Thermal Stability and Recrystallization of Titanium Grade 4 with Ultrafine-Grained Structure

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Abstract

The paper examined annealing behavior of ultrafine-grained Ti Grade 4. The ultrafine-grained microstructure was produced by equal-channel angular pressing (ECAP) technique by using a Conform scheme and was characterized by a mean grain size of d=0.3 μm and non-equilibrium grain boundaries. The ultrafine-grained structure was found to be stable up to 400°C. The excellent thermal stability was attributed to a strain-ageing, i.e., the enhanced diffusion of interstitial solutes resulting in a formation of solute atmospheres at/near grain boundaries and dislocations. At 450–500°C, a rapid growth of strain-free grains was observed to occur. This process eliminated severely-deformed microstructure and gave rise to abrupt material softening. A further increase of the annealing temperature above 600°C resulted in precipitation of lenticular dispersoids as well as iron-rich globular β-particles. This surprising phenomenon promoted a subtle hardening effect.

1. Introduction

Due to excellent biocompatibility characteristics, commercial-purity titanium (CP Ti) is often considered as a promising material for biomedical applications [1]. A considerable strengthening of CP Ti achieved by a formation of ultrafine-grained (UFG) structure had recently provided a good perspective to essentially widen its practical use. In this context, examination of thermal stability of the UFG Ti is becoming of interest. Considering a relatively high energy stored in the UFG structure [2], such material are typically expected to be intrinsically unstable at elevated temperatures. Nevertheless, several recent works have demonstrated that severely-deformed (SPD) Ti experiences no significant microstructural changes up to 300oC [3, 4]. Moreover, a remarkable hardening effect is sometimes observed in this temperature range [3-6]. On the other hand, a further increase of the annealing temperature to 400oC usually leads to material softening and essential restoration of ductility [4, 7-10], thus evidencing a recovery process [10]. Recrystallization of SPD CP Ti is often found to occur within the temperature interval of 400–500°C [4, 8-10]. This process has been reported to develop via a discontinuous mechanism [4], i.e., it involves nucleation and subsequent growth of recrystallization nuclei. The recrystallization normally results in microstructural coarsening and therefore the UFG structure is lost [11]. At higher annealing temperatures, the recrystallization is usually followed by a grain growth. This process has been reported to be governed by the normal mechanism and thus leads to minor changes in texture [12]. The activation energy for the grain growth has been established to be close to that for the self-diffusion in α-titanium [12]. It is also worth noting that annealing of SPD Ti has been sometimes reported to lead to precipitation of carbide-based particles [13, 14]. The titanium carbide (δ phase) have been reported to precipitate at ether 350°C [14], 500°C [13] or near-beta-transus temperatures [13] and is characterized by {0001}α//{111}δ, $\{1\bar{1}20\}$α//{110}δ orientation relationship with titanium matrix [13]. The particle precipitation may affect grain-boundary migration and therefore this process may be important for thermal stability of UFG Ti. So far, however, this issue has not been studied well, to the best of the authors' knowledge. Accordingly, the present work attempted to shed some light to this unusual phenomenon.

2. Material and experimental procedures

The material used in the present investigation was CP Ti Grade 4 (manufactured by Dynamet Incorporated) with the chemical composition shown in Table 1. The relatively high interstitial content in this grade imparts significant solid-solution strengthening, thus making it particularly attractive for biomedical applications. In the as-received condition, the material had a well-annealed microstructure with a mean grain size of ~20 μm, fraction of high-angle boundaries of 95%.

Table 1. Chemical composition (wt%) of the project material

Ti	C	Fe	O	N	H
Balance	0.05	0.15	0.36	0.007	0.0021

Ultrafine-grained microstructure of Ti Grade 4 was produced by equal-channel angular pressing technique by using a Conform scheme (ECAP-C) and a B_C route [15]. ECAP-C was performed at 200°C (~0.24 Tm, where Tm is a melting point) at a speed of 33 mm/s using a 120° angle die with square channels. The material was subjected to 12 successive ECAP-C passes resulting in a total accumulated effective strain of ~8.4 with a mean grain size of 0.3 μm

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[16]. To investigate the annealing behavior of the severely-deformed titanium, the ECAP-C processed material was furnace annealed over a range of temperatures from 50°C (~0.16 Tm) to 850°C (~0.57 Tm). In all cases, specimens were heated to a particular temperature at a rate of ~100 °C/min, held for 1 h, and then water quenched. In order to facilitate interpretation of microstructure evolution during annealing, microhardness was measured. Vickers microhardness values were determined by applying a load of 1 kg for 10 s. For each material condition, 50 measurements were made to obtain an average value. For microstructural observations, the ECAP-processed billet was sectioned perpendicular its longitudinal direction and prepared by using conventional metallographic techniques. The examinations were performed by optical microscopy, transmission electron microscopy (TEM), electron probe microanalysis (EPMA), and energy-dispersive x-ray spectroscopy (EDS). TEM and high-resolution EDS examinations were conducted using a JEOL JEM 2100 transmission electron microscope (equipped with the INCA X-sight EDS system) operated at an accelerating voltage of 200 kV. The beam spot size employed for local chemical analysis was 15 nm. EPMA measurements were conducted using JEOL XM-85300FBU FEG-SEM operated at an accelerated voltage of 15 kV.

3. Results and Discussion

Room-temperature microhardness measurements provided broad insight into the microstructural changes that had occurred during annealing at various temperatures (Fig. 1a). At the temperatures below 450°C (0.37 Tm), the microhardness changed only slightly. Nevertheless, a subtle hardening at 200°C (0.24 Tm) and minor softening at 400°C (0.34 Tm) were noted, both of which agreed well with the previous results published in scientific literature [3-4, 6-10, 17]. To comprehend the hardening effect, it is necessary to realize that interstitial solutes in CP Ti become sufficiently mobile at low annealing temperatures and thus can form atmospheres near dislocations [5]; moreover, solute segregation has also been observed at grain boundaries [18]. The solute atmospheres may exert a pinning force on dislocations, thus giving rise to material hardening; this phenomenon is well-known as a strain-aging effect [5]. On the other hand, the minor softening observed after annealing at 400°C was most likely associated with a recovery process. In the range of 450–500°C (0.37–0.39 Tm) the material softened noticeably. This effect has also been found previously during annealing of severely-deformed titanium and has been usually attributed to recrystallization [4, 8, 9, 10]. A further increase in annealing temperature to 600°C (0.44 Tm) resulted in a gradual softening followed by a slight strength increase at higher temperatures. The latter observation cannot be explained in terms of grain growth which might be expected for this temperature interval.

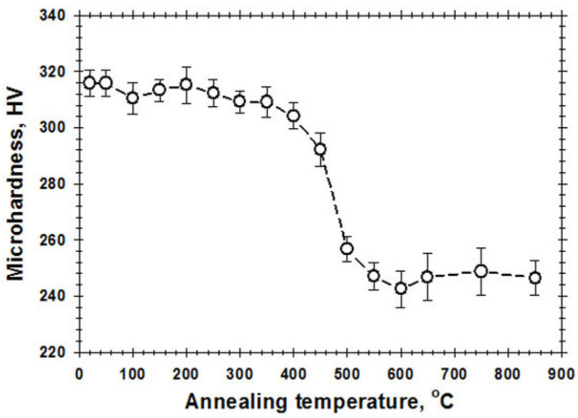

Fig. 1. Effect of annealing temperature on mean microhardness

To get a further insight into annealing-induced processes, microstructure of the heat-treated samples was closely examined. Figures 2 and 3 summarize the typical microstructures observed. Annealing below 300°C (0.29 T_m) provided no significant microstructural changes: the material was still comprised by ultrafine grains (d~0.3 μm) thus being broadly similar to the original SPD Ti (Fig. 3a). It can be clearly seen that new recrystallized equiaxed grains appear after annealing at T=450°C with a mean size of 0.6 μm (Fig. 2a). However, there were still left some areas with the deformed matrix. The appearance of a great number of small recrystallized grains at T=450°C results in the microhardness drop (Fig. 1).

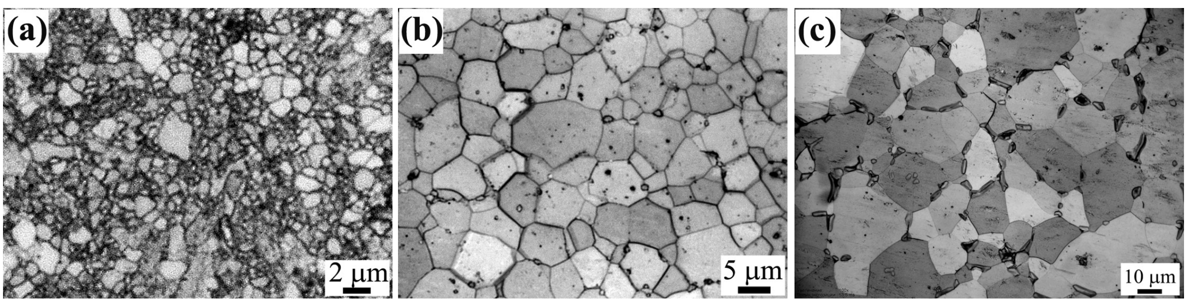

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Fig. 2. Optical micrographs showing microstructures of Ti Grade 4 after ECAP-Conform and subsequent annealing at (a) T=450°C; (b) T=600°C, and (c) T=850°C

The recrystallization process was completed only after annealing at 500°C, thus promoting an abrupt material softening (Fig. 1). A further increase of the annealing temperature to 600°C and 850°C resulted in substantial microstructure coarsening and the mean grain size achieved 5.5 µm (Fig. 2b) and 17 µm (Fig. 2c), respectively. The presence of precipitates at grain boundaries (at triple points, principally) after annealing at T=850°C is of special interest (Fig. 2c).

TEM study of the Grade 4 fine structure revealed several peculiarities. As indicated earlier, the recrystallization of UFG Grade 4 starts at about ~450°C. An example of a partially recrystallized structure (subjected to annealing at T=450°C) containing pure equiaxed grains and a deformed matrix with high defect density is shown in Fig. 3b. Annealing of UFG Ti at 600°C resulted in complete recrystallization of the material. Unusual particles were observed at the boundaries of recrystallized grains and at triple joints (Fig. 3c). Local elemental analyses of these particles detected an increased iron content ~7 at. %. On the other hand, micro-diffraction measurements showed clear evidences of β -phase (Fig. 3c). Although the allotropic transformation in pure titanium is known to occur at ~882°C, the lower transformation temperature found in the present work was most likely attributable to the relatively high content of iron, a strong β stabilizing element, in the program material. Besides, a precipitation of nanoscale, lenticular particles was observed in grain interior (Fig. 3d). A specific strain-field contrast near the particles suggested a coherent (or semi-coherent) relationship with the α-titanium matrix [19]. Moreover, the dispersoids were aligned along a common direction within each grain (Fig. 3d) thus indicating a preferred orientation for the nucleation process. It was also found that the length of the precipitates increased from ~ 90 nm at 600°C to ~ 500 nm at 850°C.

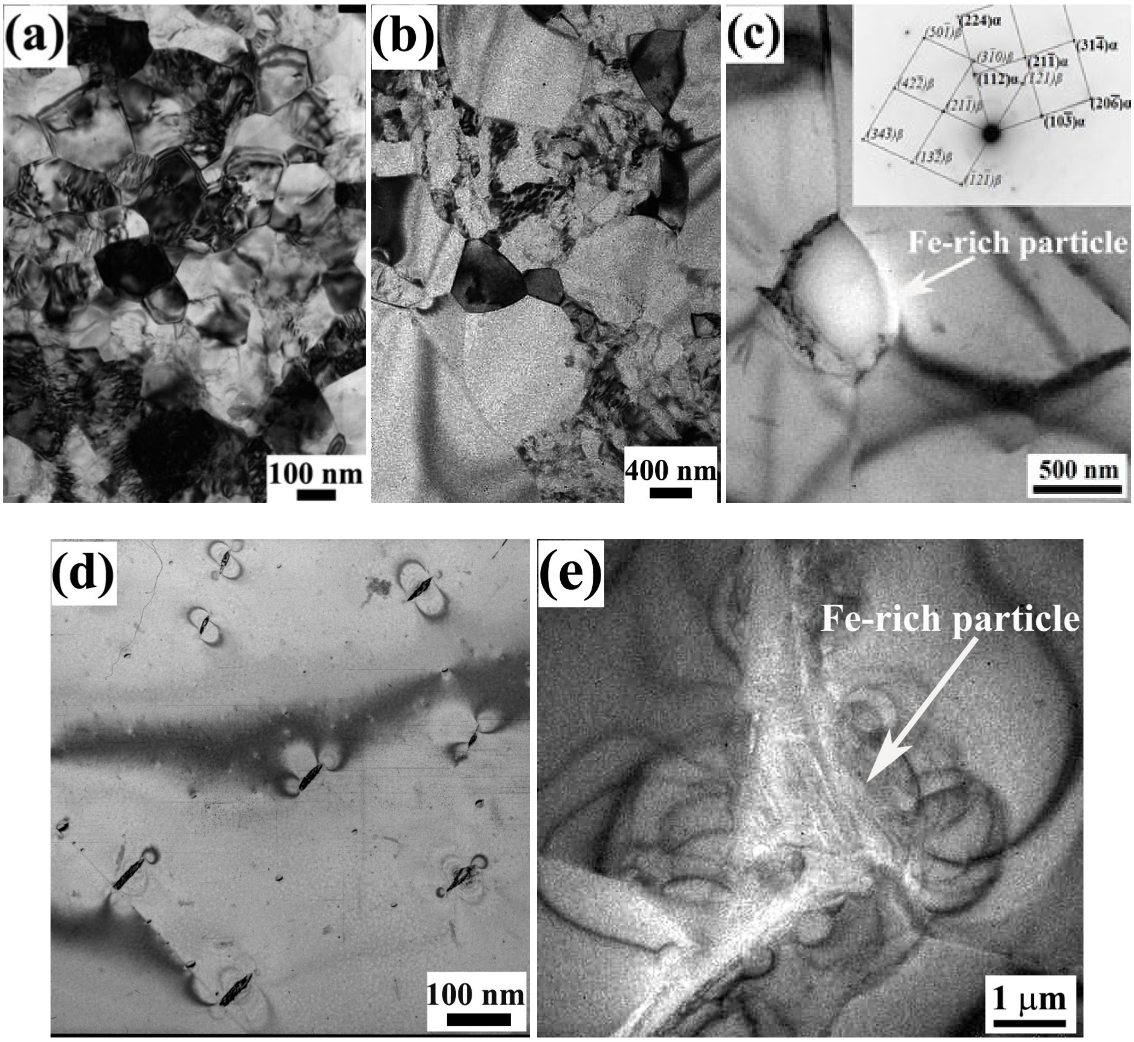

Fig. 3. Typical TEM images of the microstructure in the as-ECAP-processed condition (a) as well as after subsequent annealing at 450°C (b), 600°C, low magnification (c), 600°C high magnification (d) and 850°C (e)

TEM analysis of the structure annealed at 850°C (Fig. 3e) confirmed the presence of rather large particles located at grain boundaries with a thickness of 0.5~1 µm. These particles can be well seen through a light microscope as well (Fig. 2c). EPMA and EDS studies were performed to clarify the cause of iron-rich particles' appearance following the annealing. The particles were observed both in the state after ECAP-C and after high-temperature annealing at T=750°C (Fig. 4).

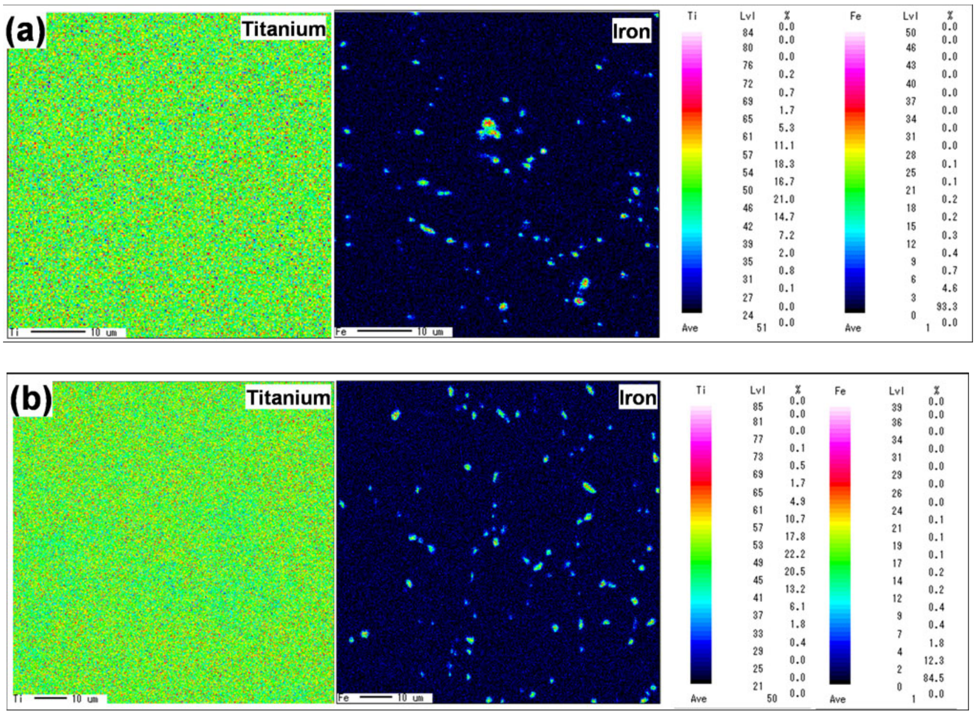

Fig. 4. EPMA maps showing distribution of titanium and iron in (a) the as-ECAP-processed material and (b) after subsequent annealing at 750°C

The studies revealed a mean content of Fe in particles after ECAP-C at about 7.2 at %, with the reduction to 5.2 at % after annealing at 750°C. The local EDS analysis of the chemical composition of particles also confirmed the trend for Fe content reduction with the increase in the annealing temperature (especially, for temperatures above 600°C). This can be accounted for the accelerative Fe diffusion from particles towards Ti matrix with the annealing temperature increase. The EPMA measurements revealed no evidence of carbides. Enhanced diffusion Fe within Ti matrix and to give rise to nanoscale lenticular particles can be one of the reasons for abnormal hardening effect after annealing at 600-850°C. This intriguing phenomenon will be studied in more detail in the next work.

5. Conclusions

1) The ECAP-processed UFG Ti exhibited excellent thermal stability up to 400°C (0.34 T_m). This was likely associated with the strain aging process in this temperature range.

2) A subsequent increase of the annealing temperature to 400^{o}C or 500^{o}C resulted in recovery or recrystallization, respectively, and the concomitant material softening.

3) The lenticular and globular iron-rich particles were found to precipitate during annealing above 600°C. Micro-diffraction analysis of such globular particles showed clear evidences of β phase. A further increase of the annealing temperature provided a reduction of concentration of iron in the globular β-particles, which was most likely related with diffusion of iron from the particles towards Ti matrix. The formation of lenticular particles in grain interior gave rise to a subtle hardening effect.

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