

The evolution of hydriding and nitridding reactions during ball milling of titanium in ammonia

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Recently it has been demonstrated that a range of metal nitrides can be easily produced by ball milling elemental metals at room temperature in an environment of nitrogen or ammonia [1, 2]. However, details of the reaction processes which take place during milling and the possible phase transformations which occur during subsequent annealing have not been established. In many cases, milling in ammonia is found to enhance the nitridding process compared with milling in nitrogen gas [3, 4]. This raises the question of the role of ammonia in determining the reaction sequence leading to the final nitride phase. In a previous study [5], we reported on the formation of Ti_2AlN by ball milling of Ti-Al elemental mixtures in an ammonia atmosphere. The reaction process was studied by monitoring changes in gas pressure during milling. It was found that the adsorption of ammonia gas on newly exposed particle surfaces created by ball impact or shearing resulted in an initial decrease of the milling chamber pressure. Further milling appeared to induce the decomposition of adsorbed ammonia and, ultimately, the evolution of hydrogen as indicated by an increase in the milling chamber pressure. In this paper, we have studied the reaction process of a simple gas-solid system NH_3 -Ti in some detail by monitoring gas pressure changes and correlating these with compositional and phase analysis of milled powders. Our results provide considerable insight into the mechanochemical process occurring during milling.

In this experiment, we used high purity elemental titanium powders (99.9%, 100 mesh) and anhydrous ammonia as starting materials. The milling process was performed in a vertical planetary ball mill. A stainless steel cell was loaded with 4 g of Ti powder and several hardened steel balls (diameter = 12 mm), and sealed with a Viton o-ring. In order to avoid oxygen contamination, the mill was purged with NH_3 several times and a pressure of 200 kPa was maintained prior to milling. The pressure of the milling chamber was monitored with a pressure gauge, over the pressure range from -100 kPa to 300 kPa.

The structural development of powders at various stages of milling was investigated by X-ray diffraction (XRD) analysis using Co radiation ($\lambda = 0.1789$ nm). The annealing behaviour of milled powders was studied using a Shimadzu differential thermal analyser (DTA) at a heating rate of 20 °C/min in a dried argon flow. The H and N

contents of as-milled powders were determined using combustion elemental analysis (Carlo Erba 1106).

Fig. 1 shows the observed pressure variations as a function of milling time. The pressure initially decreased rapidly, dropping to a minimum pressure of -95 ± 5 kPa (partial vacuum) at the end of 51 h. During further milling the pressure increased and attained the maximum measurement limit of the gauge (300 kPa) after 120 h milling. This pressure was maintained during continued milling up to 329 h. This final pressure is much higher than the starting ammonia pressure (200 kPa). Such a pressure variation is similar to that observed in the TiAl- NH_3 system [5]. In order to establish the relation between the powder composition, structural changes and observed pressure variations, the milling process was halted at different milling times to give samples corresponding to different pressure changes. These samples were firstly examined for composition and the analysis results are illustrated in Fig. 2. It is clear that the N content increases with increased milling time, but the H content decreases for milling at times beyond the minimum in the mill chamber pressure.

The evolution of microstructure during milling is illustrated by the typical XRD patterns of the milled samples in Fig. 3. A sample milled for 18 h, where the pressure had dropped to 50 kPa, has a complex structure. An fcc TiN phase appears to have been formed as indicated by peaks represented by the solid symbols. Appreciable unreacted Ti (crosses) was also found. A third phase (indicated by the open

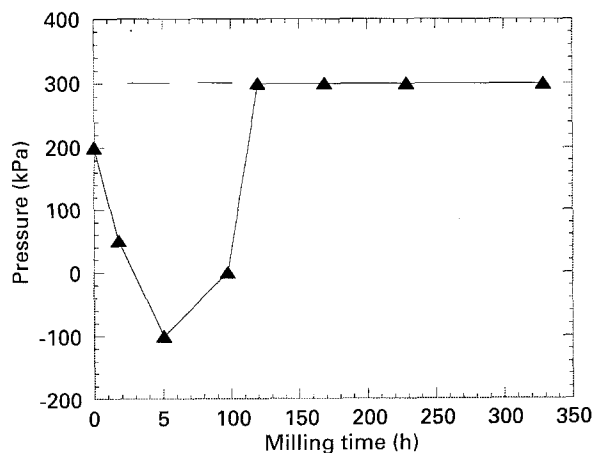


Figure 1 Pressure variation of milling chamber as a function of milling time.

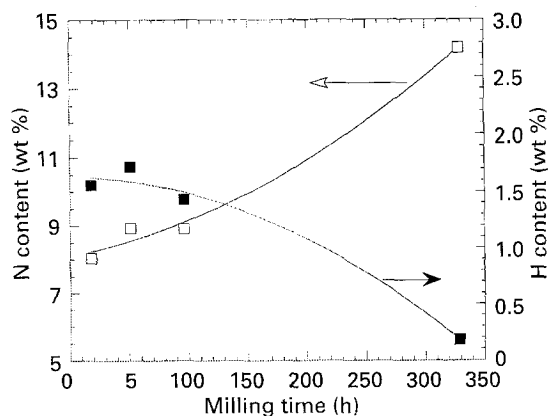


Figure 2 Evolution of H and N contents of as-milled powders as a function of milling time.

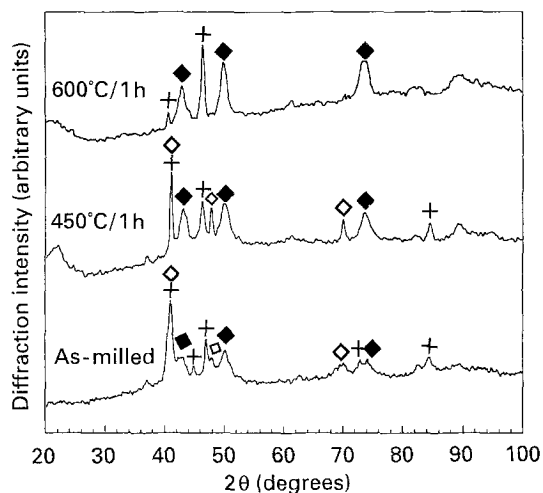


Figure 3 XRD patterns of Ti powders milled in ammonia at room temperature for different milling times; +:Ti, ◆:TiN, ◇:TiH_{1.9}.

symbols) was also identified in this spectrum. Comparison with annealed powders (see Fig. 5) indicated that this phase is cubic titanium hydride TiH_{1.9}. In contrast, the XRD pattern of the sample milled for 329 h shows only the TiN phase. Consistent with the XRD results, the samples milled for short times showed high N and H contents (Fig. 2) whereas the sample milled for 329 h exhibited a very high N content and almost no H. We can conclude that both TiH_{1.9} and TiN are formed during the early stages of milling. Furthermore, the TiH_{1.9} decomposes during prolonged milling and the dissociated hydrogen is released into the milling chamber and results in a pressure rise.

To examine the thermal stability of the as-formed phases, thermal analysis was carried out on as-milled powders at various milling times. Two typical DTA curves are shown in Fig. 4. A featureless trace was obtained for the 329 h as-milled powder, indicating that a full transformation of metal Ti to stable TiN had occurred during milling. In contrast, two different thermal reactions were indicated for the 18 h as-milled powder during heating: an exothermic peak at 410 °C and an endothermic peak at 560 °C. To determine these reactions, the 18 h as-milled powder was annealed for 1 h each at 450 °C and 600 °C. The first annealing temperature was be-

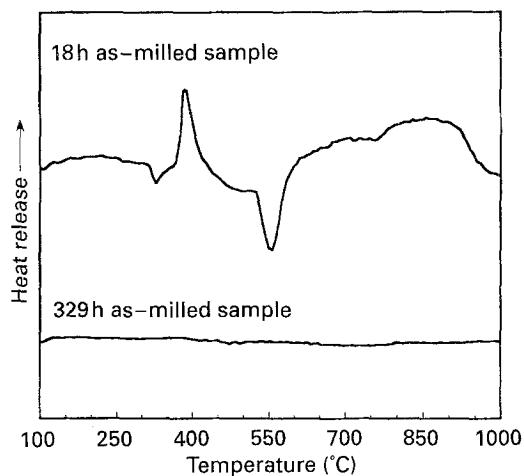


Figure 4 DTA curves of as-milled powders at heating rate of 20 °C/min in Ar flow; +:Ti, ◆:TiN, ◇:TiH_{1.9}.

tween the two reaction temperatures, the second one immediately followed the exothermic peak. The XRD patterns of these annealed powders are shown in Fig. 5, together with that for the as-milled powder for comparison. In the XRD pattern of the 450 °C annealed sample, a full set of very pronounced diffraction peaks from TiH_{1.9} is observed, indicating a substantial amount of large crystalline grains of this phase. TiN and some unreacted Ti were also observed after annealing at 450 °C. However, in the XRD pattern of the sample annealed at 600 °C, all TiH_{1.9} peaks have disappeared, and only pure Ti peaks and TiN are observed. Thus, we conclude that the first exothermic reaction is presumably related to the formation of TiH_{1.9} and/or TiN (from unreacted H and N), and the second endothermic peak indicates the decomposition of TiH_{1.9}. In addition, 1.1 wt % H was measured in the 450 °C annealed sample, but the H content is zero in the 600 °C annealed sample. Therefore, these data are consistent with the decomposition of TiH_{1.9} at about 550 °C.

From the above results we suggest the following reaction processes during milling of Ti in NH₃ gas. First, NH₃ molecules are absorbed on to new Ti particle surfaces created by pulverization during ball

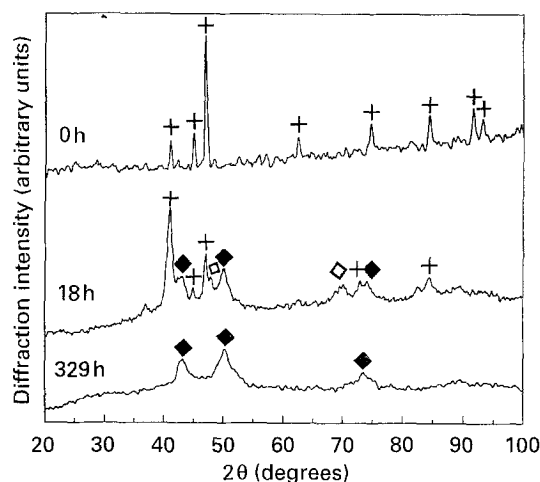
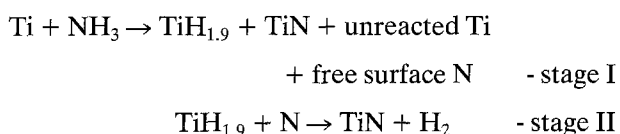


Figure 5 XRD patterns of 18 h as-milled powders annealed at different temperatures for 1 h in Ar flow.

impact. The adsorbed NH_3 can be decomposed under ball impacts [5] and the dissociated H and N atoms (or ions) are available to form hydride and nitride with Ti. When the particle size is large in the early stage of milling, only a thin TiN layer is formed as result of diffusion-limited reaction of N with Ti. However, more hydrogen is available for reaction, it is more mobile in Ti and has a high dissolution rate, thus giving thicker regions of $\text{TiH}_{1.9}$ compared with TiN formation. At this stage, $\text{TiH}_{1.9}$, TiN and free Ti phases, together with surface N, coexist. As the milling continues, the particle size is reduced, creating new surfaces for reaction with N and an increase in TiN formation. When no more free Ti is available for reaction with N, we speculate that free N atoms react with $\text{TiH}_{1.9}$ to form the more stable TiN phase and liberate H_2 gas. Hence, the mill chamber pressure rises. The two reaction stages are therefore as follows:



The formation of metal hydrides by ball milling has previously been reported [6, 7]. Indeed, Nb milled in hexane (C_6H_{14}) results in the formation of niobium hydride as an intermediate stage to the formation of niobium carbide with hydrogen evolution [8]. From our data, it would appear that the reaction of Ti in NH_3 is very similar to the Nb-hexane reaction. In addition, hydrogen has also been observed to have a catalytic role in the milling process [3]. The temporary formation of hydride can convert the ductile Ti metal to brittle $\text{TiH}_{1.9}$, a process which can enhance the rate of fracturing and particle size reduction [9]. This effect, together with the fact that NH_3 should be more easily dissociated (under milling) to atomic form than N_2 gas, may account for

the observed more efficient nitridation of Ti in NH_3 than N_2 . However, this aspect warrants more detailed study.

In summary, ball milling of pure Ti powder in a NH_3 atmosphere induces the formation of $\text{TiH}_{1.9}$ as well as TiN during the early stages of milling. The $\text{TiH}_{1.9}$ decomposes during further milling upon reaction with N to liberate H_2 and give complete conversion of Ti to TiN.

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