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Unusual hardening in Ti/Al₂O₃ nanocomposites produced by high-pressure torsion followed by annealing

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Abstract

Nanocomposites of Ti–18 vol.% Al₂O₃ were fully consolidated by applying severe plastic deformation to powder mixtures using high-pressure torsion (HPT). The HPT-processed composites exhibited an unusual increase in the hardness from 350 Hv to 650 Hv when they were annealed at 973 K for 1 h. Microstructural observations including elemental mappings were conducted using scanning electron microscopy with an electron probe X-ray micro-analyzer and scanning transmission electron microscopy with an energy dispersive X-ray spectrometer. It was shown that the Al₂O₃ particles are fragmented and the grain size of the Ti matrix is reduced to the nanometer level (<100 nm) after processing with HPT. Following the annealing, the fragmented Al₂O₃ particles with particle sizes less than ~400 nm are reduced to Al in the Ti matrix and the average grain size of Ti is coarsened to ~500 nm in conflicting with the hardness increase. The hardness increase after annealing is attributed to the dissolution of Al and O atoms in the Ti-matrix and the formation of reaction product, Ti₃Al intermetallic, at the interface and improvement of mechanical connectivity. Enrichment of Al along grain boundaries confirmed that Al atoms diffuse fast through the grain boundaries and move towards the grain interior from the grain boundaries.

Keywords: Titanium-matrix composite; Ultrafine grain; High-pressure torsion; Severe plastic deformation; Consolidation.

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1. Introduction

Composites of Al₂O₃-reinforced Ti are promising candidates for aeronautical, automobile and biomedical applications because of their high strength to weight ratio, good high temperature properties and high biocompatibility [1,2]. Fabrication of Ti/Al₂O₃ composites, especially with large fractions of Al₂O₃, is difficult using conventional techniques such as hot-press sintering because of the high sintering temperature and long sintering time [3]. Cold consolidation of Ti/Al₂O₃ composites using the high-pressure torsion (HPT) method can be an effective solution to avoid the limitations of hot-press sintering [4].

In the HPT method, which is usually used to achieve ultrafine-grained materials, a thin disc specimen is placed between two massive anvils under high pressure and intense shear is introduced by rotating the two anvils with respect to each other [5–10]. In addition to grain refinement, the HPT is also applicable as a processing tool for consolidation of metallic powders [11,12], composite powders [13,14], amorphous powders [15,16], ceramic powders [17], metallic machining chips [18,19] and amorphous machining chips [20] without sintering process. The current authors used HPT for consolidation of Ti/Al₂O₃ composites and found that the composites with the Al₂O₃ fraction of up to 50 wt.% were successfully consolidated by HPT at room temperature [4]. They reported that despite a full consolidation after processing by HPT, the composites with different Al₂O₃ fractions exhibit exceptional increases in the hardness by ~300 Hv after annealing around a temperature of 800–900 K. Although, all their results suggest the importance of post-HPT annealing in improving the hardness of the composites, the mechanism for this unusual increase is not clearly understood.

In this study, Ti–18 vol.% (20 wt.%) Al₂O₃ powder mixtures are selected as model composites and subjected to HPT and post-HPT annealing and microstructural analyses are conducted to examine the mechanism of the hardness increase following the annealing.

2. Experimental procedures

Materials used in this study were high purity Ti (99.9%) powders with ~70 μ m diameter and commercially pure α -Al₂O₃ powders with ~1 μ m particle size. The morphology of Ti and Al₂O₃ powders was reported in an earlier paper [4]. The Ti powders were mixed with 18 vol.% Al₂O₃ powders using mechanical agitation. The HPT facility consists of upper and lower anvils having a shallow hole of 10 mm diameter and 0.25 mm depth at the center. The details concerning the HPT anvils were reported elsewhere [21]. Approximately 0.5 g of the powder mixtures was put in the hole located at the center of the lower anvil and HPT was conducted at room temperature at a rotation speed of $\omega = 1$ rpm for $N = 10$ revolutions under a pressure of $P = 6$ GPa. The HPT-processed samples were annealed at 973 K for 1 h in an argon atmosphere.

The HPT-processed samples before and after annealing were evaluated through measurements of density and Vickers microhardness and were analyzed by scanning electron microscopy (SEM) equipped with an electron probe X-ray micro-analyzer (EPMA) and scanning transmission electron microscopy (STEM) equipped with an energy dispersive X-ray spectrometer (EDS). First, after processing by HPT and after annealing, disc samples were polished to a mirror-like surface and the Vickers microhardness was measured at 4 mm from the disc center in 8 radial directions using an

applied load of 1 kg for a duration of 15 s. Second, the sample density was determined by Archimedes' principle using an electronic balance with an accuracy of 0.1 mg. Third, SEM with EPMA was performed at 20 kV for examining the distribution of Al_2O_3 particles in the Ti matrix at 4 mm from the disc center. Fourth, for STEM, thin foils were prepared from the discs at 4 mm from the center with a focused ion beam (FIB) system. STEM was performed at 200 kV for microstructural observation and for recording EDS analysis and elemental mapping. The details concerning the microstructural observations were reported elsewhere [22].

3. Results and discussion

Table 1 documents the microhardness, measured density and relative density for the composites after processing with HPT, and after post-HPT annealing at 973 K for 1 h. The microhardness and density values calculated using the rule of mixtures are also included in **Table 1** using the data taken from Refs. [4,17,23,24]. It should be noted that the hardness values after HPT correspond to the steady state in the plot of hardness against equivalent strain as reported in an earlier paper [4]. The density measurements show that powder mixtures can be fully consolidated to a relative density level as high as 100% by HPT. It should be noted that an earlier paper reported that the temperature increases during the HPT processing is not significant [21], and thus, the full consolidation achieved in this study cannot be attributed to the temperature increase during the HPT process. The consolidation, however, appears to be a high-strain induced process, although the compression may have an appreciable influence on the process [25]. **Table 1** shows that post-HPT annealing results in a marked increase in the hardness, but no change in the density.

Table 1. Hardness, density and relative density for as-HPT-processed sample and for HPT-processed sample after annealing.

	HPT	Post-HPT Anneal	Rule of Mixtures
Microhardness (Hv)	350	650	540-760
Density (g.cm^{-3})	4.44	4.44	4.44
Relative Density (%)	~100	~100	---

In order to clarify the effect of annealing temperature on the hardness, hardness data are reproduced from Refs. [4,17] and plotted in **Fig. 1**. **Fig. 1** shows the variation of microhardness against the annealing temperature for Al_2O_3 , Ti (99.9%) and Ti-18 vol.% Al_2O_3 after consolidation by HPT and post-HPT annealing. While the hardness decreases in pure Ti and is very low in Al_2O_3 after annealing at 973 K, the composites containing 18 vol.% of Al_2O_3 exhibit an abrupt increases in the hardness around a temperature of 800–900 K. The increase in hardness may be due to three reasons: (1) the connectivity between Ti particles improves by post-HPT annealing; (2) the connectivity between agglomerated Al_2O_3 particles is improved by post-HPT annealing; and (3) the

connectivity between Ti and Al_2O_3 particles improves by interface reaction of Ti and Al_2O_3 by post-HPT annealing. Regarding the first reason, an earlier investigation on consolidation of Ti powders using HPT [26] concluded that the connectivity of Ti powders after processing by HPT is perfect and is the same as bulk samples. Therefore, it is unlikely that the connectivity of Ti powders can be improved by annealing. Fig. 1 also shows no increase in the hardness for Ti powders only. Regarding the second reason, the connectivity between Al_2O_3 powders is hardly improved by the annealing at 973 K for 1 h as reported earlier for the consolidation of Al_2O_3 powders by HPT and subsequent annealing [13]. Fig. 1 also shows very low hardness values for Al_2O_3 powders only after annealing at 873 K, 1273 K and 1473 K for 2 h. It is considered that the third reason should be most probable based on the observations reported earlier for the reaction between Ti and Al_2O_3 in the Ti–Al–O system [27–31].

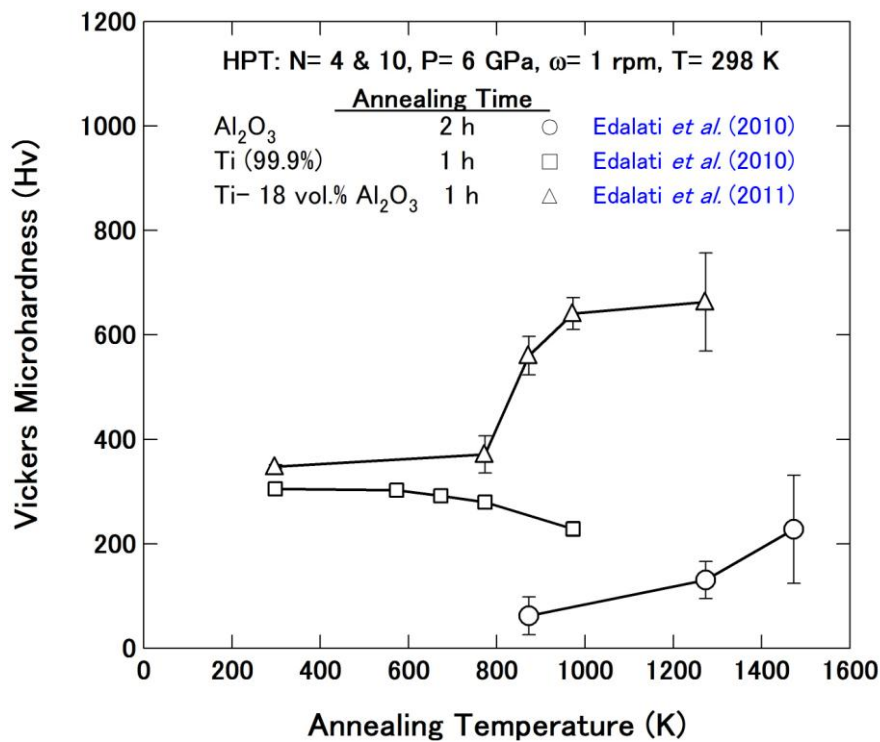


Fig. 1. Variations of Vickers microhardness with respect to annealing temperature for HPT-processed Ti composite containing 18 vol.% of Al_2O_3 including HPT-processed pure Ti and Al_2O_3 powders. Data were taken from Refs. [4,17].

SEM micrographs obtained using backscatter electrons (BSE) including the corresponding EPMA mapping of Al (right) are shown in Fig. 2(a) and (b), respectively, for the HPT sample and in Fig. 2(c) and (d), respectively, for the post-HPT annealed samples. Note that the blue color in EPMA mappings of Fig. 2(b) and (d) represents Al-enriched regions. From the EPMA analysis, the dark areas in Fig. 2(a) and (c) correspond to Al_2O_3 particles. It is shown that the microstructures consist of a uniform distribution of Al_2O_3 particles. However, there are some dark areas of which sizes are up to $\sim 50 \mu\text{m}$. Since the initial particle size of Al_2O_3 powders was $\sim 1 \mu\text{m}$, this indicates

that some fractions of the Al_2O_3 particles are present in an agglomerated form. When Fig. 2(a) is compared with Fig. 2(c), it appears that the volume fraction of Al_2O_3 particles decreases by post HPT-annealing.

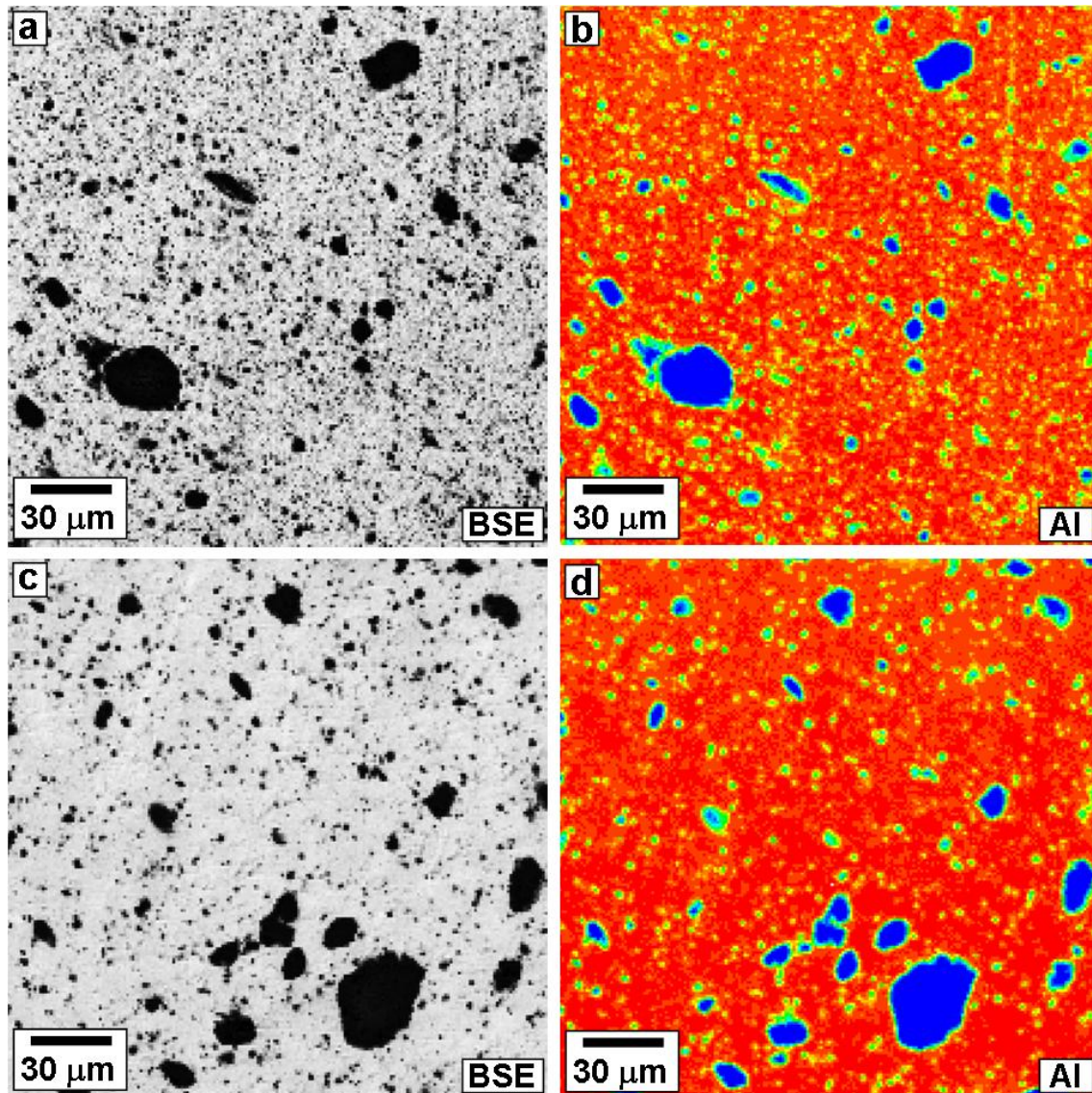


Fig. 2. SEM micrographs obtained using BSE (left) and corresponding EPMA mappings of Al (right) for samples after (a)–(b) HPT, and (c)–(d) post-HPT annealing.

Micrographs taken by STEM are shown in Fig. 3 for the sample after HPT processing. Fig. 3(a) is an overall view of the thin sample fabricated by FIB and recorded using secondary electrons (SE), and Fig. 3(b) a dark-field (DF) image and Fig. 3(c) a bright-field (BF) image, both of which are a magnified view of the rectangular area marked in Fig. 3(a). It should be noted that the dark areas in Fig. 3(b) and bright areas in Fig. 3(c) correspond to the Al_2O_3 particles. It is apparent from Fig. 3 that the HPT-processed sample contains various sizes of Al_2O_3 particles in the range from several micrometers to less than 100 nm. In particular, the particles sizes well below $\sim 1 \mu\text{m}$ are clearly visible in the DF image shown in Fig. 3(b). This indicates that the Al_2O_3 particles are fragmented during HPT processing. Close examination of the microstructure in Fig. 3(c) reveals

that grains in the Ti matrix are surrounded by ill-defined grain boundaries and their average grain size is less than 100 nm which is consistent with an earlier observation by conventional TEM [4]. This grain size is smaller than the value reported earlier for bulk Ti after processing by HPT [24].

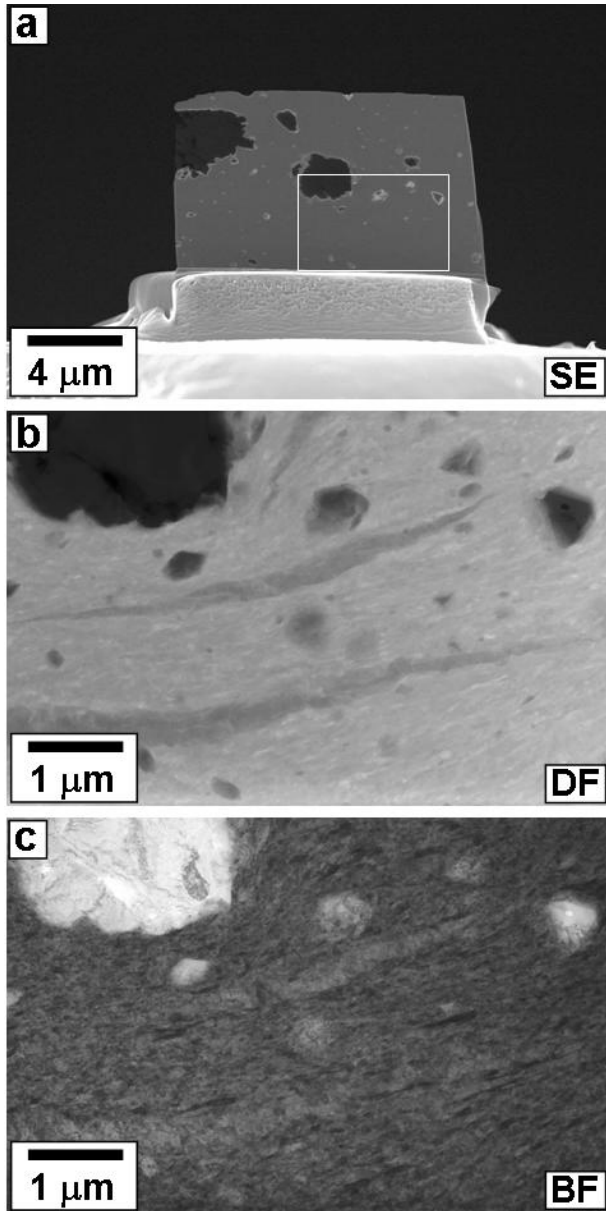


Fig. 3. STEM micrographs for sample after HPT: (a) overall view after fabrication by FIB recorded using SE, (b) DF image, and (c) BF image.

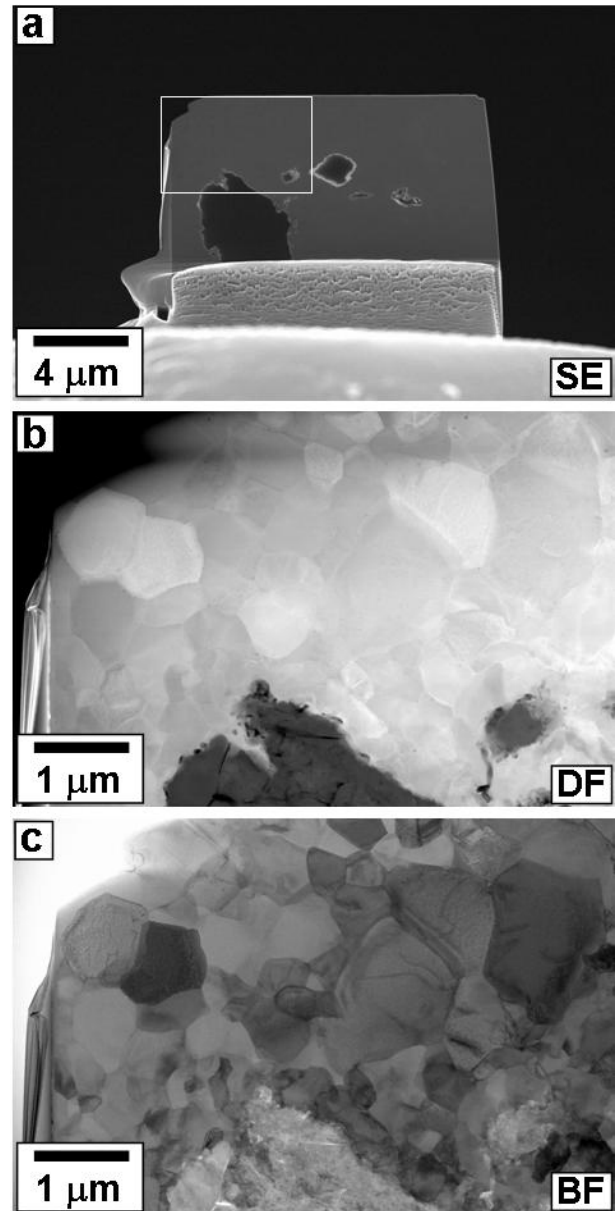


Fig. 4. STEM micrographs for sample after pos-HPT annealing: (a) overall view after fabrication by FIB recorded using SE, (b) DF image, and (c) BF image.

Fig. 4 shows STEM micrographs after annealing of the HPT-processed sample: (a) an overall view of the thin sample fabricated by FIB and recorded with SE mode, and (b) a DF image and (c) a BF image magnified from the rectangular area in (a). Examination of **Fig. 4** indicates that the Al_2O_3 particles fragmented to the sizes smaller than 400 nm are now not seen and this is well confirmed

by the DF image in Fig. 4(b). The absence of the smaller particles is also consistent with the observation shown in Fig. 2 that the volume fraction of Al₂O₃ particles decreases by the post HPT annealing. Observation of Fig. 4(c) shows that the average grain size of the Ti matrix is increased to 500 nm and grain boundaries become straight and well defined after the annealing. Now, there is a clear contradiction between the hardness measurements and the microstructural observations: the disappearance of Al₂O₃ which is a very hard phase and the coarsening of the grain size must lead to a softening, whereas the hardness value significantly increases after the annealing, as documented in Table 1 and Fig. 1. EDS analyses are further carried out to clarify the reasons for this contradiction.

Figs. 5 and 6 show (a) STEM-DF images and the corresponding EDS mappings of (b) Al, (c) Ti and (d) O, for the sample after HPT processing and after post-HPT annealing, respectively. It is apparent from Fig. 5 that Al and O are present only in the Al₂O₃ particles and no alloying occurs in the Ti matrix or in the Al₂O₃ particles through the HPT processing. However, inspection of Fig. 6 reveals that Al and O are now present in the Ti matrix. In particular, larger amounts of Al are detected more in the grain boundaries, as shown in Fig. 6(b). Here, for the reference, the traces of the grain boundaries visible in Fig. 6(a) are depicted in the elemental mapping of Fig. 6(b)–(d) by dotted lines. This suggests that Al atoms diffuse through the grain boundaries and move towards the grain interior. Although the Al₂O₃ phase is stable at the annealing temperature of 973 K, the reduction of Al₂O₃ to Al occurs thermodynamically in the presence of active Ti matrix at this temperature [27].



The distribution of O appears to be more uniform in the Ti matrix when compared with Al because of faster its diffusivity through the Ti matrix, although there may be a certain fraction of O which leaves from the material in the form of O₂ [31]. One reason for the increase in the hardness may be attributed to the presence of Al and O in the Ti matrix because these elements are known to be typical elements for the solid solution hardening of Ti [32].

The results of quantitative analysis are shown in Fig. 7 where EDS spectra are given in (a) and STEM-DF images are in (b) and (c) for the sample subjected to annealing after HPT processing. The EDS spectra in Fig. 7(a) were acquired by positioning the incident electron beam on the four points marked A, B, C and D in the STEM-DF images in Fig. 7(b) and (c). Positions A, B, and C and D are selected at the distances of 50 nm, 150 nm and more than 1 μm from the Ti/Al₂O₃ interface, respectively. It was found that positions A and B contain ~30 at.% of Al and positions C and D ~7 at.% of Al. According to the Ti–Al binary equilibrium phase diagram [32], the former composition corresponds to Ti₃Al intermetallic and the latter to a solid solution phase of Al in Ti. Therefore, the reaction at the interface may follow the form as [28]

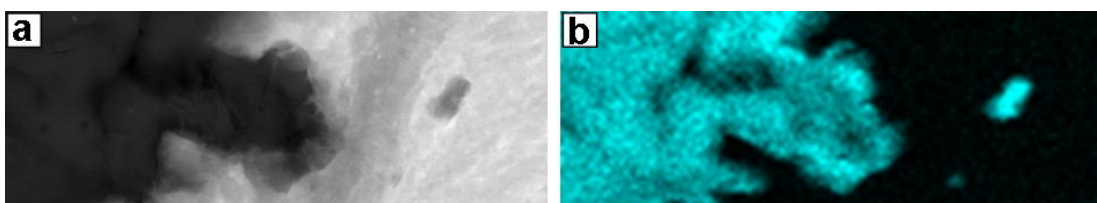


Fig. 5. (a) STEM-DF image and corresponding EDS mappings with (b) Al, (c) Ti and (d) O for sample after HPT.

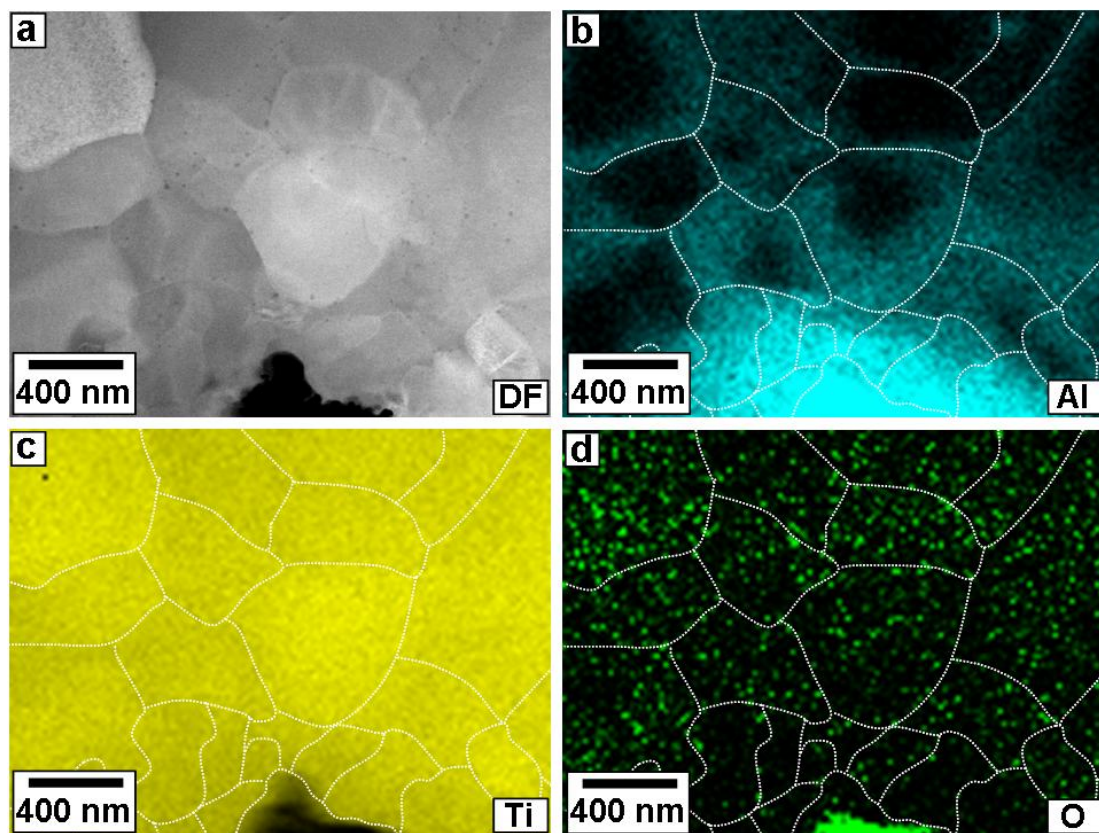


Fig. 6. (a) STEM-DF image and corresponding mappings with (b) Al, (c) Ti and (d) O for sample after post-HPT annealing.

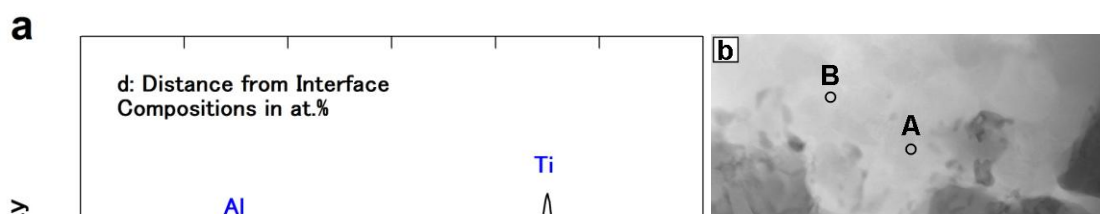


Fig. 7. (a) EDS spectra for sample after post-HPT annealing taken from positions A and B in (b) and positions C and D in (c), where (b) is STEM-DF image containing Ti/Al₂O₃ interface and (c) is STEM-DF image away from Ti/Al₂O₃ interface.

It should be noted that this reaction occurs through some intermediate reaction paths and O may present in the reaction product to some levels [27–31]. This indicates that the reaction takes place by the expense of the Al₂O₃ phase with high hardness and pure Ti with relatively low hardness to form Ti₃Al intermetallic with high hardness. It should be noted that since the fraction of Ti₃Al is very low when compared to the total fractions of Ti and Al₂O₃, it could not be detected using X-ray diffraction analysis.

It has been confirmed in Table 1 that the rule of mixtures is not applicable for the composite after HPT processing. This is because of the complexity in deducing the connectivity between the Al₂O₃ particles and the Ti matrix as well as the size and distribution of the Al₂O₃ particles for the HPT-processed sample. However, the marked increase in hardness after the annealing indicates that the formation of Ti₃Al at the interface and the dissolution of Al and O in the Ti matrix are well sufficient to exceed a hardness decrease due to a loss of Al₂O₃ particles. The rule of mixtures is now applicable for the composite after annealing because of not only a hardness increase through the formation of Ti₃Al and the solid solution effect on the matrix but also through a significant improvement of the connectivity at the interface. It should be noted that the findings reported in this study for Ti–18 vol.% nanocomposite are applicable to all other compositions that were used in an earlier paper [4].

4. Summary and conclusions

Nanocomposites of Ti–18 vol.% Al₂O₃ powder mixtures were consolidated by high-pressure torsion (HPT) and post-HPT annealing. The following findings and conclusions were obtained from this study.

1. The hardness of HPT-processed composite unusually increases from 350 Hv to 650 Hv when it anneals at 973 K for 1 h.
2. The grain size of the Ti matrix is refined to less than 100 nm after processing by HPT but the average grain size of the Ti matrix is increased from the nanometer level to ~500 nm by post-HPT annealing. This suggests that the unusual increase in the hardness is not due to the grain refinement of the Ti matrix.
3. An appreciable fraction of Al₂O₃ particles are fragmented to the sizes below ~400 nm during HPT processing and they are totally reduced to Al in the Ti matrix by the subsequent annealing. There is also a formation of Ti₃Al intermetallic at the interface between the Ti matrix and Al₂O₃ particles with larger sizes than ~400 nm.
4. Al atoms diffuse fast along the grain boundaries and they move towards the grain interior from the grain boundaries and O atoms diffuse uniformly through the grains and grain boundaries, resulting in the formation of solid solution of Al and O in the Ti matrix.
5. The unusual hardness increases is attributed to the formation of Ti₃Al intermetallic at the interface and resultant improvement of the connectivity as well as solid solution hardening through the dissolution of O and Al atoms in the Ti matrix.

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