alloys, where hardness continued to increase while YS did to decrease with grain refinement [8]. This behavior has been understood that the strengthening effect by grain refinement is more pronounced than the softening effect by texture anisotropy in hardness test where deformation occurs locally and non-uniformly, whereas the softening effect by texture anisotropy is more dominant in tensile test where deformation occurs more macroscopically and uniformly. It is well known that the dislocation density in the grain interiors and other microstructural factors, such as solute elements and particle distribution, can also influence the slope of the Hall–Petch equation (k_y and k_H) in commercial alloys. However, pure Ti has no influence

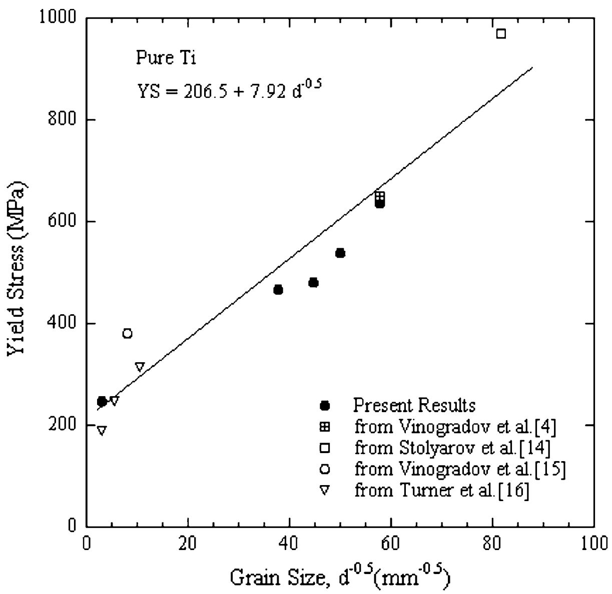

Fig. 6 Hall-Petch behavior of pure Ti

due to these factors. Thus, only dislocation density works as obstacles to the dislocation movement. The standard Hall–Petch relation for YS and hardness in the ECAPed Ti implies that the ECAPed Ti samples have similar texture. And, the effect of grain size on strength may prevail over the effect of texture on the strength in Ti.

Conclusions

Microstructure evolution and the mechanical behavior of UFG commercially pure Ti (grade 2) produced by ECAP were investigated. After the sixth pass was finished, the recrystallized grains were observed as similar as the fourth pass. However, the size distribution of the grains after the sixth pass was more uniform than that of the fourth pass. From the relation of H_v against $d^{-1/2}$, the H_v values are in good agreement with the other experimental data of Ti produced by severe plastic deformation processes. The grain size dependence of $k_y$in the Hall–Petch relation for the present samples was $7.9\,MPa\,\sqrt{mm}$. Aftersix-pass ECAP, the ultimate tensile strength was increased by 60%. This is most likely due to considerable grain refinement through severe deformation by ECAP.

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