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# Synthesis of titanium diboride $TiB_2$ and Ti-Al-B metal matrix composites

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Titanium diboride $TiB_2$ and TiAl aluminide composites reinforced with in situ borites have been synthesized from the elemental powders of Ti and B, and Ti, Al and B respectively using mechanical alloying technique. No progressive diffusion between Ti and B was observed. The formation of $TiB_2$ was found to be governed by strong and fast exothermic heat release. This indicates that the formation of $TiB_2$ compound in local area of mechanically alloyed powder generated high energy which in turn ignited and promoted the formation of new compound in the rest of the area. Because of the presence of Al in Ti-Al-B system, the concentration of Ti or B was diluted. The exothermic reaction between Ti and B was consequently delayed. However, grain refinement of Ti and Al in this system down to nanometer scale is faster than that in Ti-Al system due to the contribution of B. Using X-ray analysis, strong but broad TiAl, and weak TiB and $TiB_2$ peaks had been detected at 50 h of mechanical alloying indicating the formation of nano TiAl composite reinforced by TiB and $TiB_2$. However, TiB was, however, not a stable phase; it later was transformed into equilibrium phase of $TiB_2$ after annealing at 800 °C.

## 1. Introduction

Titanium borides are particularly attractive for high temperature applications owing to their high modulus, excellent refractory properties and chemical inertness [1]. From Fig. 1 it can be seen that $TiB_2$ is much more refractory than TiB while the latter is the stable compound in equilibrium only with titanium-rich alloy [2]. Hence, $TiB_2$ is an ideal reinforcement with titanium aluminides.

$TiB_2$ has a hcp structure with lattice parameters of $a = 3.03034$, $c = 3.22953$ and $c/a = 1.066$. Several methods have been utilized in the synthesis of $TiB_2$ materials. Tani [3] used a carbothermal reaction from $TiO_2$, $B_4C$ and C materials. By adding B into Ti-Al solid solution (ss), $TiB_2$ could be synthesized during heating via the following route:

$$\mathrm{Ti(Al)ss} + \mathrm{B} \rightarrow \mathrm{(Ti, Al)B_2}$$

$$\mathrm{Ti} + \mathrm{(Ti, Al)B_2} \rightarrow \mathrm{TiB_2} + \mathrm{(TiAl)ss}$$

Although much attention has been devoted to a novel in situ formation of composites in Ti-Al alloys, the reinforcements employed are generally in the form of fibres [4]. The major problem in fibre reinforced Ti alloys is the difference in coefficient of thermal expansion between the reinforcements and the matrices. Extensive cracks in the matrices due to thermal mismatch can be induced during thermal cycling [4]. Another problem is the chemical instability of the reinforcements if they are not carefully selected. As long as the ternary Ti-Al-B system (Al-rich) considered, formation of $TiB_2$ is therefore thermodynamically more stable. The phases evolving from the monovariant reaction have been found to change from $\beta + \mathrm{TiB}$ to $\beta + \mathrm{TiB_2}$ to $\alpha + \mathrm{TiB_2}$ and eventually to $\gamma + \mathrm{TiB_2}$ as the aluminium content increases [2].

More recently, mechanical alloying (MA) technique has been used as a mechanochemical process by which fine grained ceramics can be synthesized [5]. This technique provides a unique means to synthesize compounds and alloys at room temperature [6]. Different types of materials have been successfully produced via the MA technique. The formation of borides by combustion synthesis during MA of Ti, Zr-B system has been reported [1]. The effects of milling ball size, power to ball weight ratio on the process of formation composites and combustion behaviour have also been investigated. It was found that exothermic temperature spike took place during MA indicating the formation of new compounds.

The present study investigates the formation of $TiB_2$ in Ti-B system and the possibility of formation of $TiB_2$ in Ti-Al-B system via MA technique.

## 2. Experimental

Commercial Ti, Al and B (amorphous) powders of purity 98%, 99% and 98% respectively were first blended in their stiochiometric ratio of Ti-66.7at%B and Ti-18.7at Al-15at%B for 60 min in a V-blender. MA of the Ti-B system was carried out using a Fritsch PM/5 planetary ball mill operating at 250 rpm while for the

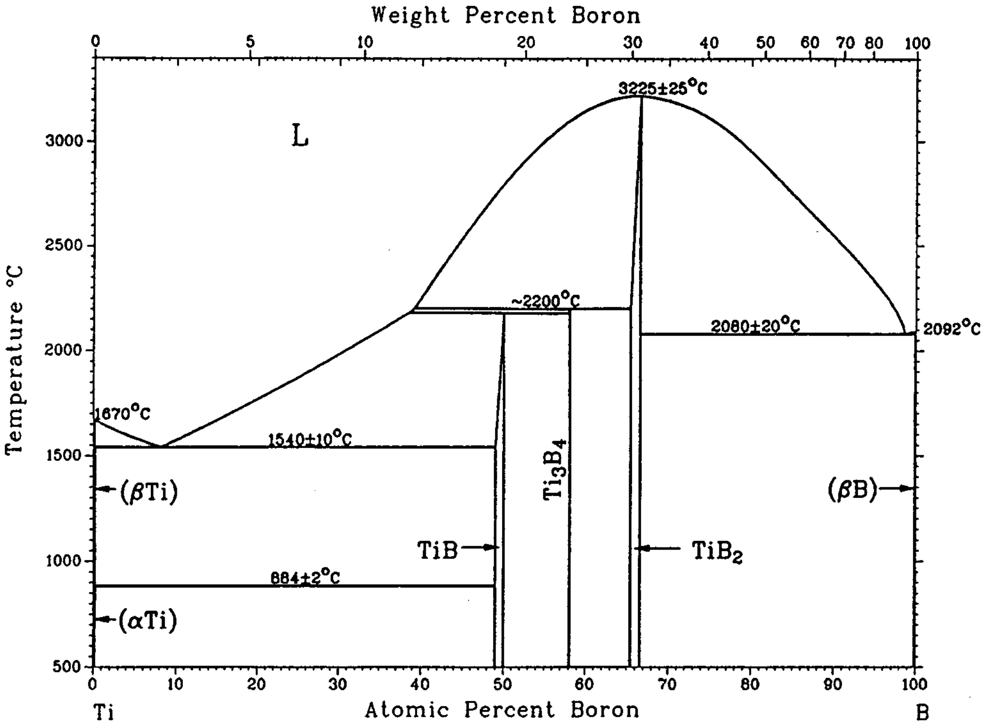


*Figure 1* Ti-B phase diagram.

Ti-Al-B system, 200 rpm. The vial was cooled with forced air during milling to prevent excessive temperature rise. For MA of the Ti-B system, 40 g of powder mixture of Ti and B was loaded into a stainless steel vial, while for the Ti-Al-B system, 10 g of powder mixture was used. Hardened steel balls of 19.05 mm diameter were employed. The ball to powder weight ratio was maintained at about 20 : 1 throughout the investigations.

To minimize oxidation, nitriding and hydriding of the blended powders, the steel vial was first filled with research grade argon and then evacuated with a vacuum pump. 1% by weight of stearic acid was added as a process control agent (PCA) to prevent excessive cold welding of the powder mixture during milling. This ensures a balance between cold welding and fracturing of the powders during milling.

Milling was carried out in steps of 30 min at a time, followed by an equal length of time for cooling to room temperature before milling was resumed. The cover and the rim of the steel vial were gently brushed to remove any loosely adherent powder when the vial was opened. Small amounts of sample powder were collected at regular time intervals for analysis.

The changes in structures of the mechanically alloyed (MAed) powder mixtures at different ball milling durations were characterized using X-ray diffraction (XRD) on a Phillips PW1729 X-ray diffractometer with $\mathrm{CuK}_\alpha$ radiation operated at 30 kV and 20 mA settings. Phases present in the composites were identified by comparing the peak positions and intensities with those from the JCPDS databases. A TA 1600 differential thermal analysis (DTA) was employed for examination of thermal behaviour of the MAed powder particles. Calibration of the DTA was performed by using Al and Ag.

## 3. Results and discussion

### 3.1. Mechanical alloying of Ti-B system

### *3.1.1. X-ray analysis*

Fig. 2 shows the XRD patterns of Ti-B as a function of milling duration. Pattern of the as-received mixture of Ti and B is shown in Fig. 2a as a reference. All the major peaks were found to correspond to that of Ti as the B used was amorphous and did not therefore contribute to any significant peaks in the diffraction pattern.

Fig. 2b shows the XRD pattern after 30 min of ball milling. No peak shifts could be detected. The diffraction pattern appears to be similar to that of Fig. 2a suggesting that no new phase had formed. However, significant changes took place after 60 min of ball milling as evidenced in Fig. 2c. Characteristic peaks of $TiB_2$, (100), (101), and (110) occurring at diffraction angles of 34.1°, 44.4° and 61.1° respectively can be observed. A comparison is made with the XRD pattern of commercial $TiB_2$ as shown in Fig. 2d. The two patterns match very well with each other. Based on this observation, the formation of $TiB_2$ from MAed Ti-66.7at%B powder mixture is confirmed. Fig. 2e and f show the diffraction patterns of Ti-66.7at%B MAed for 60 min and annealed at 600 and 1000 °C respectively. No structural change has taken place after annealing; from which it can be deduced that the MAed $TiB_2$ is in an equilibrium state which is very stable thermodynamically.

The rapid formation of $TiB_2$ from Ti-66.7at%B powder mixture can be explained by the highly exothermic reactions taking place during milling. Formation of borides, carbides, nitrides, ceramic composites and other refractory compounds are usually accompanied by strong exothermic reactions. Such reactions are capable of being self-sustained and are thus defined as

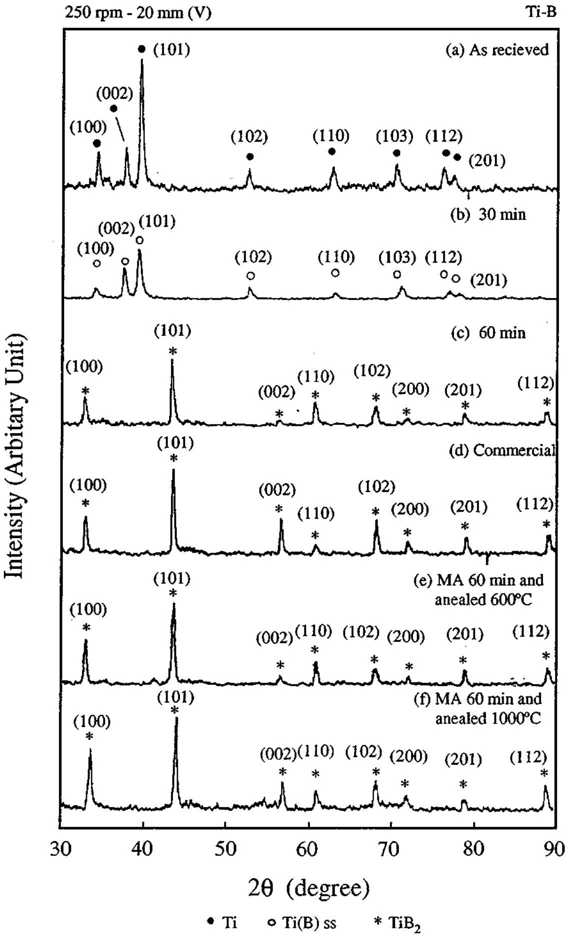


*Figure 2* XRD patterns of mechanically alloyed Ti and B mixture, commercial $TiB_2$ and annealed powder mixture.

self-propagating high temperature synthesis (SHS) [7] or combustion synthesis.

Combustion synthesis reactions during MA were reported in the literature. Park *et al.* [1] reported the formation of $TiB_2$ from combustion synthesis while milling Ti-B powder mixture in a vibratory ball mill. An exothermic temperature spike was seen to occur during milling. Formation of $TiB_2$ was detected after the occurrence of the temperature spike. Combustion synthesis was also reported during MA of metal oxide systems [8]. In both cases, abrupt change in temperature was observed. This sudden rise in temperature is perceived as the occurrence of combustion. The abrupt formation of $TiB_2$ suggests that the powder mixture must have experienced an abrupt temperature rise.

The rate of formation of $TiB_2$ from Ti-66.7at%B clearly shows that MA is a technique that can be used to increase reaction rate in the solid state. The formation of $TiB_2$ does not seem to follow the conventional diffusion theory proposed to explain the MA process because the conventional diffusion in MA normally takes a long time by gradual diffusion through formation of lamellaed layers of the constituent elements. As a result, there is a progressive change in the structure of the milled material before the formation of the final product.

MA is a room temperature process. The temperature during milling is not expected to increase significantly. It can be high if the reaction enthalpy of the material being milled is considered [8]. From thermodynamics data available, the enthalpy of formation of $TiB_2$ at room temperature is −323.8 kJ/mol [9]. The negative sign indicates that it is a highly exothermic reaction. Davis *et al.* [10], and Schwartz and Koch [11] successfully modelled the temperature rise due to collision events during milling. However, these models did not take into account the reaction enthalpy of the materials being milled. This can be very significant for materials whose formation results in large amounts of energy release as in the case of $TiB_2$. In highly exothermic systems, heat generated by the reaction enthalpy is faster than it is dissipated [12]. In addition, the creation of new surfaces for reaction and very finely distributed B in Ti during the MA process can increase the possibility of fast reactivity between the Ti and B elements. This enhancement of reactivity creates better conditions for self-propagating high temperature synthesis to take place. Once the reaction has taken place in a small local volume, the highly exothermic reaction will provide the energy for initiating reactions in the neighbouring regions [13]. The reaction becomes self-sustaining and thus greatly increases the reaction rate to form $TiB_2$. Hence, the formation of $TiB_2$ is attributed to the combustion synthesis caused by the high formation enthalpy between Ti and B elements under high impact energy. The condition for combustion synthesis was induced by MA and thus the formation of $TiB_2$ is described as mechanical alloy induced combustion synthesis.

### *3.1.2. DTA analysis*

Fig. 3 shows the DTA curves of MAed Ti-66.7at%B as a function of milling duration. Fig. 3a shows the DTA curve for blended Ti-66.7at%B while Fig. 3b, c and d, represent the curves after milling for 30 and 60 min and that for the commercial $TiB_2$ respectively. The dashed lines in the figures represent the second DTA run of the respective samples. The purpose of the second DTA analysis is to determine if the thermal events recorded in the first analysis are reversible or irreversible reactions.

A strong exothermic peak can be found at about 700 °C for the blended sample as shown in Fig. 3a. This peak represents the crystallization of amorphous B which occurs at about 575 °C (tangent temperature) and 728 °C (peak temperature), and the reaction between Ti and B elements to form $TiB_2$. DTA curve for the sample milled for 30 min shows significant changes from that of the blended sample. It appears that the former curve represents at least three overlapping curves. Although there are significant changes in the thermogram, the XRD patterns at the corresponding stage of milling (Fig. 2b) show no change when the hcp crystalline peaks of Ti are observed.

Two exothermic peaks centred at about 550 and 750 °C are present in the sample milled for 60 min (Fig. 3c). To identify and understand the significance of these two peaks, the sample was annealed at 600 and 1000 °C. Since the annealed samples represent the products of the two thermal events centred at 550 and 750 °C, XRD analysis of the annealed samples should

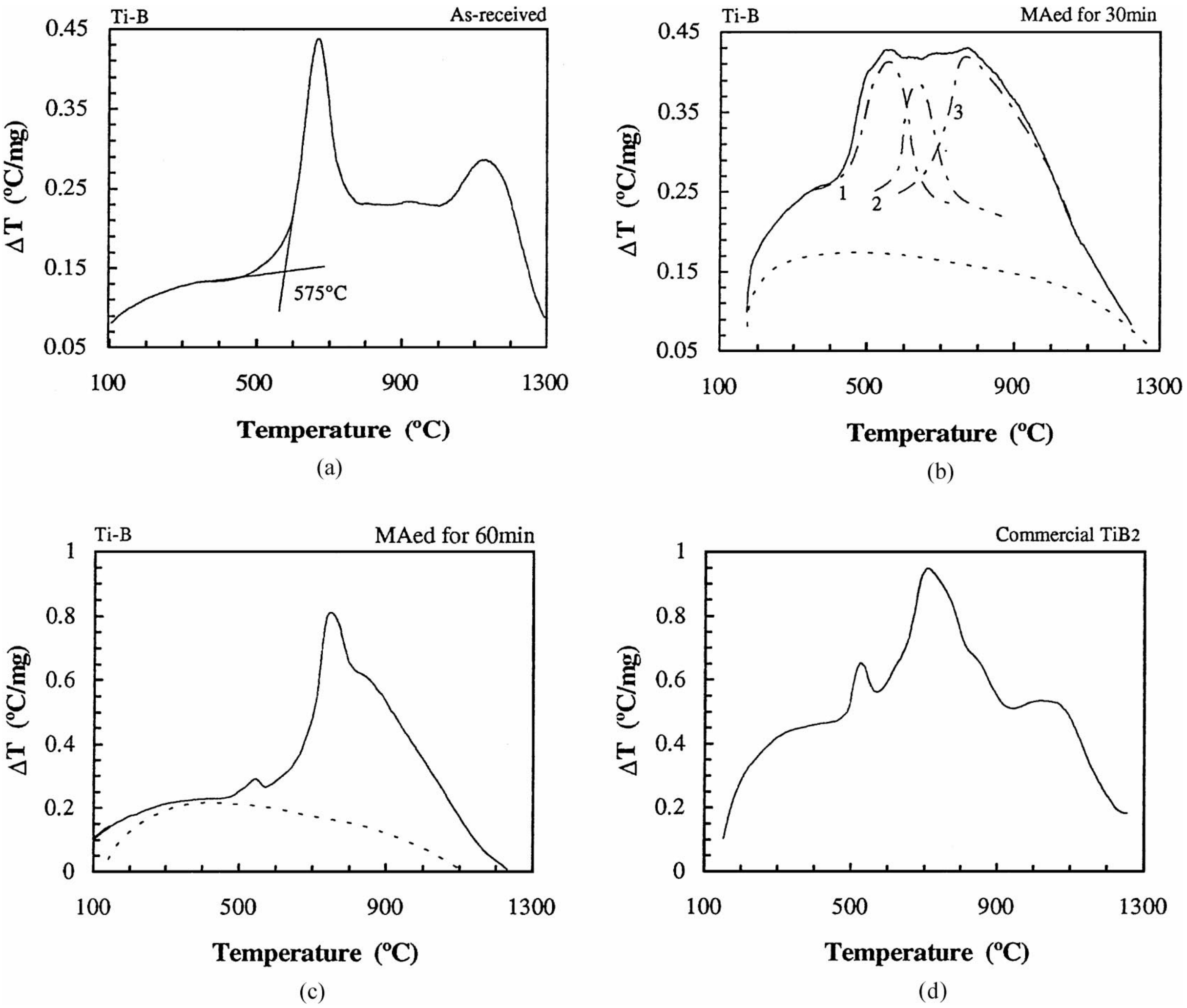


*Figure 3* DTA thermograms of mechanically alloyed samples and commercial powder mixture. (a) Ti-B mixture, (b) MAed for 30 min, (c) MAed for 60 min, and (d) commercial $TiB_2$.

reveal the type of thermal transitions occurring at the two observed temperatures. XRD analysis of the annealed samples however did not show any significant difference from the patterns before annealing (Comparing Fig. 2c with e and f). This suggests that there is no formation of new phases after annealing and that the two thermal events are not the representation of new phase transition. It also means that the MAed $TiB_2$ is thermally stable for at least up to 1000 °C. Therefore, the first weaker exothermic peak centred at 550 °C is probably due to recovery. The second exothermic peak centred at 750 °C can be attributed to recrystallization and grain growth as the XRD analysis shows no new phases after annealing. The peaks of the annealed sample appear to be sharper than the XRD peaks before annealing.

Comparison of the DTA curves of sample MAed for 60 min and that of commercial $TiB_2$ (Fig. 3c and d respectively) showed that the two curves are almost identical confirming the XRD analysis (Fig. 2c and d) that $TiB_2$ is indeed formed after 60 min of milling. The second run curves of the blended and MAed samples showed that the thermal events are irreversible processes. From the Ti-B equilibrium phase diagram of Fig. 1, no phase transitions are expected to take place at the composition of $TiB_2$. Therefore, the dashed curve of the MAed $TiB_2$ after 60 min of milling (Fig. 3g) is expected.

## 3.2. Ti-Al-B composite

With the information on the formation of $TiB_2$ from Ti-B system, the formation of $\gamma$ phase composite reinforced in situ borite through MA of Ti, Al and B elements is expected. The intended reaction is of the form:

$$2Ti + Al + 2B \rightarrow TiAl + TiB_2$$

with a ratio of TiAl/15wt%$TiB_2$. It is assumed that there is no reaction between the Al and the B elements.

### *3.2.1. XRD analysis*

Fig. 4 shows the XRD patterns of the MAed Ti-Al-B mixture as a function of milling durations with that of the as mixed elemental Ti, Al and B shown as a reference in Fig. 4a. Fig. 4b and c represent the initial stages of the MA process up to 120 min. As there is no appearance of new peaks, it is deduced that no structural changes have taken place during this period of time. The slight shifts in diffraction angles of Ti and Al are

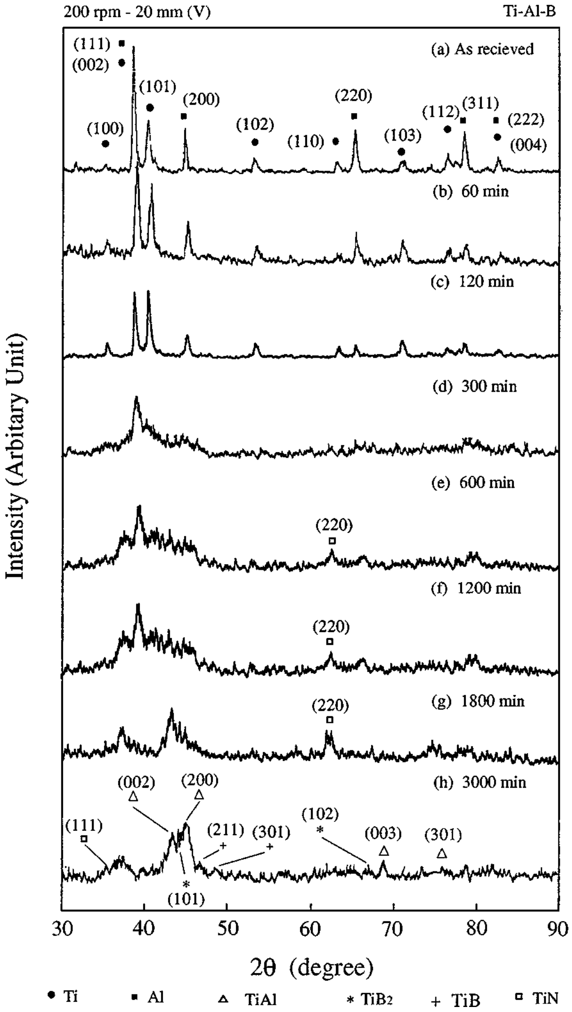


*Figure 4* XRD patterns of mechanically alloyed Ti, Al and B mixture.

attributed to the formation of solid solution between Ti, Al and B. Because the diffusivity of Al into Ti is larger than that of Ti into Al, more Al diffused into Ti. Among the three elements, the atomic radius of B is very much smaller than that of Ti and Al (0.98, 1.47 and 1.43 Å for B, Ti and Al respectively). Hence, B is the fastest diffuser into Ti and Al. Although formation of $TiB_2$ or TiB within a short time of MA of the Ti-B system was expected, there was no evidence of formation of borides. The reason may be attributed to the dilution of Al in Ti. Similar phenomenon has been observed by Malchere and Gaffet [14] when Si-C and Al-Si-C systems were MAed. Apart from the absence of formation of borides, an increase in the intensity of the (101) peak of Ti relative to the (200) peak of Al has also been observed. The weakening of the Al peak may be due to the dissolution of Al into Ti. The qualitative comparison of the relative proportion of the phases in a mixture can be estimated by using the following equation [15]:

$$\frac{I_A}{I_B} = \frac{R_A c_A}{R_B c_B}$$

where $I_A$ and $I_B$ are the integrated intensities of the diffraction lines of phases $A$ and $B$ respectively, and $c_A$ and $c_B$, the volume fractions of phases $A$ and $B$ in the mixture. Values of $R_A$ and $R_B$ can be calculated from:

$$R = \frac{1}{v^2}\left(|F|^2 p \frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)\exp(-2M)$$

where $v$ is the volume of unit cell of phase $A$ or $B$, $F$, the structure factor, $p$, the multiplicity factor, $\theta$, the diffraction angle and $\exp(-2M)$, the temperature factor.

Fig. 4d represents the XRD pattern after 300 min of milling. Considerable changes have taken place as evidenced by the broadening and overlapping of crystalline peaks. It is estimated that the milled mixture had already reached a nano-size of about 27 nm.

Since the reaction between Ti and B elements is highly exothermic, it is speculated that the large energy release during the reaction can accelerate the MA process. This leads to a faster nanocrystallization at an early stage of MA. Another consequence may be the interstitial diffusion of B elements into the Ti(Al) solid solution. As with the case of milling in atmospheric conditions, segregation of B atoms to the grain boundaries of the lamellae structure results in accumulation of strain and hence high density of dislocations. This hinders defect mobility and thus the rate of work hardening is higher.

XRD patterns at milling duration longer than 300 min appear to be similar to those of the Ti-Al system. However, with the presence of B elements, it is expected that there would be formation of compounds of Ti and B during milling. Given the high diffusivity of Al into Ti and the relatively small amount of B, it is assumed that there would be a solid solution of Al in Ti with traces of B situated interstitially at the interfaces of the lamellaed layers of Ti and Al. Thus, the first step in the formation of the MMC may be:

$$\text{Ti} + \text{Al} + \text{B} \rightarrow \text{(Ti,Al)(B)ss}$$

The reaction between Ti and B is expected to take place first before the reaction between Ti and Al. As far as the formation of $TiB_2$ is concerned, however, there is excess of Ti in the Ti-Al-B powder mixture. Consequently, any reaction between Ti and B elements would result in TiB being formed first rather than $TiB_2$. From the equilibrium phase diagram of Ti-B system, TiB is the first phase existing in titanium rich regions. Some of the peaks in Fig. 4g and h match those of TiB. However, more conclusive evidence is needed given the difficulties in identifying the relevant peaks from the broad and overlapping profile of the XRD pattern. There are two possible hypotheses to account for the formation of $TiB_2$. In the first hypothesis, it is assumed that all the B firstly reacted with Ti since the reaction between Ti and B is much faster than that between Ti and Al, and there is no reaction between B and Al:

$$\text{Ti} + \text{Al} + \text{B} \rightarrow \text{TiB} + \text{TiB}_2 + \text{(Ti, Al)Bss}$$

With formation of TiB in the initial stages, the remaining Ti is assumed to react with Al to form Ti(Al)ss (solid solution). It is believed that beside the formation of TiB and $TiB_2$, B still exists in the solid solution of Ti(Al)ss.

If the reaction is based on the amount of Ti remaining, any reaction between Ti and Al would form $TiAl_3$ due to the rich concentration of Al as compared to Ti. TiB and $TiAl_3$ are intermediate metastable products of MA process. As equilibrium compositional homogeneity requires the formation of $TiB_2$ and TiAl as the end products, the second hypothesis is

$$\mathrm{Ti} + \mathrm{Al} + \mathrm{B} \rightarrow \mathrm{TiAl_3} + \mathrm{TiB} + \mathrm{Ti(Al)ss}$$

As milling continues, the reaction will proceed as follows:

$$\mathrm{TiAl_3} + \mathrm{TiB} + \mathrm{Ti(Al)ss} \rightarrow \mathrm{TiB_2} + \mathrm{TiAl}$$

Reaction of this unconventional nature through MA has also been reported by others. Suryanarayana *et al.* [15] milled compounds of $TiAl_3$ and $TiH_2$ to obtain TiAl according to the equation:

$$\mathrm{TiAl_3} + 2\mathrm{TiH_2} \rightarrow 3\mathrm{TiAl} + 2\mathrm{H_2}\uparrow$$

The second hypothesis appears not so evident. Based on the work of Kim [16], it was discovered that the $TiAl_3$ phase was formed by precipitation from supersaturated Al(Ti) during annealing. The Ti in Al shares other merits of transition metal additions. The maximum solubility of Ti in Al obtained from the MA process was limited to 2.46 wt % [16]. This solubility is far from that of $TiAl_3$. Therefore, it is not possible to synthesize $TiAl_3$ from a hyper-peritetic Ti-Al system.

After MA time of 1800 min, the XRD pattern of Fig. 4i shows a significant change although TiAl and $TiB_2$ had not clearly been detected. The inability to detect these compounds may be due to two possibilities. Firstly, TiB/$TiB_2$ may not have been formed at this stage. The second possibility may be that the formation of $TiB_2$ takes place but in nanocrystal form. Fig. 4h presents the XRD patterns after 3000 min of MA. At this stage of milling, at least three different phases were found to be present, namely TiAl, TiB and $TiB_2$. The main (101) peak of $TiB_2$ corresponding to a diffraction angle of 44.4° is overlapped by peaks corresponding to TiAl in the lower angle regions. Furthermore, the amount of $TiB_2$ is small relative to TiAl. Because of its fine grain size and small quantity, it was not evident with XRD measurement. It was evident, however, that there was a formation of fct phase of TiAl. Hence, based on the above data, the reaction sequences in Ti-Al-B system most likely follow the form:

$$\mathrm{Ti} + \mathrm{Al} + \mathrm{B} \rightarrow \mathrm{(Ti,Al)Bss} \rightarrow \mathrm{TiB} + \mathrm{TiB_2} + \mathrm{TiAl(B)ss}$$

### 3.2.2. *DTA analysis*

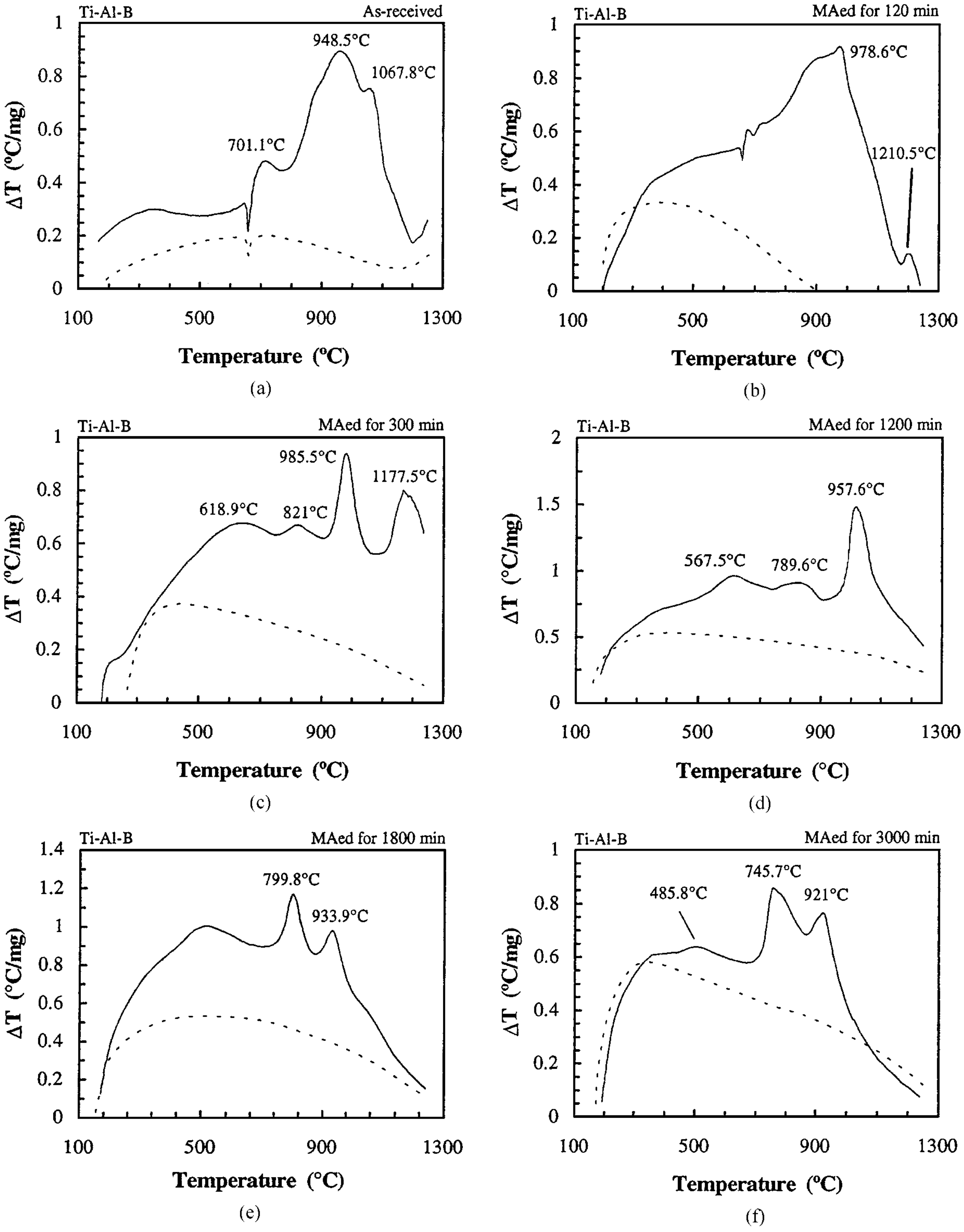
The DTA curves of the Ti-Al-B MMC are given in Fig. 5. The dashed lines show the DTA curves of the second runs. Fig. 6 shows the XRD patterns after annealing. The purpose of annealing the samples at specific temperatures related to the thermal events of the DTA analysis and then analysing them by XRD is to identify any phase changes or formation of new phases as a result of thermal events occurring within the sample as it is being heated up from room temperature.

Fig. 5a shows the DTA curve of Ti, Al and B mixture. Cross reference to DTA curves of Ti-66.7at%B (Fig. 3a) and Ti-58at%Al is necessary since the Ti-Al-B MMC is likely to show features common to the latter two sets of DTA curves. There may be overlapping of peaks if the thermal events between Ti and B elements or Ti and Al elements occur within the same temperature region. The endothermic peak at 660 °C represents the melting of Al. Reaction between elemental Ti and B is expected to take place at a temperature of 700 °C as evidenced from Fig. 3a. Fig. 5a suggests that the reaction between Ti and Al was inhibited by the presence of B. The endothermic peak during the second DTA run represents the large concentrations of residual Al after the first heating. The original assumption that B is a stronger reacting species with Ti as compared to Al in the Ti-Al-B mixture appears to be justified.

Fig. 5b and c show the changes in thermal events with MA duration. Although no borides were formed at this stage of MA, Diffusion of B into (Ti, Al)ss has already occurred. Clearer exothermic peaks could be observed. Fig. 5c shows that the peak at 1210.5 °C at MA of 120 min has been shifted to 1177.5 °C at MA of 300 min. This has not been observed in the Ti-Al system before and thus it is believed that some new structure could have been formed after heating to that temperature. However, this observation disappeared after longer time of MA (Fig. 5d).

Fig. 5e and f appear similar to those of the Ti-Al system. Two exothermic peaks centred at about 799.8 and 933.9 °C have been observed for the sample milled for 1800 min. Another weak peak at about 520 °C can also be observed. The significance of these exothermic peaks may be explained as follows.

The first weak peak at 520 °C can be attributed to the precipitation of $TiAl_3$ from supersaturated Al(Ti)ss while the exothermic peak centred at about 799.8 °C may be caused by the formation of $TiB_2$. Excess Ti released from the dissociation of Ti in TiB reacted with the $TiAl_3$ present to form TiAl intermetallic phase. To investigate the validity of this assumption, samples milled for 1800 min were annealed at 720 and 850 °C to identify the phases formed as a result of this thermal event. XRD patterns of the powders annealed at 720 and 850 °C are respectively shown in Fig. 6a and b. The presence of Ti and Al elements can easily be discerned. It is also clear that $TiAl_3$ has formed after the annealing treatment. Although some very weak peaks corresponding to TiB and $TiB_2$ are detectable, no affirmative conclusion on this formation could be established at this stage. However, TiB and $TiB_2$ phases can readily be detected when the powder was annealed at 850 °C while the Ti and Al phases are almost undetectable. As the reaction temperature for the formation of $TiB_2$ is below 800 °C [17], it is not surprising that the formation of borides took place after annealing because the heating of the sample to 800 °C provided a



(a) (b) (c) (d) (e) (f)

*Figure 5* DTA thermogram of mechanically alloyed and commercial powder mixture. (a) Ti-Al-B mixture, (b) MAed for 30 min, (c) MAed for 120 min, (d) MAed for 300 min, (e) MAed for 1800 min, and (f) MAed for 3000 min.

driving force for the formation of TiB and $TiB_2$ from the dissolution of (Ti, Al)Bss and reaction from Ti. Since the equilibrium phase of $TiB_2$ could be obtained from Ti-Al-B system after annealing at 800 °C, it is believed that with prolonged heating at 800 °C, full $TiB_2$ phase will be obtained. Accordingly therefore, the exothermic peak centred at about 779.8 °C represents borides.

Fig. 5f shows the DTA curve of the sample milled for 3000 min. Qualitatively, the curve appears similar to that milled for 1800 min (Refer to Fig. 5e). In detail, however, some differences occurred in the significance of their DTA peaks. The identity and significance of the last exothermic peak centred at 921 °C has been confirmed by annealing the sample milled for 3000 min at 1000 °C and then analysing by XRD. Fig. 6c shows the results of the XRD patterns after annealing. The presence of two equilibrium phases of TiAl and $TiB_2$ can be observed. It is therefore believed that MA produces metastable TiAl, TiB and $TiB_2$ phase. The phases may contain high Al solid solution which subsequently may be transformed to equilibrium phases after annealing at 1000 °C.

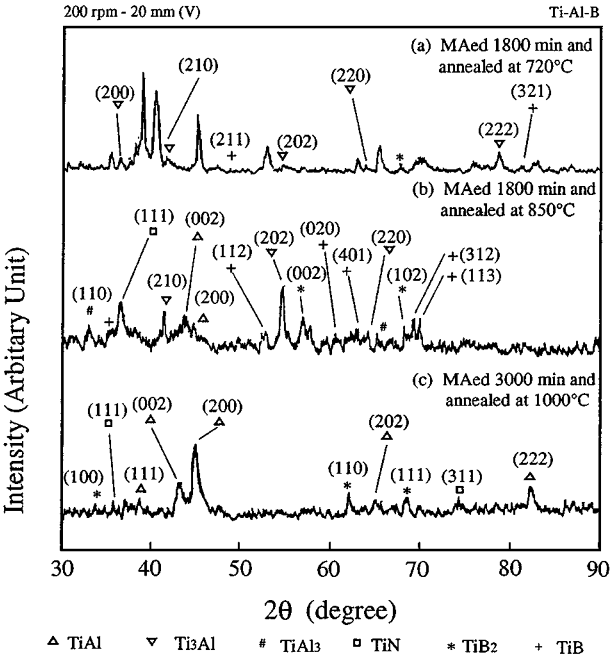


*Figure 6* XRD patterns of the MAed Ti, Al and B mixture after annealing at different temperatures.

## 4. Conclusions

$TiB_2$ could be rapidly synthesized within 60 min by mechanical alloying at 250 rpm. Because high exothermic reaction was involved, large amount of heat was released at the time of reaction. This ignited a combustion process in a local region which it led to an increase in pressure in the milling vial. Hence, extreme care had to be taken during mechanical alloying.

$TiAl/15\%TiB_2$ has been successfully fabricated from Ti, Al and B. This most likely, exothermic reaction route of this process may be $Ti + B + Al \rightarrow (Ti, Al)Bss \rightarrow TiB + TiB_2 + (TiAl)Bss \rightarrow TiB_2 + TiAl$ after annealing. Because of the presence of Al in the Ti-Al-B system, the concentration of Ti or B was diluted leading to the exothermic reaction between Ti and B being delayed. However, grain refinement of Ti and Al in this system went down to nanometer more rapidly than that in Ti-Al system as a result of contribution from B.

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