

Article

Nanocrystalline Ti Produced by Cryomilling and Consolidation by Severe Plastic Deformation

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Abstract: We report on a study of the nanocrystalline structure in Ti, which was produced by cryogenic milling followed by subsequent consolidation via severe plastic deformation using high pressure torsion. The mechanisms that are believed to be responsible for the formation of grains smaller than 40 nm are discussed and the influence of structural characteristics, such as nanometric grains and oxide nanoparticles, on Ti hardening is established.

Keywords: Ti; cryomilling; high pressure torsion; nanostructure; strengthening

1. Introduction

For the past decade or so, the interest in the application of severe plastic deformation (SPD) techniques to manufacture nanostructured Ti has been motivated by several factors [1–15]. First, the reports on the formation of an ultrafine-grained structure from SPD processing and its influence on the mechanical behavior have led to interesting fundamental questions [1–13]. Second, the published studies suggest that nanostructuring of Ti and its alloys can result in significant enhancements in strength, ductility and fatigue life [10,14], which provide a pathway to the structural and medical applications.

Grain refinement in commercially pure Ti by various SPD methods typically leads to ultrafine grain (UFG) structures with an average grain size in the range of 100–600 nm [3–6,12–15]. However, it has been reported that the consolidation of the metal powders via SPD methods can be implemented to prepare high-density samples with grain sizes that are smaller than 50 nm [16,17]. In the view of the above discussion, in the current study, we report on a novel processing approach for producing nanocrystalline commercially pure (CP) Ti with grain sizes that are smaller than 40 nm. Accordingly, we describe experimental results obtained by consolidating cryomilled CP Ti using the SPD techniques and discuss the influence of the nanostructure on the mechanical behavior.

2. Results and Discussion

Figure 1 shows a SEM image of the Ti powder after pre-compaction (a) and after subsequent consolidation by high pressure torsion (HPT) (b). The separated powder particles with irregular morphologies and an average particle size of about 17 μm are evident (see Figure 1a). The microstructural analysis revealed the presence of pores between the powder particles (see Figure 1a); the volume fraction of porosity was estimated to be approximately 40% of the total area. The volume fraction of porosity decreased significantly after HPT (see Figure 1b), with separate pores smaller than 1 μm and a fraction <3 vol.% in the central part of the sample (within a radius of up to 2 mm from the center). The pores were not observed in the peripheral region of the disk.

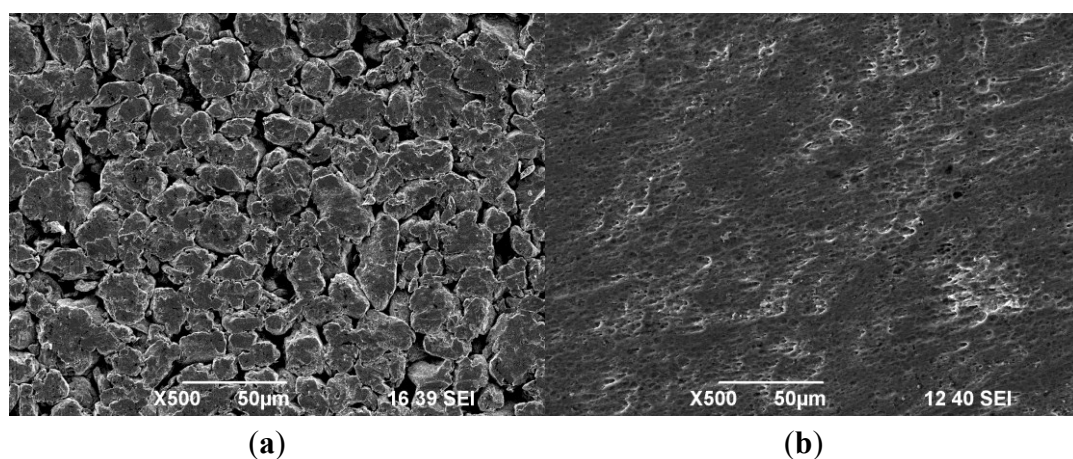


Figure 1. (a) The morphology of Ti Grade 2 powder produced by cryogenic milling and pre-compacted under a pressure of 1.95 GPa; (b) the sample's surface in the peripheral part of the sample after five turns of high pressure torsion (HPT) at 573 K.

Figure 2 shows bright-field and dark-field TEM images of the microstructure at the peripheral zone (approximately 3 mm from the center) of the sample after HPT. As noted above, this region does not show any significant porosity. The microstructure of Ti consists of ultrafine grains with an average size ranging from 25 to 40 nm (see Figure 2a). However, some coarser grains with an average size of 120 ± 50 nm were also observed in the microstructure (see Figure 2b). The fraction of the large grains in the microstructure did not exceed 7%. It is likely that the large grains in the Ti sample were formed during HPT through coalescence of the initial small grains in the cryomilled Ti powders. A similar phenomenon was observed in Cu powders subjected to HPT [18]. In this study a possible mechanism of non-uniform grain growth can be also associated with dynamic recrystallization, because SPD processing was performed at elevated deformation temperatures ($T = 573$ K) when grain boundary diffusional processes are activated.

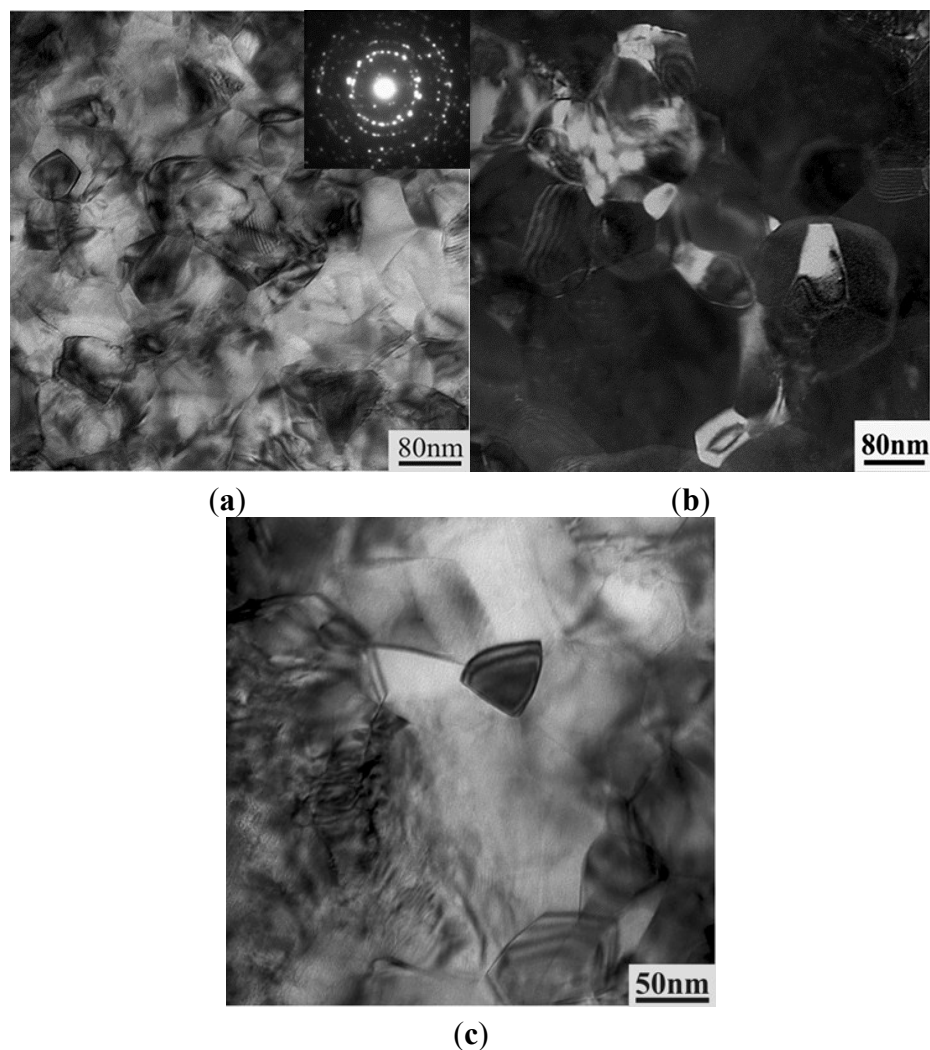


Figure 2. (a,b) Bright-field and dark-field images of ultrafine grains formed in peripheral part of the sample; (c) ultrafine grains.

The appearance of non-uniform contrast inside the grains in the dark-field images indicates the presence of a high lattice distortion (see Figure 2c). The total dislocation density at grain interiors was estimated to be approximately $2 \times 10^{14} \text{ m}^{-2}$. The spots on the SAED patterns formed concentric circles (see Figure 2). This feature is consistent with the formation of high-angle boundaries, which is typical

of nanostructured materials produced by HPT under conditions that involve a high number of rotations [1].

The microstructure in the central region of the sample revealed a non-uniform distribution of grain sizes ranging from 25 to 240 nm (see Figure 3). Such non-uniformity of the structure formed in the center of HPT samples can be attributed to the competing processes of deformation, dynamic recrystallization and grain growth, which are likely to be activated at elevated temperatures (573 K) [13]. The microhardness measurements along the disk radius from a sample center to its periphery showed a decrease in hardness from 4050 MPa in the peripheral region to 3600 MPa in the sample center. However, the microhardness was significantly higher in comparison with that of nanostructured monolithic Ti after HPT at room temperature reported in [4], where the minimum grain size was about 80 nm, and the microhardness averaged 3000 MPa.

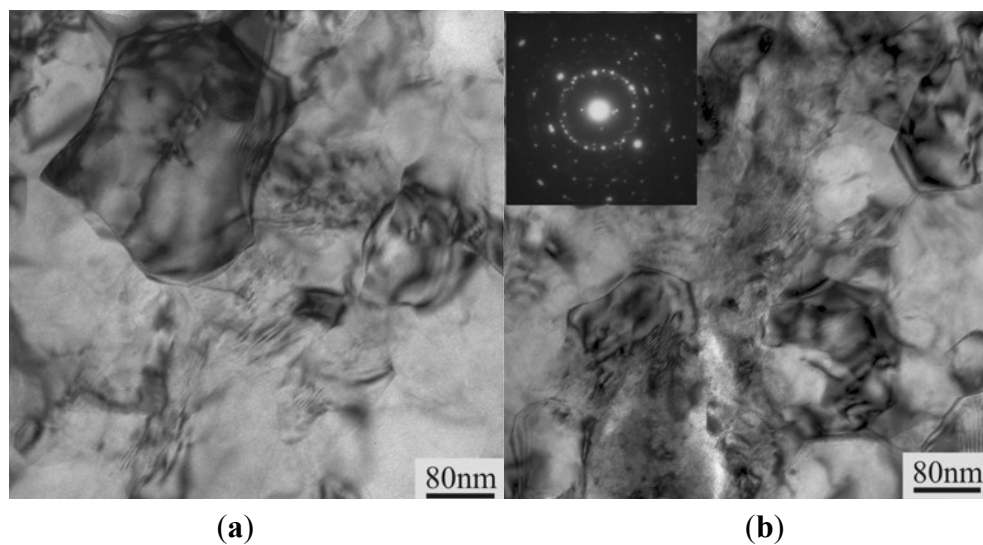


Figure 3. (a) TEM micrographs coarse grains; (b) ultrafine grains in the center of the sample.

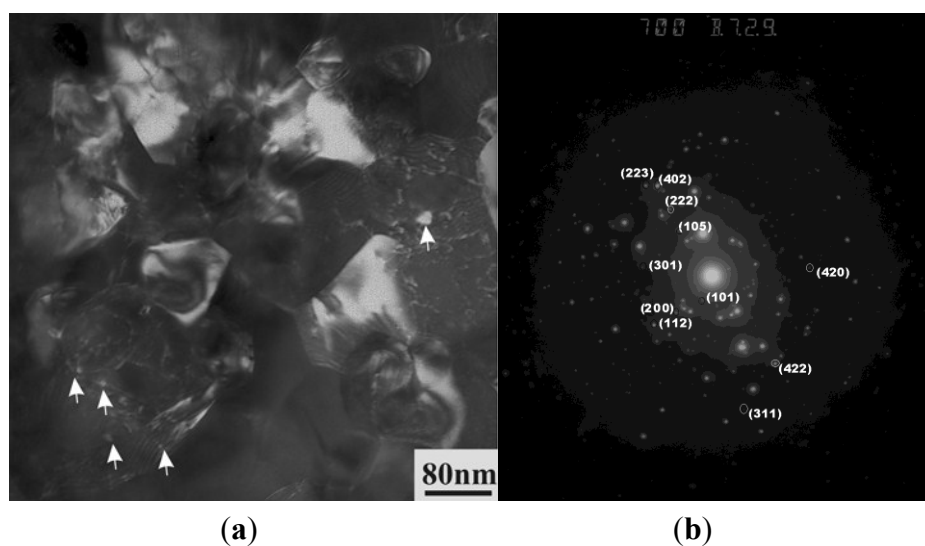


Figure 4. (a) TEM dark-field images and (b) diffraction pattern showing precipitates.

As is known, the strong affinity between Ti and O leads to the formation of a thin oxide layer in Ti, regardless of the environmental conditions used during ball milling [18,19]. Accordingly, during structural analysis of the HPT samples, particular attention was paid to the dispersed nanoparticles with a size less than 10 nm, which we observed along the grain boundaries (see Figure 4). Diffraction patterns taken from the area of 0.5 μm showed the spots with interplanar distances that correspond not only to Ti, but also to its oxides and nitrides, such as TiO_2 and TiN (see Figure 4b). Analysis of the TEM-images of the structure showed that the volume fraction of such oxide particles was very small and did not exceed 0.1% by volume.

The results presented herein support the hypothesis that it is possible to synthesize nanostructured CP Ti Grade 2 samples of high density by using a new approach involving HPT processing of powder after cryomilling. In this work, we have managed to produce a nanocrystalline structure with a mean grain size below 40 nm in CP Ti for the first time. It has been demonstrated in an earlier study [17] that the obtained nanostructure depends greatly on the size of the initial powder particles and the method of their preparation. It is known that, during milling, the material is subjected to high-strain-rate deformation of a very high degree. Here, a high level of internal stresses is created due to a high density of dislocations, disclinations, vacancies and other defects of the crystal lattice, introduced during deformation [19]. As the deformation degree increases, sub-boundaries forming in the powder particles transform into new high-angle boundaries, and the efficiency of structure refinement grows considerably in the conditions of low temperatures as a result of cyclic plastic deformation during milling in combination with limited recovery at low temperatures [19]. One benefit of cryogenic milling in an inert medium (in liquid nitrogen or argon) is that it hinders recovery processes (by virtue of the low mobility of defects at low temperatures) and thereby diminishes the time required to attain a nanocrystalline microstructure, as compared to the mechanical alloying, for example [19]. After cryogenic milling the average size of nanocrystals forming in the particles can reach 20–30 nm [19].

Subsequent compaction of ultradispersed powders should, first, ensure the fullest consolidation of the sample, and second, preserve the nanostructure of the initial ultradispersed powder [20,21]. To attain a high density of samples, sintering and/or pressing at elevated temperatures is normally used during compaction, but an intensive recrystallization occurring in the material during this process leads to a noticeable grain coarsening [21]. It is evident that the preservation of the nanocrystalline range of grain sizes can be achieved only through a decrease in the temperature and/or an increase in the pressure during pressing. As is shown in the results of present work, an efficient method of consolidation is severe plastic deformation via high pressure torsion (6 GPa) at a temperature of 573 K, at which recrystallization processes in Ti are impeded. Nevertheless, note should be made that we did not manage to completely exclude recrystallization processes in Ti at the given temperature due to high internal stresses accumulated in the particles after their milling. As a result of such intensive straining, macro- and micro-pores were practically absent in the microstructure of the samples, and the minimum grain size reached 40 nm. At the same time, the non-uniformity of deformation in the central and peripheral parts of the sample led to a noticeable inhomogeneity of the microstructure, which affected the microhardness values (3600 and 4050 MPa, respectively).

Figure 5 shows experimental points that are plotted for CP Ti Grade 2 processed by ECAP with a grain size of 600 nm [15], processed by HPT at room temperature when the average grain size reached 80 nm [4], and for Ti Grade 2 with a nanocrystalline structure and an average grain size of around

40 nm produced within the present work ($H\mu \sim 3\sigma_{0.2}$). For the sake of comparison, the Hall-Petch relationship (1) was extrapolated to the ultrafine-grained region, where the grain size dependence of yield stress in Ti is described by the following equation:

$$\sigma = \sigma_0 + K_{H-P}d^{-1/2} \quad (1)$$

where σ_0 is the lattice friction stress, and K_{H-P} is the hardening coefficient in the Hall-Petch equation. The variation σ_0 and K_{H-P} can be due to the difference in material composition and process. It should be noted that these σ_0 and K_{H-P} values are somewhat different to those reported previously, for example, well-annealed pure Ti had $\sigma_0 = 78$ MPa and $K_{H-P} = 0.40$ MPa·m^{1/2} [22], CP Ti subjected to cryogenic channel die compression with an intercept of 249 MPa, and a slope of 0.27 MPa·m^{1/2} [23]. In this work, the value of σ_0 was experimentally determined as the yield stress ($\sigma_{0.2}$) of commercially pure Ti Grade 2 with a grain size of 25 μm and it was assumed that the value of K_{H-P} was 0.24 MPa·m^{1/2} [24]. It can be seen that strengthening of Ti by ECAP processing is quite adequately described by the Hall-Petch relationship. At the same time, with the grain sizes decreasing to 80 [4] and 40 nm (present work) the yield stress of Ti is somewhat lower than the predicted classic curve. Such a deviation from the Hall-Petch relationship and even its inverse dependence has been observed in other nanocrystalline metals, normally at grain sizes of 20–30 nm [25]. This is related, in the first place, to the realization of grain boundary sliding [25]. In developing these observations, a new aspect is the fact that in Ti the deviation from the classic Hall-Petch relationship is observed already at 80 nm, evidently, conditioned by the involvement of the grain sliding mechanism in the deformation, which can take place at room temperature [4]. However, this requires a more detailed study of the nature of this unusual phenomenon.

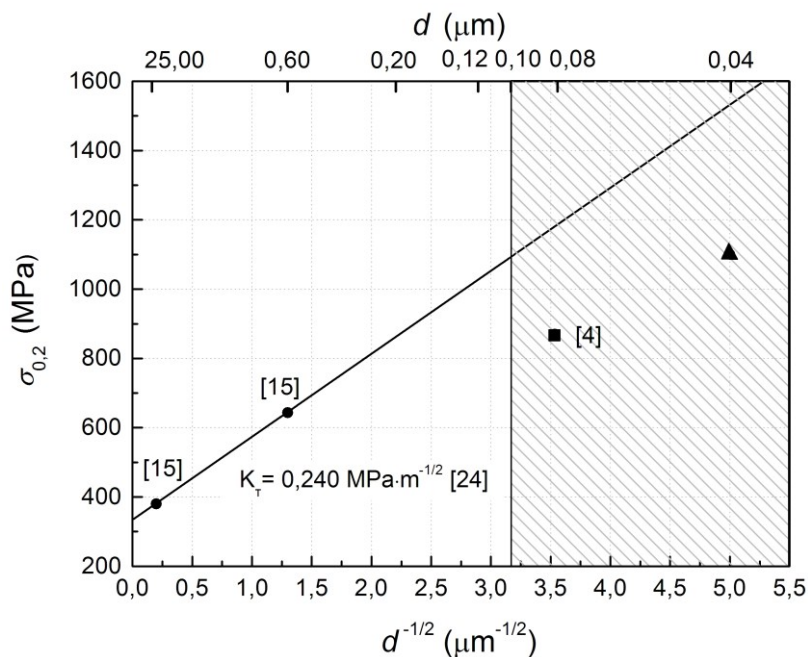


Figure 5. The relationship between grain size and yield stress ($\sigma_{0.2}$) and the experimental values for commercially pure (CP) Ti Grade 2 from earlier [4,15] and present works.

To provide insight into the influence of dispersed oxide particles on the strengthening mechanisms in CP Ti, the Orowan-Ashby equation was used to estimate their potential contribution to strength [26].

$$\Delta\sigma_{SD} = 0.16 \frac{Gb}{\lambda} \ln \frac{r}{b} \quad (2)$$

where r is the average radius of nanoparticles (~ 10 nm), G is the shear modulus (41.4 GPa for Ti) and λ is the average distance between them,

$$\lambda = \left(\frac{4\pi r^3}{3f_o} \right)^{1/3} \quad (3)$$

where f is the volume fraction of oxide particles in the structure (about 0.1%). The Burgers vector was assumed to be 0.336 nm for $a + c$ slip systems along the pyramidal plane, which were the most active ones in CP Ti during HPT [27]. Estimates show that the contribution of the oxides to the flow stress of nanocrystalline Ti is marginal (~ 4.7 MPa). According to the work [10], the changes in the concentration of oxygen near boundaries can also considerably affect the strength and ductility of UFG Ti after annealing at 623 K. From this work, it appears that the changes in the concentration of alloying elements near grain boundaries and the accompanying grain boundary segregations with their influence on the plastic deformation response should be also investigated in more detail during further study.

3. Experimental Section

CP Ti Grade 2 powder with the following chemical composition (Ti-base, -0.015H-0.052C-0.24O-0.3Fe-0.015N, wt.%) was used as the initial material for our studies. The powder was fabricated by cryogenic milling of commercial CP Ti in a liquid argon medium; the experimental details are available in the published literature [19]. The cryomilled powder was then subjected to preliminary compaction at a pressure of 1.95 GPa (described hereafter as pre-compaction), followed by SPD processing using high pressure torsion (HPT) at 573 K with 5 rotations under a pressure of 6 GPa. The samples were shaped as disks with a diameter of 10 mm and a thickness of 0.2 mm. Transmission electron microscopy was performed on a Philips CM 20 (TEM Philips is a trademark of Philips Electronic Instruments Corp., Mahwah, NJ, USA) operating at 200 kV with a condenser aperture with a 100 μm nominal diameter and a nominal beam diameter of 55 nm. TEM foils were prepared by twin-jet polishing in a solution of 5% perchloric acid and 95% methanol using a Struers Tenupol 5 electropolisher (Struers A/S, Ballerup, Denmark) at a temperature of -248 K. The operating voltage was 50 V. Observations were made in both bright and dark field imaging modes, and the selected area electron diffraction (SAED) patterns were recorded from the areas of interest using an aperture of 0.3 μm nominal diameter. The dislocation density was calculated on five bright and dark field TEM micrographs at magnification of 88,000 times with two tilting using intercept method, where the foil thickness was determined from intensity oscillations in the two-beam convergent beam electron diffraction (CBED) patterns. Microhardness was measured using a Micromet 5101 microhardness tester (BUEHLER LTD, Lake Bluff, IL, USA) at a load of 100–150g for 20 s.

4. Conclusions

For the first time, the possibility of producing in Grade 2 CP Ti a nanocrystalline structure with a grain size below 40 nm has been demonstrated. This is made possible due to high-strain-rate deformation at a cryogenic temperature in the powder milling and its subsequent consolidation by HPT at a high pressure (6 GPa) and a temperature of 573 K.

The discovered deviation of the experimental data on microhardness and yield stress from the typical Hall-Petch relationship for Ti Grade 2 extrapolated into the ultrafine-grained region may be associated with the involvement of the grain boundary sliding mechanism into deformation in nanostructured Ti already at a grain size below 100–80 nm.

Acknowledgments

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Author Contributions

Irina Semenova: idea of the paper and major preparation of text; Ilana Timochina: transmission electron microscopy of samples; Rinat Islamgaliev: high pressure torsion (HPT) of samples and discussion of the experimental results; Enrique Lavernia: cryomilling of powders, the preliminary compaction of experimental samples and discussion of the experimental results; Ruslan Valiev: discussion of the experimental results.

Conflicts of Interest

The authors declare no conflict of interest.

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