Synthesis of titanium oxynitride by mechanical milling

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The synthesis of a titanium oxynitride phase by mechanically milling elemental titanium powder in air at ambient temperature has been studied. X-ray powder diffraction, transmission electron microscopy and chemical analysis showed that milling resulted in the formation of a nanocrystalline f c c oxynitride phase having the composition $TiNO_{0.5}$. The effects of milling time and subsequent heat treatment on the structure and lattice parameters are reported. The results indicate that mechanical milling significantly increases the reactivity of titanium with nitrogen.

1. Introduction

Mechanical alloying has attracted considerable attention in recent years as a new method for synthesizing materials. It has been demonstrated that high-energy mechanical milling of powders can cause both alloy formation and disproportionation [1–4], and induce chemical reactions [5, 6]. During ball-to-ball and ball-to-container collision events, powder particles experience unique and complex conditions of repeated pulses of high temperature and pressure [7, 8], through which highly reactive particles with nanoscale substructures are produced. As a result, chemical reactions between the milling constituents and atmospheres such as oxygen, nitrogen or air are possible.

There have been several recent reports of gas–metal reactions during mechanical milling. Alonso *et al.* [9] reported the formation of face-centred cubic structures by mechanically milling rare-earth elements such as neodymium, samarium, gadolinium and dysprosium. It has been shown that the f c c structures were NaCl-type oxynitride phases formed by reaction of the powder with air during milling [10]. Fu *et al.* [11] observed the formation of f c c ErN by ball milling of erbium and iron in leaking steel vials. It was suggested that iron acts to catalyse the dissociation of nitrogen molecules, enabling rapid nitriding to occur [11]. Guo *et al.* [12] reported the formation of an f c c (Ti,O)N phase as a result of air contamination during the mechanical milling of titanium. More recently, Calka [13] reported the formation of titanium nitride by mechanically milling elemental titanium powder in a nitrogen atmosphere.

Despite the experimental evidence of the formation of metal nitrides and oxynitrides during mechanical milling, few studies on structural characterization and reaction kinetics have been reported. In this paper we report the formation of a face-centred cubic titanium oxynitride phase during the mechanical milling of pure titanium powder in air. The kinetics of the

formation of the oxynitride phase, and its structural evolution are discussed.

2. Experimental procedure

The material used in this study was − 325 mesh, 99.7% titanium powder. The as-received powder was milled for up to 24 h using a Spex 8000 mixer/mill. Two different vials were used: a tungsten carbide vial with 10 tungsten carbide balls (diameter 11 mm) and a hardened steel vial with 10 steel balls (diameter 12.5 mm). The vials were loaded in air and had their O-ring seals removed to allow the ingress of air during milling. The ball-to-powder mass ratio was 13:1. The as-milled powder samples were annealed at 1173 K under vacuum for 12 h in sealed silica tubes.

To characterize milling kinetics, the structural evolution of the titanium powder was followed by X-ray powder diffraction (XRD) at time intervals of 2, 4, 6, 8, 10 and 24 h. XRD was carried out using a Siemens D5000 diffractometer with CuK_{α} monochromatic radiation. A Philips 430 transmission electron microscope (TEM) was used to characterize the morphology and microstructure of the milled powder. The total weight of the vial was monitored during mechanical milling and the mass change was measured at 1 h time intervals. The oxygen and nitrogen content of the as-milled and annealed powder were measured using a LECO TC136 nitrogen/oxygen analyser.

3. Results

X-ray diffraction patterns of the as-received titanium and the powder milled in the tungsten carbide vial for 24 h are shown in Fig. 1, curves (a) and (b) respectively. The transformation of titanium from the α h c p phase into an NaCl-type f c c structure is clearly seen after milling. To verify the single-phase structure in the as-milled powder, a sample was annealed at 1173 K
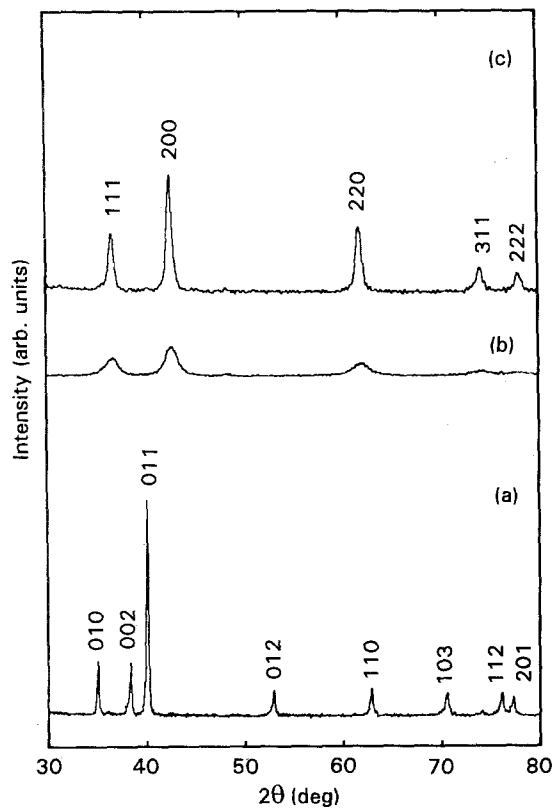
Figure 1 X-ray diffraction patterns of (a) as-received powder, (b) as-milled, and (c) annealed samples.

Figure 2 Dark-field image of as-milled titanium particle, with selected-area diffraction pattern (insert).

under vacuum. The XRD pattern of the annealed sample is also shown in Fig. 1 as curve (c). Only a single set of diffraction peaks associated with the f c c phase is observed. The lattice parameter of the f c c phase is determined to be 0.424 nm. Similar results were also obtained for milling in the hardened steel vial with steel balls. The average crystallite size estimated from XRD peak broadening based on the Scherrer equation [14] after 24 h milling is approximately 6 nm.

A typical TEM image (dark-field) of the as-milled powder is shown in Fig. 2. The as-milled powder consisted of thin, flake-shaped particles, containing many crystallites with size ranging from 6–10 nm. By tilting the sample in the microscope, it was observed that crystallites occupied the entire volume of the particles, i.e. no amorphous regions were observed. Selected-area electron diffraction showed well-defined ring patterns (Fig. 2 insert). The rings were indexed to an f c c structure with a lattice parameter of 0.424 nm, in agreement with the XRD measurements.

Chemical analysis showed that after milling for 24 h the powder contained approximately 40 at % N and 20 at % O, indicating that the f c c phase is the titanium oxynitride phase, $TiNO_{0.5}$.

The structural change of the titanium powder during milling in a steel vial was characterized by X-ray diffraction, as shown in Fig. 3. After 2 h, the main phase remained h c p with no apparent shift in diffraction peaks relative to the starting material. However, significant peak broadening was evident, indicating a reduction in the average crystallite size as a result of milling. An additional diffraction peak was also ob-
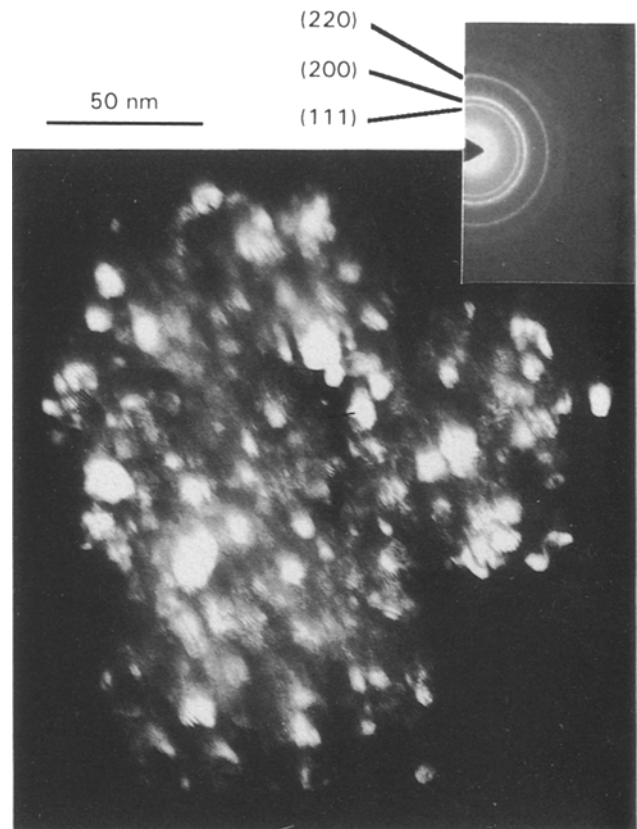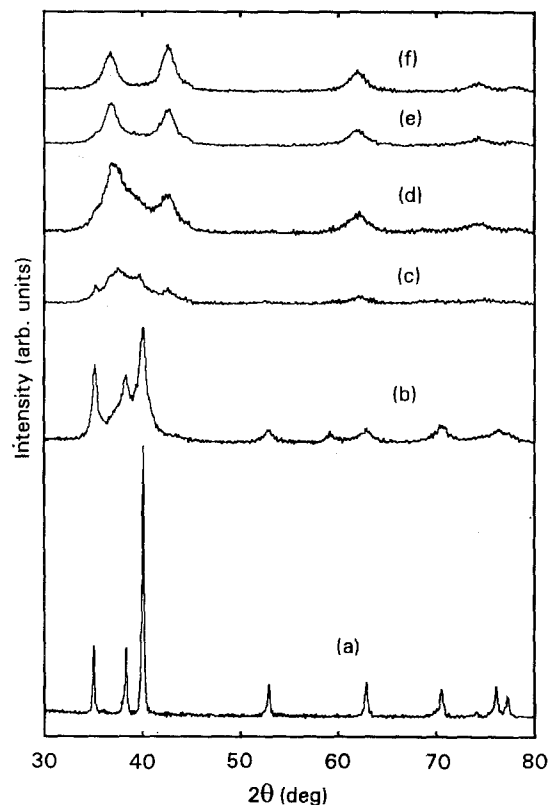

Figure 3 X-ray diffraction patterns of as-received titanium and as-milled powder for various milling times; (a) as-received, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, (f) 10 h.

served at $2\theta \sim 58°$, which could be an indication of the formation of an intermediate phase during milling. A significant change in the XRD pattern was observed after milling for 4 h, and after 6 h milling the f c c

structure clearly evolved. In addition, a subtle change in relative intensities of the (1 1 1) and (2 0 0) diffraction peaks of the f c c phase was observed as a result of further milling: the intensity of the (1 1 1) diffraction peak decreased with milling time, whereas the intensity of the (2 0 0) peak increased.

XRD patterns of samples annealed after milling are shown in Fig. 4. Two structures were observed in samples milled for different time intervals. For samples milled for 6 h or less, annealing resulted in a single h c p (α) phase, despite the f c c structure present in the 6 h as-milled sample (Fig. 3, curve d). On the other hand, for samples milled for 8 h or longer, in which an f c c structure was established after milling, annealing retained the f c c structure but sharpened its diffraction peaks, although a small peak corresponding to the major diffraction line of the α phase was still evident for both samples milled for 8 and 10 h.

A close examination of the diffraction patterns of the annealed samples showed that the diffraction peaks of the h c p phase shifted to lower angles progressively with increasing milling time. The lattice parameters of the h c p phase, a and c, were measured and the c/a ratio is shown as a function of milling time in Fig. 5. A progressive lattice expansion is evident which appears to level off after 6 h milling without the c/a ratio reaching the ideal value of 1.633. To illustrate the lattice parameter shift in forming the f c c phase, the d-spacings for two sets of crystallographically equivalent planes between the h c p and f c c structures, namely $(1\,1\,\bar{2}\,0)/(2\,2\,0)$ and $(0\,0\,0\,2)/(1\,1\,1)$ are also shown in Fig. 5.

Measurements of the weight gain during milling are

Figure 5 Lattice parameters of milled and annealed samples.
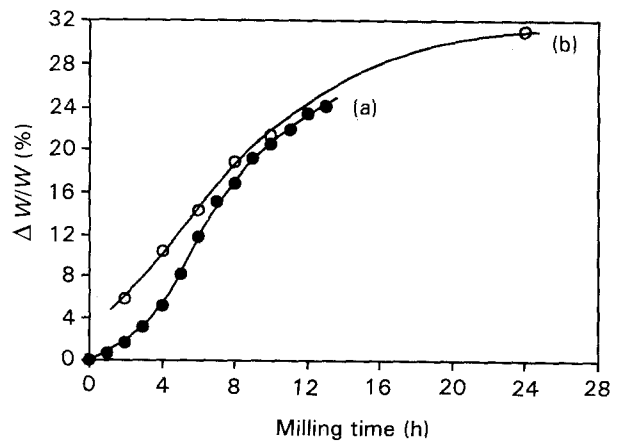
Figure 6 Relative weight change during milling based on (a) weight monitoring during milling, and (b) chemical analyses.

shown in Fig. 6 (curve a). It is seen that the rate of mass increase reached a maximum after a milling time of $\sim$ 6 h. The mass gain reached a value of 24% of the original mass of the powder after 12 h milling. Comparison with the stoichiometric oxygen and nitrogen content in $TiNO_{0.5}$, the observed 24% weight gain is equivalent to an 85% transformation from titanium to $TiNO_{0.5}$.

Results of the chemical analysis for powder samples milled for different time intervals are shown in Fig. 7. It is seen that both the nitrogen and oxygen contents increased with milling time, apparently reaching saturation values after $\sim$ 24 h milling. The total weight gain due to the absorption of oxygen and nitrogen calculated on the basis of chemical analyses is plotted in Fig. 6 as curve (b). The two curves are in good agreement. Chemical analyses were also carried-out on annealed samples, with oxygen and nitrogen contents being in agreement with those obtained in the as-milled samples.
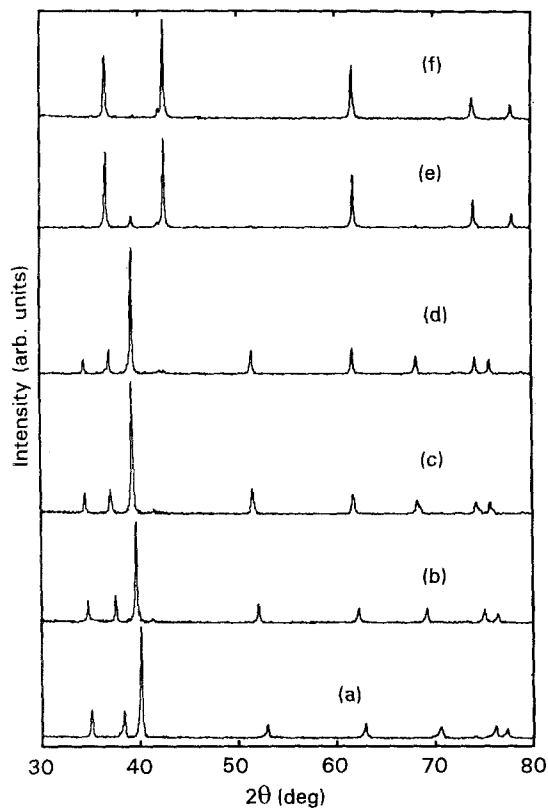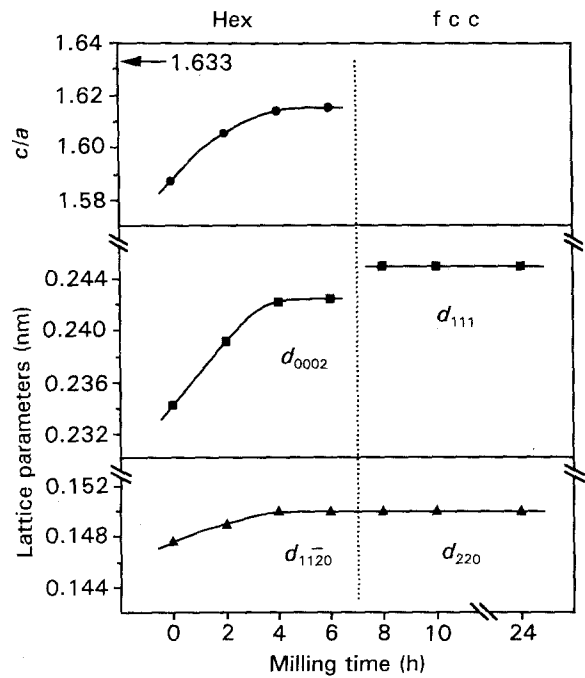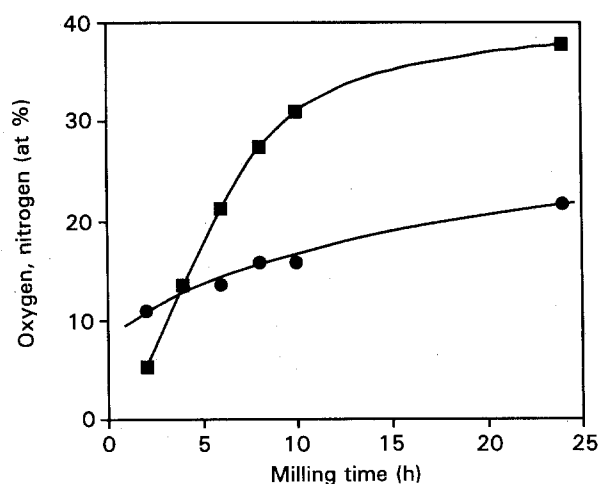

Figure 4 X-ray diffraction patterns of annealed samples. (a) As-received, (b) 2 h, (c) 4 h, (d) 6 h, (e) 8 h, (f) 10 h.

Figure 7 Effect of milling time on (●) oxygen and (■) nitrogen content.

4. Discussion

In this work, a nitrogen-rich titanium oxynitride phase was formed by mechanically milling pure titanium powder in air. Thermodynamically, titanium has a higher tendency to react with oxygen than with nitrogen. The reaction free energies are -309, -513 and -889 kJ mol^{-1} at 298 K for TiN, TiO and TiO$_2$, respectively [15]. Previous studies on the reactivity of titanium with air at elevated temperatures have shown that the titanium–oxygen reaction predominates, and this was ascribed to the slow diffusion rate of nitrogen in titanium and the instability of titanium nitride relative to the oxide at high temperatures in air [16]. Similar behaviour was also observed in this study. It was found that the as-received titanium powder reacted with oxygen to form the tetragonal TiO$_2$ phase when heated to 923 K in air. However, no reaction occurred when titanium powder was heated to 923 K in nitrogen for up to 3 h.

The drastic increase in reactivity of titanium with nitrogen during mechanical milling suggests that the kinetic conditions during milling favour the titanium–nitrogen reaction. The mechanical milling process produces ultrafine powder of sub-micrometre particles which consist of nanosize crystallites. The powder–atmosphere reaction occurs mainly on the surfaces of particles and long-distance diffusion is not required, because the repeated fracturing and welding of particles induced by milling continuously produces rough and atomically clean surfaces for reaction, and fragments the newly formed products to assist further reactions. As a result, the slow diffusion rate of nitrogen in titanium is no longer an obstacle for the reaction, rather the reaction kinetics are determined by the milling parameters such as the collision frequency and impact energies, and by surface reactivities instead of diffusion path lengths [6, 7].

An increased reactivity of erbium with nitrogen during mechanical milling with iron has been observed [11]. It was suggested by Fu *et al.* [11] that the formation of erbium nitride was due to a catalytic effect of iron in the dissociation of nitrogen molecules. In this study, the titanium oxynitride phase was

formed by milling titanium powder in both hardened steel and tungsten carbide vials. Thus, the increased reactivity of titanium with nitrogen during milling was not associated with any catalytic effect of iron in dissociating nitrogen molecules.

The XRD measurements of the as-milled powder indicate that mechanical milling did not result in an increased solubility of oxygen and nitrogen in the α-Ti phase. No shift in the lattice parameters was observed after milling up to 4 h. It is likely that the increase in oxygen and nitrogen content during milling resulted in the formation of a second phase, having its diffraction peaks obscured by the broadened α-phase peaks. On the other hand, the lattice parameters of the α-phase in the annealed specimens shifted progressively with the increasing milling time, indicative of a significantly higher solubility of oxygen and nitrogen in the α-phase at high temperatures. The increased solubility at high temperature is also responsible for the change in structure in the samples milled for 4 and 6 h, from fcc to hcp, on annealing. The present results are consistent with the room-temperature solubility of the α-phase being of the value of the starting oxygen and nitrogen content of the titanium powder (i.e $\sim$ 1500 p.p.m.) and the combined oxygen and nitrogen solubility at high temperatures being $\sim$ 36 at %. Although the Ti–O–N phase diagram does not appear to have been measured at high oxygen and nitrogen concentrations, these results are in agreement with that expected from the variation of solid solubility with increasing temperature in the binary Ti–O and Ti–N systems.

As shown in Fig. 5, the c/a ratio of the α-phase in the annealed specimens increased with increasing oxygen and nitrogen content, but did not reach the ideal value of 1.633 for spherical bonding. The transformation from α-phase to fcc was characterized by the increase in $d_{1\,1\,1}$ (fcc) relative to the corresponding $d_{0\,0\,0\,2}$ in hcp, while the $d_{2\,2\,0}$ (fcc)/$d_{1\,1\,\bar{2}\,0}$ (hcp) did not change. The constant value of lattice parameters of the fcc phase with further milling is due to there being a two-phase mixture, as is evident by the presence of the major hcp diffraction peaks in samples milled for 8 and 10 h.

The formation of a titanium oxynitride phase with similar concentration of oxygen and nitrogen has also been recently reported by Shin *et al.* [17]. In their work, a series of oxynitride compounds was prepared via thermal reaction of TiO$_2$ with NH$_3$ at temperatures above 1073 K. The highest molar ratio of oxygen and nitrogen to titanium was 1.53:1 (TiN$_{0.83}$O$_{0.70}$), being similar to the present result of 1.50:1 for TiNO$_{0.50}$. However, at high nitrogen contents, a rapid decrease in oxygen resulted in TiN$_{0.92}$O$_{0.07}$. In this work, the O/N ratio approached a constant value of 0.5 for milling time longer than 4 h.

Titanium oxynitrides have potential applications as catalysts for reactions traditionally catalysed by noble metals [17]. Syntheses of titanium oxynitrides with high specific surface areas to promote their catalytic activity are normally carried out by thermal reactions such as the plasmochemical method and temperature-programmed synthesis, all of which involve high-

temperature (> 850 K) processes [17]. It has been demonstrated in this study that mechanical milling provides an attractive way to synthesize titanium oxynitride at ambient temperatures. The nature of the mechanical milling process ensures that the product exhibits an attractive microstructure, characterized by a small particle size and high surface area, for catalytic applications.

Acknowledgements

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