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Abstract

Mechanically induced reactive synthesis of TiN via magnetically controlled ball milling of titanium under nitrogen gas was investigated using X-ray diffraction, advanced electron microscopy and Raman spectroscopy. Ball milling of titanium powder with nitrogen gas was performed in Uni-Ball-Mill, with external temperature of the vial and initial pressures of the nitrogen gas monitored, while the milled samples were taken out periodically, both before and after detection of an exothermic ignition point. Before ignition, nitrogen-enriched Ti, small proportions of TiN and very minor amounts of Ti₂N are formed, in addition to the heavily deformed Ti. Raman spectroscopy revealed the pre-ignition products to include off-stoichiometric nitrides (TiN_x) and oxynitride skin (TiO_xN_y). The formation of the new TiN and Ti₂N products before ignition was attributed to the diffusion of highly polarized active N atoms into the mechanically activated clean surfaces of Ti, followed by local reaction. This local reaction is likely promoted by numerous cycles of induced local temperature rise and rapid quenching, large surface area and accumulation of deformation defects. After the exothermic ignition, there was rapid nucleation of new TiN crystals, and simultaneous growth of the pre-existing TiN and the newly formed TiN crystals. This understanding explains the reaction pathways leading to the formation of small proportions of TiN and very minor amounts of Ti₂N before ignition and the thin-plated TiN after ignition.

Disciplines

Engineering | Science and Technology Studies

Publication Details

Oghenevweta, J. E., Wexler, D. & Calka, A. (2018). Understanding reaction sequences and mechanisms during synthesis of nanocrystalline Ti₂N and TiN via magnetically controlled ball milling of Ti in nitrogen. *Journal of Materials Science*, 53 (4), 3064-3077.

Understanding reaction sequences and mechanisms during synthesis of nanocrystalline Ti₂N and TiN via magnetically controlled ball milling of Ti in nitrogen

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ABSTRACT

Mechanically induced reactive synthesis of TiN via magnetically controlled ball milling of titanium under nitrogen gas was investigated using X-ray diffraction, advanced electron microscopy and Raman spectroscopy. Ball milling of titanium powder with nitrogen gas was performed in Uni-Ball-Mill, with external temperature of the vial and initial pressures of the nitrogen gas monitored, while the milled samples were taken out periodically, both before and after detection of an exothermic ignition point. Before ignition, nitrogen-enriched Ti, small proportions of TiN and very minor amounts of Ti₂N are formed, in addition to the heavily deformed Ti. Raman spectroscopy revealed the preignition products to include off-stoichiometric nitrides (TiN_x) and oxynitride skin (TiO_xN_y). The formation of the new TiN and Ti₂N products before ignition was attributed to the diffusion of highly polarized active N atoms into the mechanically activated clean surfaces of Ti, followed by local reaction. This local reaction is likely promoted by numerous cycles of induced local temperature rise and rapid quenching, large surface area and accumulation of deformation defects. After the exothermic ignition, there was rapid nucleation of new TiN crystals, and simultaneous growth of the pre-existing TiN and the newly formed TiN crystals. This understanding explains the reaction pathways leading to the formation of small proportions of TiN and very minor amounts of Ti₂N before ignition and the thin-plated TiN after ignition.

Introduction

Reactive synthesis of titanium nitride (TiN) by high energy ball milling of elemental titanium powder under high-purity nitrogen gas atmosphere has been studied in the past [1–7]. Similarly, TiN synthesis has been explored by ball milling or deformation of elemental titanium powder under different media and powder mixtures including air (mixture of nitrogen, oxygen and carbon dioxide) [8], pyrazine compound (C₄H₄N₂) [9], ammonia gas [4, 10, 11] and urea [12]. Other methods such as combustion synthesis by thermal heating of Ti under nitrogen gas or ammonia gas [13, 14], direct heating of Ti–Si ingot under combined atmosphere of N₂–H₂–Ar [15] and direct reaction of titanium powders with nitrogen gas at very high temperature [16] have been reported as typical routes to produce TiN. More recently, electrical discharge-assisted mechanical milling (EDMM) of titanium powders under nitrogen plasma has been carried out to produce TiN [17]. Of all these approaches, high-energy ball milling of elemental titanium powders under nitrogen atmosphere has been identified as one of the most convenient and easy routes to produce TiN in powder form [1, 18].

Mechanochemical reaction between Ti and N has been reported to either occur gradually, a typically process often known as mechanically induced solid state diffusion reaction (MDR) [7, 8, 19, 20], or occur suddenly, a phenomenon that is termed as mechanically induced self-propagating reaction (MSR) [1–3].

In MSR, an ignition is known to occur due to action of mechanical impacts, and this is associated with instantaneous exothermic reaction accompanied by great evolution of heat. The released heat helps to set up a combustion heat front that self-propagates extremely rapidly throughout the powder charge [1–3, 32]. Gotor et al. [1] reportedly attributed the self-propagating reaction to the extremely high spinning rate (960 rpm) and high pressure of the nitrogen gas (11 bars) used. Similarly, Chin et al. [2, 3] attributed the self-catalytic reaction to large impact energy and large surface area provided by the smaller particles.

Whether the reaction will occur gradually or suddenly typically depends on the milling conditions [1, 18, 20–23]. High-energy ball milling of titanium powders under nitrogen atmosphere is typically classified as metal–gas reaction system. In a typical metal–gas reaction, transfer of the gas to the interface of the metal, nucleation and growth of the new phase and adhesion of first reacted layer to the unreacted metallic layer are distinctive steps involved in the reaction mechanism. However, in ball milling, the reaction mechanism is rather complex, probably due to different milling parameters, and other mechanical effects that usually occur during the process [8, 24–26].

Typically, during ball milling of Ti and N, the starting metallic titanium particle is expected to be heavily deformed, fractured, work-hardened and eventually cold-welded. Such mechanical events are well known in generating deformation defects such as vacancies, dislocations, twinning, large amount of strains and formation of mechanically fresh and clean surfaces. Also, local temperature and pressure rise of the powders, reduced crystallite sizes and finer grains of Ti are more likely to occur. The transfer of the nitrogen molecules unto the Ti surfaces has been reported to occur preferential within clean surfaces [7, 27, 28]. In [29], clean surface membranes made from transitional metals such as vanadium (V) (or metals from Group V metals) or vanadium alloyed with ruthenium (Ru) have been reported as preferential catalytic sites for molecules of N₂ to adsorb and subsequently dissociate to form N atoms. In case of ball milling, freshly clean metallic surfaces have been reportedly generated during the stages of plastic deformation and repeated fracturing [1, 27, 28]. These clean metallic surfaces may likely represent preferential sites for adsorption of the molecules of nitrogen unto the metallic surfaces and subsequent dissociation into N atoms. The N atoms have been suggested to diffuse into the Ti crystal lattice by hooping through the interstitial Ti sites unto the subsurface and bulk Ti layers to facilitate nucleation and growth of TiN [1, 27–30].

In our previous work involving controlled ball milling of Ti with C (graphite) [31] and Ti with amorphous boron (B) [32], significant new insights were obtained, which parallels the previous understanding on the formation mechanism of MSR synthesis route. Apparently, these systems (Ti–C and Ti–B) represent metal–metalloid compositional mixtures, where the formation mechanism may likely differ from metal to gas system (Ti–N). This present research is conceived in order to further understand the detailed sequence of phase evolution induced by mechanical milling of Ti in nitrogen gas with particular emphasis on the reaction pathways leading to and after ignition.

Materials and experimental procedure

Ball milling of elemental powder of titanium (Sigma Aldrich®, 99.9% purity, $\leq 250\mu\text{m}$) was performed using 10g of titanium powder in nitrogen gas at pressure of 800kPa in a magnetically controlled Uniball mill. Other milling conditions include using four hardened steel balls, each having a diameter of 25.40mm and weight of 66.84g; corresponding to BPR of 27:1, and 80rpm. The pressure of the nitrogen gas was continuously monitored and recorded at every 1-5 h using pressure gauge. Likewise, the outside temperature of the milling vial was monitored using a pyrometer connected to the data logged computer. At different milling times, milling was interrupted and small milled products were collected in an air-tight glove bag filled with high purity helium gas. Both the pressure of the nitrogen gas and the outside temperature of the vial were plotted against time of milling. X-ray diffraction (XRD) was performed using a GBC diffractometer with Cu K α radiation radiation, Graphite Monochromator and Traces™ software and the PC-PDF software to analyse diffractometer output. Rietveld method of structural refinement (Materials Analysis Using Diffraction (MAUD)) was used to estimate the crystallite sizes, particle sizes, lattice parameters and lattice strains from the XRD profiles. The Rietveld MAUD software method typically uses a non-linear least square algorithm (Marquardt least-squares), as earlier described by Ghosh *et al* [33]. The XRD profiles were fitted with pseudo-Voigt (pV) function parameter until the quality factor (GOF) is very close to unity was obtained (within good fitness factor converges more readily between 1.2 and 1.5). Results of the quantitative analyses were extracted after sufficient convergence was obtained [34].

Field emission scanning electron microscopy (FESEM) was performed using JEOL JSM-7001F Schottky field emission gun-scanning electron microscopy (FEG-SEM) equipped with a 80 mm² X-Max^N energy dispersive X-ray spectroscopy (EDS) silicon drift detector. TEM and high resolution images were acquired using both the 200 kV JEOL JEM-2011 analytical TEM (imaging resolution 0.16nm) equipped with a LaB₆ electron source, Gatan Orius CCD camera and a JEOL SiLi energy dispersive x-ray detector (EDS) and the JEOL ARM-200F high resolution TEM (110pm) and STEM (78pm), and energy resolution (0.5eV) analytical instrument equipped with Cold Field Emission Gun source, Gatan UltraScan 1000XP CCD camera (2k x 2k) and a JEOL Centurio SDD EDS detector with 100 mm² detection area and also fitted with advanced Cs spherical aberration-corrector for the condenser lens. Selection electron diffraction patterns (SAD) were acquired at standard objective lens settings with the brightness control fully clockwise. This ensured consistent diffraction measurements and meant the internal calibration of the microscope could be relied up (to within $\pm 1\%$). Direct measurement of the reciprocal distance from the pattern centre to a diffraction spot or ring could then be converted directly into a d-spacing, by taking the reciprocal value. These diffracted rings/spots are indexed using the Ellipse Fitting Analytical (EFA) method, as described by D.R.G Mitchell [35] and also present in the DiffTools program in the Gatan DigitalMicrograph software by the same author [36]. The ellipse fitting analytical (EFA) method was employed because it enables correction due to possible pattern distortion errors (typically $<1\%$) which are always present in TEM-based diffraction systems.

Raman spectroscopy was conducted using a John Yvon HR800 HeNe 632.81nm laser line equipped with a thermoelectrically cooled (-70°C) CCD detector and a long working distance (LWD) confocal X50 objective

lens. During spectra acquisition, a notch-type optical laser blocking filter was inserted to block the highly intense laser beam from possible surface contamination while maintaining the acquisition time for each spectrum at 50 x 5 seconds while the acquired Raman spectra were analysed using LabSpec 5 software.

Results

Temperature and pressure measurement and XRD analysis of Ti-N milled products

Figure 1a, b shows the respective plots of the external temperature of the vial and the initial pressure of the nitrogen gas (P_{N_2}) measurements with increasing milling times. At the commencement of milling, the outside temperature of the vial typically increases progressively until a steady-state of temperature variation was attained at about 5 h. Within milling interval of approximately 5-28.5h, the temperature did not change significantly. However, there was an instance when the temperature slightly increases to about 1.5°C above the steady-state and then decreases back to the base temperature within a short period of time (Fig. 1a). Such a characteristic abrupt temperature increment represents an ignition stage in reactive ball milling [1-3]. The ignition effect was observed to be instantaneous and is typically known to be activated either by collision between the balls or between a ball and the wall of the vial [1-3, 31, 32]. As shown in Fig. 1a, the sudden temperature increment is relatively very small, which is not consistent with higher temperature increment earlier detected by Chin *et al* [2, 3] during milling of Ti and N, and also compared with the ball milling of Ti with C [31], and Ti with B powders [32], where the sudden temperature spike rises to about 25-30°C above the based temperature. Moreover, the typical change in the sound of the balls motion was not detected here, probably suggesting a much slower transformation of the products. On the other hand, the P_{N_2} was observed to slightly decrease within 0-25h of milling however; it rapidly decreases immediately when the slight temperature spike was detected, a result that is consistent with the earlier works of Chin *et al* [2, 3]. Thereafter, the pressure continues to decrease until about 80 h when its reduction was marginal.

Figure 1a, b Respective plots of external temperature of the vial and initial pressure of nitrogen gas (P_{N_2}) with milling time, and (c) XRD results obtained for the Ti-N milled products, sampled at different milling times

Figure 1c shows the XRD patterns obtained for milled products of Ti-N, sampled at different milling times. After milling for 5 h, the Ti peaks are slightly broadened, reduced in intensity and slightly shifted to lower Bragg's angles (Fig. 1c 5h)). The XRD analysis of milled products sampled after 10 h of milling shows continuous Ti peaks broadening and shifting to lower Bragg's angle while a very weak peak located at $2\theta = 36.6^\circ$ was observed, matching the reflection of TiN peak. The broadening of the Ti peaks within these periods of milling is probably due to reduction of the crystallite sizes. The slight lower diffraction angles may be due to formation of solid solution of nitrogen in Ti, (α Ti) or Ti(N), consistent with [1, 7]. Notably, when Ti was ball

milled in Argon (without nitrogen gas), a Ti peak shift to lower angle was not detected, rather some peaks slightly shifted to higher angles with increased milling time (XRD patterns not inserted), suggesting the likely possibility of the lower angle shifts as product of formation of Ti(N).

After 25 h of milling, the XRD analysis of the milled products revealed peaks that match Ti and a new well-defined peak, although very weak, was precisely match to be TiN (Fig. 1c (25 h)), using PDF card # 38-1420 (lattice parameter, $a = 4.24173$, space group Fm-3m (225)). After ignition, products that were sampled after 29 h show weak Ti peaks while the TiN peak intensities increase greatly. However, the TiN peaks are broad as compared to the peaks associated with Ti (Fig. 1c (29 h)), suggesting possibly the formation of nanostructural TiN. Between 29-50 h of milling, the TiN peaks increases again while the Ti steadily decreases until the Ti peaks eventually disappeared after 100h of milling (Fig. 1c). Most significant is that the TiN peaks shift to higher angles as the time of milling increases.

Table 1: Estimated values of wt.%, lattice parameters, lattice strain, crystallite sizes and particles for Ti and TiN with increasing milling times using Rietveld method of analysis

Milling time (hr)	Phase present	wt.%	Lattice parameter ($\text{\AA}$)		Lattice strain ($\times 10^{-3}$)	Crystallite sizes (nm)
			a	c		
0	Ti	100	2.9490	4.6792	-	145
5	Ti(N)	100	2.9510	4.6823	3.01	54
10	Ti(N)	98.35	2.9562	4.6906	3.11	32
	TiN	1.65	4.2210	-	1.03	3.6
25	Ti(N)	88.73	2.9638	4.7026	3.18	22
	TiN	11.27	4.2213	-	1.08	4.1
29	Ti(N)	31.9	2.9647	4.7042	3.08	13
	TiN	68.1	4.2321	-	2.02	4.3
50	Ti(N)	16.3	2.9648	4.7043	2.25	6.1
	TiN	83.7	4.2404	-	3.53	4.8
100	TiN	100	4.2483	-	3.41	8.2

Table 1 shows the average estimated crystallite sizes, lattice strain and parameters, in addition to the percent weight of each of the Ti(N) and TiN present in the milled products obtained at different milling times using the Rietveld MAUD software. As expected, the wt.% of TiN increases with increased milling time, in contrary to Ti which decreases with time of milling. Also, with increased milling time, the crystallite sizes of Ti were observed to decrease while that of TiN increases. Crystallite reduction is usually associated with increased mechanical milling of the Ti grains while the TiN crystallite increment may suggest an increase in the TiN crystals. Both the lattice parameters and strains obtained for TiN and Ti slightly increases with increasing time of milling. Increase in lattice parameters of Ti is probably due to lattice expansion due to introduction of interstitial nitrogen atoms into the Ti lattice to form Ti(N). While the increment in the lattice parameter of TiN may suggests an evolution from off-stoichiometry to stoichiometry. Likewise, the lattice strains for both TiN and Ti were observe to initially increase and thereafter decreases (Table 1). The slight decrease in the strain values of TiN with increased milling time is most likely associated with the grain refinement of the TiN grains, as earlier reported by Fecht [37]. The same trend of significant lattice strain reduction was also observed for Ti after milled products that were sampled after milling for 25 h were analysed.

Microstructural characterization of the Ti–N milled products

Figure 2 shows the FESEM backscattered images obtained for Ti-N milled products sampled before (10 and 25) and after (29 and 100 h) ignition. After 10 h of milling, FESEM (Fig. 2a) reveal large Ti particles that are severely deformed, fractured and form a typical pancake lamella structure, consistent with the evolution of a deformed metallic microstructure during ball milling [21]. Note that there are some bright regions in the images, where it is believed that nitrogen uptake is low. After 25 h of milling all the light coloured regions, believed to be associated with the starting Ti, have disappeared, the product colour is a darker grey, consistent with higher levels of nitrogen present. The product comprises a mixture of agglomerates with smaller particles, and also regions comprising of agglomerates formed by cold welding of the Ti(N) particles (Fig. 2b), and additional regions comprising darker regions within the agglomerates, believed to comprise of TiN while the slightly lighter grey regions of the agglomerates are likely Ti(N). The occurrence of some TiN after 25 h is consistent with XRD analysis of the same sample (Fig. 1c (25 h)), and also in agreement with the observation of [1-3]. Interestingly, the appearance of the milled products was observed to change from metallic grey to black

colour. In addition, there was slight iron contamination in the milled products, confirmed by EDS mapping (image not presented).

After ignition (29 h of milling), the different grey levels in the backscattered FESEM image reveals, combined with EDS analysis (described later) indicate the presence of regions comprising Ti(N), TiN and Fe contamination (lightest in colour) (Fig. 2c) and regions of unreacted Ti particles. Moreover, the appearance of the milled products was observed to significantly changes to brownish red at ignition, without the presence of the well-defined grains structure that typically characterised MSR products that are sampled immediately after ignition during milling of Ti and C (graphite) [31], and titanium and boron (amorphous) [32]. With increased milling time up to 100 h, the colour of the products later progresses from brownish red to gold colour while the FESEM image revealed mixtures of nano and agglomerates of TiN particles (Fig. 2(d)).

Fig. 2: Backscattered FESEM images obtained for Ti-N milled products, sampled after milling for: **a** 10 h, showing heavily deformed Ti particles with lamellar or pancake morphology, **b** 25 h, showing regions of heavily deformed Ti and mixtures of Ti and/or TiN particles, **c** 29 h, showing heterogeneous mixtures of Ti and/or TiN particles, and Fe contamination (lightest colour), and **d** 100 h, showing regions of nano and clusters of TiN particles.

Figures 3, 4 and 5 show TEM combined with SAD and HRSTEM results obtained for products that were sampled after milling before (10 h) and after (29 and 100 h) ignition. Before ignition, the TEM image (Fig. 3a) reveals heterogeneous mixtures of particles, confirmed by SAD to include Ti, TiN and Ti_2N . In the SAD pattern, the diffraction spots that match the reciprocal d-spacing of 0.226 nm and 0.259 nm for the respective planes of (111) and (101) of Ti_2N tetragonal crystal structure (PDF card # 17-0386, lattice parameters $a=4.9452 \text{ \AA}$, $c=3.0342 \text{ \AA}$ and space P42/mnm (136)), were found. Additional spots that match TiN and well-defined diffraction rings of Ti are also indexed. The HRSTEM image (with an insert) obtained for the same sample (Fig. 3b) revealed crystal fringes of nano Ti_2N and TiN. These newly nucleated Ti_2N and TiN crystals were found to be located in the vicinity of product interface and the nano titanium crystals. However, there is every probability that these new phases might also be found to be distributed in other regions (not necessary at the interface), as confirmed by EDS mapping of the nitrogen distribution in the milled products (image not inserted). After 25 h of milling, electron diffraction of the some selected regions (image not inserted) shows large numbers of spots that match d-spacing of Ti_2N , probably suggesting the formation of more volume fractions of Ti_2N in the milled products.

Figure 3: Ti-N milled products sampled after milling for 10 h showing: **a** TEM image and its corresponding SAD pattern and **b** HRSTEM image revealing fringes corresponding to Ti, Ti_2N and TiN crystals.

Figure 4: Ti-N products sampled after milling for 29 h showing: **a** TEM image and its corresponding indexed SAD pattern revealing d-spacings that match Ti and TiN, **b** HRSTEM image and inserts revealing fringes corresponding to TiN crystals and **c** Dark-field image acquired using the $\text{TiN}(200)$ ring, revealing thin-plated TiN particles.

Figure 4 shows TEM combined with SAD, and HRSTEM results obtained for products that were sampled after ignition (29 h of milling). Diffraction rings/spots that match TiN and Ti are found to be present in the milled products (Fig. 4a and b), consistent with the XRD results of the same sample (Fig. 1c (29 h)). In the dark-field image (Fig. 4d) acquired using the (200) ring revealed thin-plated TiN particles while the HRTEM image revealed crystal fringes that matched TiN (Fig. 4c). Similar microstructural evolutions of thin-plated TiN were observed for products that were sampled after milling for 100 h (Fig. 5) however; some of the crystals appear clumping on each other forming clusters of crystals.

Figure 5: Ti-N milled products sampled after milling for 100 h showing: **a** TEM image and its corresponding SAD pattern, and **b** HRTEM image and inserts revealing the crystal fringes that match TiN, and **c** Dark-field image acquired using the TiN(200) ring, revealing thin-plated TiN particles.

Raman spectroscopy analysis of the Ti–N milled products

Further chemical composition and bonding characteristics of the milled products were studied using Raman spectroscopy in order to obtain additional information that could help in understanding the reaction synthesis of Ti_2N and TiN. Typically, Raman scattering of stoichiometric TiN is forbidden possible due to the high O_h -symmetry that exist for the compound. However, the high symmetry that exists in the stoichiometric TiN compound was reportedly suggested to be destroyed if point defects and lattice imperfections are present [38, 39]. Such structural morphology typically exists for non-stoichiometric titanium nitride TiN_x ($x = 0.5\text{--}1.0$), reportedly Raman-active due to the presence of nitrogen vacancies and crystal imperfections [38, 39]. Typically, the presence of such defects reduces the symmetry of the stoichiometric TiN compound to allow certain atoms or perturbed crystals to display a non-zero polarizability derivatives [40].

Figure 6 shows the Raman spectra obtained for different particles regions probe by the laser line, for milled products sampled after 10 and 25 h of milling. After 10 h of milling, the spectra obtained for these regions revealed Raman signals (relatively similar and consistent with band positions) that are located in the first-order scattering frequencies (Fig. 6a). Three broad but distinct peaks are observed, all located within the frequency ranges of $225\text{--}231$, $315\text{--}318$ and $578\text{--}581\text{ cm}^{-1}$ while there was additional very weak shoulder peak that was found within $446\text{--}452\text{ cm}^{-1}$ Raman shift (Fig. 6a)). These four Raman signals has been found to be consistent with transverse acoustic (TA), longitudinal acoustic (LA), second-order acoustical (2A) and transverse optical (TO) vibrational modes inherent in the density of states for off-stoichiometric TiN_x [38, 40–43]. These bands typically correspond to A_{1g} , E_g and F_{2g} Raman-active modes caused by perturbed crystals of off-stoichiometric TiN_x . According to Spengler and Kaiser [43], vibrations in the acoustic regions ($\sim 225\text{--}452\text{ cm}^{-1}$) may likely represent scattering largely from the Ti vibrations while that of the optical regions ($458\text{--}631\text{ cm}^{-1}$) is assigned to vibration of the lighter N atoms. This implied that the vibrational intensity due to scattering from the nitrogen atoms appears to be higher than that from the titanium (Fig. 6a).

Figure 6: Raman spectra obtained for Ti-N milled products, sampled after milling (before ignition) for **a** 10 h and **b** 25 h. The intensities for Raman plots labelled (ii) and (iii) in (b) are respectively raised by approximately 6 and 8 above the zero ordinate-axis.

After 25 h of milling, the Raman spectra obtained for different particles regions were found to show variant Raman signals unlike for products sampled after 10 h that reveal similar Raman spectra. There were three distinct Raman signals found to be consistent for milled products that were probed by the laser line (Fig. 6b). The first distinct Raman signal (Fig. 6b (i)) display by several particles, with bands located within frequency range of 212-235, 319-321, and 553-577 cm^{-1} , are consistent with off-stoichiometric TiN_x [38, 40-43]. Additional peak-splitting within the 553-577 cm^{-1} band and a weak shoulder peak was also observed. These additional splits may possibly suggest some differences in the valence state or coordination of the Ti/N atoms within the Ti-N bond vibrations. The second distinct Raman signal (Fig. 6b (ii)) revealed two bands located at 227 and 574 cm^{-1} while the third Raman signal (Fig. 6b (iii)) revealed four distinct peaks (231, 340, 456 and 613 cm^{-1}) and a shoulder split-peak (546 cm^{-1}). The second and third Raman signals, not consistent with off-stoichiometric TiN_x , may likely represent additional off-stoichiometric titanium nitrides (TiN_{1+x} or Ti_{1+x}N) or off-stoichiometric oxynitride (TiO_xN_y , $x+y \leq 1$) [27]. The off-stoichiometric oxynitride may result from native oxide skin on the surface of the milled products present in the milled products. Further chemical analyses using high spatially-resolved electron energy loss spectroscopy combined with scanning TEM mode (STEM) and X-ray photoelectron spectroscopy (XPS) was use to clearly distinguish these additional chemical constituents (results not present here). It is worthwhile to mention here that these additional Raman-active bands represent Ti_2N and surface oxide skin features, as revealed from the EELS and XPS results.

Figure 7: Raman spectra obtained for Ti-N milled products, sampled after milling for **a** 29 h (after ignition), and **b** 100 h (further milling after ignition)

Figure 7 shows the Raman spectra obtained for particles probe by the laser line, for milled products sampled after milling for 29 h (just after ignition) and 100 h (further milling after ignition. After ignition, Raman probe on different particles show the three distinct peaks, consistent with off-stoichiometric TiN_x , and a lower frequency shoulder peak (165 cm^{-1}) representing a typical E_g bond vibration of surface titanium bonded with oxygen signal [44], possibly caused by surface oxidation of the milled powder during the handling process. Interestingly, the relative intensity of the TiN_x Raman band appears to increase greatly when compared to those sampled earlier (Fig. 6a and b (i)). Such increase may likely be associated to formation of more volume fractions of off-stoichiometric TiN_x with increased milling times. On the other hand, after milling for 100 h, the intensity of the TiN_x decreases significantly, suggesting possible products evolution towards stoichiometry, where the particles are not likely to be Raman-active.

Discussion

The X-ray diffraction results obtained during controlled ball milling of titanium powder under nitrogen have revealed the formation of TiN products prior to the onset of the temperature spike. Most significantly, the temperature spike was lower and the time required for it to decreases back to the base temperature was very short time (~ 30 minutes) compared when to Chin *et al* [2, 3] during milling of Ti and N, and other similar highly exothermic systems such as Ti-C and Ti-B [18, 26, 45], where higher temperature increments are recorded at the point of ignition [18, 22, 31, 32]. Such clear distinction between Ti and N and that of Ti-C and Ti-B is likely linked to the equilibrium phase diagram of Ti-N [46] compared to Ti-C [47] and Ti-B [48]. Essentially, on the Ti-N binary phase diagram [46], nitrogen is found to readily dissolve in the octahedral interstices of Ti at higher concentration, unlike that of C in Ti or B in Ti with limited solubility[47, 48]. As such, the higher content of N already present in the Ti products before the ignition may cause the reaction mechanism to change when compared to that of metal-metalloid systems [18, 26, 31, 32].

Possible formation mechanisms of Ti_2N and TiN before ignition

The reaction mechanism involved in the formation of TiN during ball milling of titanium under nitrogen atmosphere was reportedly to be a very complex process, possibly because of the different milling factors that influence its formation [6-8, 19]. Fig. 8 schematically illustrates the sequence of phase evolution during reactive ball milling of titanium powder in nitrogen gas.

During the early stages of ball milling of titanium under nitrogen atmosphere, it is believed that the molecules of nitrogen gas (N_2) are adsorbed onto mechanically activated Ti surfaces, preferentially unto clean and metal coordination sites [1, 27-29]. Under normal conditions, it is very difficult to create very clean surface which enhances preferential adsorption. However, through ball milling, repeated fracturing and deformation of the metallic particles, freshly clean and catalytic surfaces are reportedly generated continuously [11, 27, 28]. The interaction between the N_2 and the freshly cleaned Ti surfaces was reportedly suggested to be achieved by donation of $1\pi_u$ orbital states from N_2 to the surface and back-donation of $1\pi_g^*$ states from the surface of Ti [29]. Such N_2 -Ti interactions enable the metal-nitrogen bonds to be slightly stronger while the N-N bonds to be weaker, resulting to dissociation of the N_2 molecules to form highly polarized dipole N atoms. The N atoms was also reported to likely diffuse through the Ti crystal lattice by moving through the interstitial sites of the Ti unto the subsurface and bulk regions of Ti [27-29]. The diffusion of N atoms into Ti is probably promoted by the combined effects of accumulated defects (such as twinning, dislocations and induced strain), generation of large surface area as well as induced local temperature and pressure on the Ti particles during high energy ball milling [6, 7, 17, 19].

Before the detection of the ignition peak, small amount of TiN products are already present, as revealed from the XRD, Raman spectroscopy and advanced electron microscopic (FESEM, TEM/SAD and HRTEM). This clearly indicates that the incubation period is associated with reaction of Ti with N to form TiN, in addition to the grain refinement of Ti particles as well as regions showing lower and higher levels of nitrogen uptakes. Before the exothermic ignition, as schematically illustrated in Fig. 8, three key stages are likely in play (adsorption, dissociation and diffusion). Firstly, the N_2 molecules are likely to be adsorbed onto the surfaces of Ti during milling and then followed by repeated dissociation to form highly polarized active N atoms. As earlier reported by Bab *et al* [54], these active N atoms are likely to be diffuse into the catalytic clean subsurfaces of Ti and also the Ti bulk through incorporation of the N atoms within the octahedral interstices of Ti. The diffusion of N atoms into the crystal sites of Ti may thus result to possibly atomic arrangement between Ti and N to form similar crystal lattices that resemble the crystal structure of TiN [55]. The continuation incorporation of N atoms unto Ti may likely be restricted due to limited octahedral sites available for N to form such arrangement [55]. Presumably, when the concentration of the N atoms present in the mechanically-activated clean Ti surfaces exceed a critical value; the incorporation of the extra N atoms may probably followed by nucleation of TiN. This reaction sequence is likely to be promoted by numerous cycles of induced local temperature rise and rapid

quenching, large surface area, and accumulation of deformation defects (dislocations and twinning), within the vicinity of microvolumes of entrapped powders [8, 54].

Figure 8: Schematic diagram illustrating the process of reactive milling of titanium powder in nitrogen gas.

During controlled heating of titanium under nitrogen gas, the formation of Ti_2N has been suggested to occur under rapid cooling conditions [46]. In the case of ball milling, the effects of localized temperature increment combined with rapid quenching have been reported [1, 49, 50]. Different reports have shown that the local temperature could possibly rise up to $1000^\circ C$ or $2700^\circ C$ [49-53], depending on the elemental mixtures and milling conditions. The localized temperature was reportedly suggested to take place in a split nanosecond, possibly occurring in a thin strain layer of the reacting powders and then rapidly quenched within these split nanoseconds [1, 8, 49]. With repeated ball collisions, numerous cycles of induced local temperature rise and rapid quenching may occur. Such conditions may likely activate the nucleation of fewer amounts of Ti_2N crystals that are detected by TEM/SAD combined with HRSTEM.

Possible formation mechanisms of TiN after ignition

At the point ignition, it is believed that the exothermic reaction between Ti and N may simultaneous result to rapid nucleation of new TiN crystals, plus rapid growth of the pre-existing TiN crystals that are present before ignition and the newly formed TiN crystals. In addition, there is likely that the minor amounts of Ti_2N that are present in the pre-ignition products may probably be transform to TiN, since they were not detected by TEM/SAD combined with HRSTEM. Presumably, the heat released due to the exothermic reaction may probably have caused the transformation of Ti_2N to TiN to occur. In the Ti-N equilibrium diagram [46], such transformation under equilibrium condition, is reportedly to occur when the temperature of the system lies within $1100^\circ C$. In the case of reactive ball milling, even though the outside temperature of the mill may appear to be lower (Fig. 1(a)), the heat present inside the mill immediately after ignition has been reportedly to be very high, above the melting point of the one of the reactant [18, 21, 26]. Such high heats may probably cause the growth of the newly-nucleated TiN and the pre-existing TiN crystals as well as the solid-state transformation of Ti_2N to TiN. This is consistent with the products that were sampled shortly after ignition (29 h of milling) which shows thin-plated TiN particles (Fig. 4(c)). The morphologies of the TiN formed after ignition was seen to differ from the characteristic well-defined grains formed by MSR, as earlier reported during MSR synthesis of TiC [31] or TiB_2 [32] from their elemental powders. The reason may likely to be associated with the lower heat released at ignition during milling of titanium in nitrogen (Fig. 1(a)), compared with that of titanium and

graphite [31], and titanium and boron [32], where the temperature measurement taken outside of the vial was found to be relatively higher in both cases.

Conclusions

The formation mechanism of nanocrystalline TiN powder via magnetically controlled ball milling of titanium in nitrogen gas was investigated with particular attention paid to the reaction pathways that occur before and after ignition.

1. The combined techniques of XRD, TEM/SAD, HRSTEM and Raman spectroscopy revealed, before ignition, the formation of nitrogen enriched Ti, small proportions of TiN and very minor amounts of Ti₂N. The formation of TiN and Ti₂N before ignition was attributed to diffusion of highly polarized active N atoms onto mechanically-activated clean surfaces of Ti, followed by local reaction. These events were promoted by the numerous cycles of induced local temperature rise and rapid quenching, the large surface area of Ti available for reaction, and the accumulation of deformation defects (dislocations, vacancies, twinning and induced strain) generated by the plastic deformation and fracturing of the Ti particles.
2. After ignition, rapid conversion to a product containing thin rounded plates of TiN was found to occur, with significant quantities of unreacted Ti particles also present in the product. With increase milling time in nitrogen, these Ti particles are gradually converted to TiN, a result attributed to further diffusion of N atoms unto the Ti particles followed by reaction. Before the onset of this ignition, significant grain refinement was found to occur for the Ti particles, and this is accompanied by the generation of large plastic strains and high densities of dislocations and vacancies.
3. The formation of Ti₂N and TiN before ignition was associated with a change in appearance of the milled products from metallic grey colour to black, while after ignition the colour of the reacted products suddenly changes from black to brownish red and then to gold after extended milling.
4. The Raman spectroscopy revealed the pre-ignition products to include off-stoichiometric nitrides (TiN_x) and minor oxynitride skins (TiO_xN_y). These minor fractions of oxidized products were attributed to the presence of oxygen bonded to the surfaces of the TiN_x prior to analysis.

Acknowledgements

We thank the Australian Research Council (ARC)–Linkage, Infrastructure, Equipment and Facilities (LIEF) grant numbers LE120100104, LE0237478, and LE0882613 located at Electron Microscopy Centre (EMC) and Australian National Nanofabrication Facility (ANNF)– Materials node located at Intelligent Polymer Research Institute (IPRI), University of Wollongong, Australia for all the equipment use.

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