

Formation of Ti-B-N-C Ceramic Composite Materials via a Gas-Solid Phase Reaction

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Abstract Phase mixtures of Titanium boride, nitride, and carbide powder were produced by the reduction of a mixture of titanium and boron oxides with carbon via a gas-solid phase reaction. Boron oxides produce a vapour phase or decompose to a metal sub-oxide gaseous species when reduced at elevated temperature. The mechanism of BO sub-oxide gas formation from B_2O_3 and its subsequent reduction to titanium diboride for the production of uniform size hexagonal platelets is explained. These gaseous phases are critical for the formation of boride, nitride and carbide ceramics. For the production of ceramic phase composite microstructures, the nitrogen partial pressure was the most critical factor. Some calculated equilibrium phase fields has been verified experimentally. The theoretical approach therefore identifies conditions for the formation of phase mixtures. The thermodynamic and kinetic factors that govern the phase constituents are also discussed.

Key words titanium diboride, composites, gas-solid reaction, in-situ formation.

1. Introduction

Titanium diboride (TiB_2) has a hexagonal crystal structure and like other diborides, exhibits the characteristics of both metallic and covalent bonding. Its covalent character, dominated by interstitial boron packing, determines a high melting point and micro-hardness.¹⁾ The metal-metal bond, however, still persists throughout and the most important properties are due to their essentially metallic character.²⁾ Its metallic characteristic determines the thermal and electrical resistivity.³⁾ The metallic bonding also contributes to its wettability with most reactive metals. Above all, its high fracture toughness and good corrosion resistance makes TiB_2 a suitable candidate material for elevated temperature applications. The unique combination of properties offers the material a potential for a wider use as engineering ceramics in diverse applications. The material can be machined by spark erosion or electrical-discharge technique.^{4,5)} Prerequisite to the use of metal diboride for any of the above applications is the preparation of powder that is not only pure, but also has a controlled particle size, shape and state of agglomeration. The morphological factors affect and determine the physical and mechanical properties.

The present work is aimed at the production of pure TiB_2 powders, mixed diborides and partially-densified

composite materials by the reduction CVD technique, and to understand the mechanism of the complex reactions. The reduction CVD is process in which the metal oxides or their sub-oxides are evaporated under the influence of controlled low oxygen potential. The principle of BO sub-oxide gas formation from B_2O_3 and its subsequent reduction to titanium diboride for the production of uniform size hexagonal platelets has been adopted.

2. Experimental Procedure

Titanium dioxide (TiO_2 , rutile), and boron oxide (B_2O_3) were used as the starting material with carbon. Appropriate amounts of TiO_2 , B_2O_3 and carbon were weighed in stoichiometric proportions. The particle size of TiO_2 (Tioxide UK Ltd, pigment grade) was in the submicrometer range and the size of granulated boron oxide of 99.999% purity (Aldrich Chemical Co.) was 1-5 mm. The particles were crushed and ground for more than 30 minutes in an agate mortar for the production of finer particles. The grinding was carried out inside a controlled atmosphere glove box in order to avoid contamination from ambient moisture. Other types of boric anhydride were also tested for reduction experiments. Two different kinds of carbon: graphite (Hopkins & Williams Ltd, synthetic powder, Assay > 98%) and activated charcoal (Fluka Chemie Ltd, ash < 1%) were used. Each sample weighed about

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1.2 gram. The weighed materials were thoroughly dry-mixed, ground in an agate mortar and then pressed in a 6 mm inner diameter steel mould to form cylindrical shape pellets. The pressure used was $3 \text{ kN}\cdot\text{cm}^{-2}$.

A silicon carbide resistance tube furnace was employed for heating the pelletised mixture. The temperature was measured using Pt/Pt-Rh13% thermocouple placed inside the alumina tube at the bottom of the crucible which was also used as a support for the crucible. The compacted pellets were heated in the temperature range 1173 K to 1773 K. The pressed samples were transferred inside a graphite or alumina crucible and heated in the isothermally maintained zone of the resistance furnace. The crucible had holes on the sidewall and bottom in order to facilitate the flow of gases around pellet during the reaction. The dimension of each crucible was 20 mm diameter and 20 mm long. Each pellet took approximately 3-4 minutes to reach the selected isotherm. It was recorded that the weight loss sustained by a pellet during heating was insignificantly small in comparison to the total expected weight loss. Also, for a lower selected isotherm, the reduction reaction seemed to commence at a slow rate once the temperature of the pellet reached 1273 K. After a preselected reaction time, the crucible was lowered in order to cool the sample rapidly in the nitrogen atmosphere. During this procedure, the cooling rate of $250 \text{ K}\cdot\text{min}^{-1}$ was recorded up to 673 K. Depending upon the composition of the starting materials, any one of the following purge gas mixtures was selected: N_2 , N_2+H_2 , $\text{N}_2+\text{H}_2/\text{CO}$. Prior to the attainment of the reaction temperature, N_2 gas was purged through the chamber in order to rid residual oxygen. The typical gas flow rate in all experiments was $500 \text{ ml}\cdot\text{min}^{-1}$.

After reaction, the pellets were weighed for determining the percentage reduction. The phases present in the reacted pellets were examined by X-ray powder diffraction technique by using $\text{Cu-K}\alpha$ radiation. The two theta angles were measured after subtracting the $\text{Cu-K}\alpha_2$ value from the original data. The reaction products were also examined by scanning electron microscopic technique using a scanning electron microscope fitted with an energy dispersive X-ray detector to study morphology of the phases and their chemical composition.

3. Results

3.1 The effect of reaction temperature and time

The reaction for TiB_2 formation occurred rapidly leading

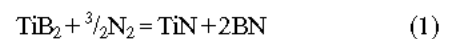
to TiB_2 crystals. The equilibrium temperature of TiB_2 formation from the reaction between titanium and boron oxides with carbon is 1613 K. But continuous removal of CO gas from the reaction chamber force to form TiB_2 even at below this temperature. The results of phase analysis of the reaction at different temperature are summarised in Table 1. Evidently the non-stoichiometric titanium oxycarbide (TiC_xO_y) and Ti_3O_5 are two important phases at 1473 K which could be responsible for indicating a change in the reaction mechanism discernible from the activation energy analysis. With increasing temperatures, oxycarbide and oxide phase mixtures transform into a combination of carbide and boride phases. At short reaction time, in this case 10 minutes, TiC still exists up to 1673 K, and this phase transformed to TiB_2 at 1773 K. From these results, it is obvious that TiB_2 is more stable high temperature phase than TiC. Once B_4C is formed in Ar gas, B_4C react with TiO_2 to form TiB_2 more easily at relatively lower temperature than that of TiB_2 formation from the reaction between phases, such as $\text{TiO}_2+\text{B}_2\text{O}_3$, $\text{TiN}+\text{B}_2\text{O}_3$, $\text{TiC}+\text{B}_2\text{O}_3$, or $\text{BN}+\text{TiO}_2$.

Table 1. The effect of reaction temperature and time on the phases produced in Ar gas.

Starting Materials	Temperature (K)	Time (hr)	Produced phases
$\text{TiO}_2 + 1.5\text{B}_2\text{O}_3 + 6\text{C}$	1473	0.17	Ti_3O_5 , TiC_xO_y
	1573	0.17	TiB_2 , TiC
	1673	0.17	TiB_2 , TiC
		0.5	TiB_2 , B_4C
		1.0	TiB_2 , B_4C
		4.0	TiB_2
	1773	24.0	TiB_2
		0.17	TiB_2

3.2 The effect of partial pressure of nitrogen

In the inert gas atmosphere, titanium diboride (TiB_2) phase easily formed with titanium carbide (TiC), whereas titanium nitride (TiN) phase formed by carbothermic reaction of TiO_2 in the nitrogen atmosphere, for example, TiN phase formed with titanium suboxide, Ti_3O_5 , within 40 min reaction time at 1473 K. But TiN did not form with boron oxide in the starting materials even after 24 hours reaction time at 1573 K. It is understood that because of the formation of BO gas, the reduction of titanium oxide was retarded.



At the temperature is 1773 K, the Gibbs free energy change of reaction (1) is -113.3 KJ which means TiN and BN are more stable phases than TiB₂ in the nitrogen atmosphere. As expected by thermodynamic data, TiB₂, TiC, and B₄C progressively transformed into TiC_xN_y and BN when nitrogen gas used with argon, and the volume fraction of TiB₂ was controlled by varying the partial pressure of nitrogen gas, time of nitridation and temperature. The results of phases formed in the nitrogen atmosphere via the reduction route are summarised in Table 2 and X-ray diffraction patterns of phases are shown in Fig. 1.

3.3 The effect of B₂O₃/TiO₂ ratio

The effect of composition of starting materials,

Table 2. The effect of partial pressure of nitrogen on the phases produced after 24 hours reaction.

Starting Materials	Temperature (K)	Atmosphere (P _{N₂} +P _{Ar} =1atm)		Produced phases
		P _{Ar}	1	
TiO ₂ +2B ₂ O ₃ +8C	1773	P _{Ar}	0.0005	TiB ₂ , TiN
			0.002	TiB ₂ , TiN, BN
		P _{N₂}	0.02	TiN, BN
			1	TiN, BN

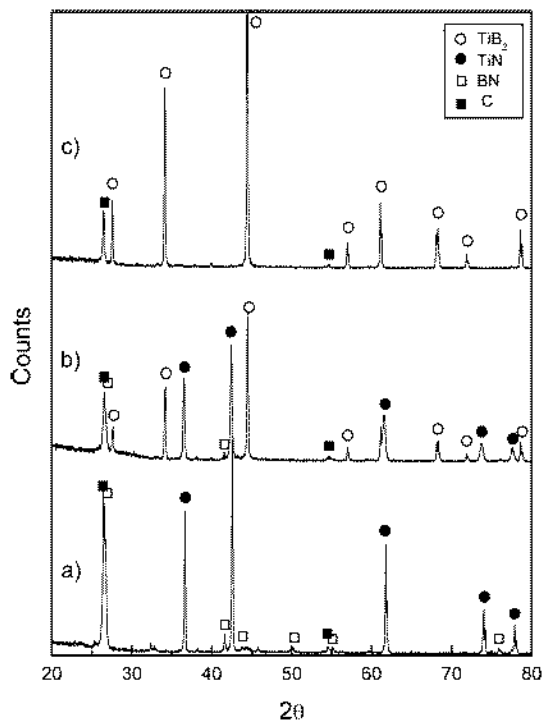


Fig. 1. X-ray diffraction patterns of the reduced samples. (P_{N₂}= (a) 0.05, (b) 0.002 and (c) 0 atm at 1773 K after 24 hrs)

especially B₂O₃/TiO₂ ratio was investigated. At short reaction time, titanium oxide reduced to suboxide (e.g. Ti₃O₅) which is subsequently reduced by carbon to form titanium carbide. When pellets with molar ratio of TiO₂:B₂O₃=1:2 in the mixture were reduced with carbon at 1623 K in an argon atmosphere, the boride (TiB₂) phase formed. At B₂O₃/TiO₂=1, the formation of Ti_{1-x}C_x phase was noticeable, which indicates that one mole of B₂O₃ for one mole of TiO₂ is not enough to maintain TiB₂ formation reaction because of the loss of B₂O₃ due to the volatilisation. But as the amount of B₂O₃ was raised, the Ti_{1-x}C_x phase became less stable and at the TiO₂/B₂O₃ ratio is 1.5, TiB₂ was the most stable phase at the same condition. Table 3 summarises the experimental condition for the formation of two or more refractory phases mixture. The observations are consistence with the overall stoichiometry of the reduction reaction that is a major subject of discussion.

Table 3. The effect of B₂O₃/TiO₂ ratio on the phases produced in Ar gas.

Starting Materials	Temperature (K)	Time (hr)	Produced phases
TiO ₂ +B ₂ O ₃ +5C	1673		TiC, TiB ₂
TiO ₂ +1.5B ₂ O ₃ +6C	1673	24	TiB ₂
TiO ₂ +2B ₂ O ₃ +8C	1773		TiB ₂

3.4 Microstructure of TiB₂

The growth characteristics of titanium diboride crystals were studied. When the minimum stoichiometric proportion of boron oxide (B₂O₃/TiO₂=1) was used for the conversion of titania to titanium diboride in argon gas atmosphere, the crystals grew with a pronounced faceting of the basal plane and the growth direction was along the c-axis of the diboride crystals. Due to enhanced volatilisation of boron oxide at elevated temperatures, the conversion of TiO₂ to TiB₂ is only partial. The excess TiO₂ converts into TiC, which is shown in Photo 1(a). The microstructure of TiC has "flaky-snow dust" type morphology. The TiC formation enhances when an active reducing agent such as charcoal or active carbon is used. However, B₂O₃/TiO₂ ratio increased to 1.5, there is an excess of boron oxide which reacts with TiC and transforms into the diboride phase and the nucleation rate is higher. This is apparent when the microstructure in Photo 1(b) is compared with the microstructure in Photo

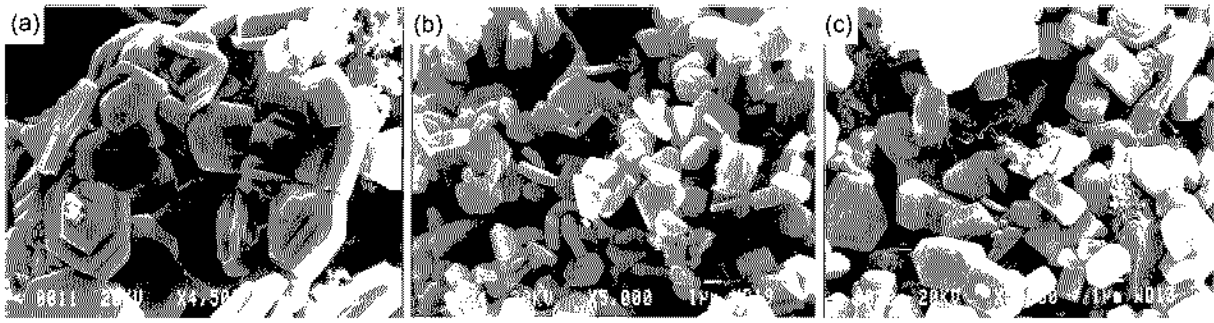


Photo 1. Scanning electron micrograph of titanium diboride when B_2O_3/TiO_2 ratio was (a) 1, (b) 1.5, after 24 hours at 1673 K in Ar, and (c) 2, after 20 hours at 1773 K in Ar/H₂(4%)+N₂(0.05%) gas.

1(a). When $B_2O_3/TiO_2=2$, with the presence of nitrogen ($P_{N_2}=0.05$ atm), appears to promote growth along the c-axis of the hexagonal crystals as shown in Photo 1(c). Titanium diboride has a small range of non-stoichiometry. The crystal could be either titanium-rich or boron-rich. The loss of boron oxide either as BO or B_2O_3 gas enhanced the titanium to boron ratio. Due to this there is a slight excess of titanium atoms in the structure which can only occupy sites along the a-axis in the MB_2 structure. The growth rate along a-axis is faster than c-axis due to a marginally larger concentration gradient of the titanium atoms in the reducing atmosphere. The diboride structure has a relatively smaller defect concentration along the a-axis whereas the interstitial defect concentration is more likely to change because it can be controlled via the gas phase. Boron deficiency in the lattice is expected when the volatilisation rate of boron oxide is expected to increase. The basis for the stability of an interstitial defect structure is similar to that of the metal ion deficiency in oxides and sulphides that is governed by the gas phase. The presence of nitrogen in the gas phase enhances the relative growth rate along the c-axis as shown in Photo 1(c). The crystallites of boride grow faster along the c-axis because nitrogen atoms compete for interstitial sites with boron. Indeed it is also possible that the solubility of nitrogen gas in the diboride structure increases due to complex interaction between Ti and B atoms. The presence of 0.05% nitrogen in the gas mixture promotes the nitriding process under which it is possible to form TiN and BN from the boride microstructure. This is via $TiB_2+N_2+xC = TiNC_x + BN$ or $TiN + BN$ reaction in the absence of carbon. Provided the partial pressure of nitrogen gas in the atmosphere reaches the critical value for compound nitride formation, the stability of a solid-solution carbonitride compound phase is possible. The presence of carbonitride

on the surface of crystals in the initial stage of nitriding and inter-granular titanium carbonitride phase is apparent from Photo 1(c).

The particle characterisation of boride powder was attempted by determining the average size of crystals at a given temperature. On the average fifty crystallites of TiB_2 were selected for size measurement at each reduction temperature. Table 4 summarizes the data at three different experimental temperatures. The average crystallite size in micrometers is also given at each time and temperature. The standard deviation of thickness was $0.4 \mu m$. The growth rate at 1673 K is insignificantly small, the average size remains virtually constant between 0 hour and 8 hours. Beyond this period, the size increases with time non-linearly. At higher temperature, the average crystal size was bigger after 10 minutes reduction.

Table 4. The average crystallite size of TiB_2 at each experimental condition.

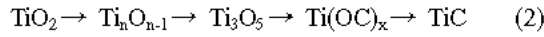
Composition	Gas	Temp. (K)	Time (hr)	Average grain size(μm)
$TiO_2+1.5B_2O_3+6C$	Ar	1673	0.17	0.44
			0.17	0.86
			0.5	0.87
			1	0.87
			8	0.87
	1773	24	1.26	
		0.17	1.60	

4. Discussion

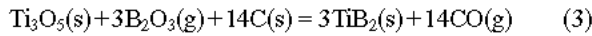
4.1 The Mechanism of TiB_2 Synthesis Reaction

Titanium dioxide and boron oxide reduce to lower oxides in the presence of carbon above thermodynamic equilibrium temperatures. The phase constitutions above the equilibrium temperature are determined by the partial

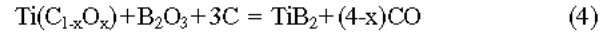
pressure of carbon monoxide gas generated as a result of the reduction reaction. For example, rutile was reduced above 1273 K, it progressively loses oxygen and transforms into non-stoichiometric sub-oxides presented in elsewhere.⁶⁾ The reduction sequence is as follows:



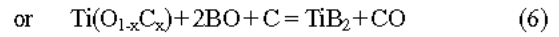
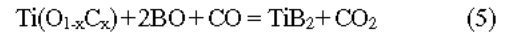
where n varies between 9 and 4. In the presence of nitrogen or ammonia gas, the last two reaction products are titanium oxynitrides/oxycarbonitrides and titanium carbonitrides/nitrides. The reduction process raises the activity of titanium metal in the sub-oxide lattice. Boron oxide (B_2O_3) similarly reduces to (BO) gas and in this way raises the activity of boron. Once the thermodynamic chemical potential of titanium and boron rises to a critical level, the formation of TiB_2 crystals takes place. On the basis of the results of X-ray powder diffraction pattern, the mechanism of reduction of titanium dioxide to titanium diboride is as follows and can be defined by the following set of chemical reactions. At low temperatures in the 1573 K temperature range:



reaction can occur. However, the reaction will only sustain in the presence of a physical contact between the non-stoichiometric oxide and carbon. It also appears to be evident is that when the ratio of $\text{TiO}_2/\text{B}_2\text{O}_3$ in the pellet is unity, only a part of the total carbon reacts with boron oxide and produces BO gas. In the same way, the rutile phase reduces to Ti_3O_5 . The formation of the oxycarbide intermediate phase succeeds the reduction of Ti_3O_5 . The presence of this phase is essential and provides a diffusion medium for carbon and oxygen. This is promoted by the available vacant sites from the non-stoichiometry of the oxycarbide phase. The absence of the titanium monoxide (TiO) phase under reducing conditions may support that both Ti_3O_5 and oxycarbide are more stable under reducing conditions. The oxycarbide phase is the intermediate phase for the transport of carbon and oxygen atoms and from this phase, the formation of diboride phase takes place. The proposed mechanism is consistent with the experimental results shown in Table 1. This means that carbon and oxygen diffusion can take place through the $\text{Ti}(\text{C}_{1-x}\text{O}_x)$ lattice and either boron oxide or BO gas can pore diffuse to facilitate the formation of titanium diboride.



At temperatures higher than 1573 K, the reduction mechanism changes because the generation of BO gas becomes thermodynamically more favourable. Therefore the oxycarbide phase can then directly react with the mixture of BO and CO gas.



The CO_2 gas produced in this way can be regenerated in-situ via the Boudouard reaction, i.e. $\text{CO}_2 + \text{C} = 2\text{CO}$ gas. The presence of BO or B_2O_3 gas in the reducing atmosphere implies that the interstitial diffusion rate of carbon and oxygen in the oxycarbide lattice is expected to increase at least by the same order of magnitude as the drop in the activity of boron from BO gas to TiB_2 . This means that the oxygen and carbon diffusion in the oxycarbide lattice rises due to the chemical potential gradient. By examining reactions given in Eq. (5) and (6), it is important that the generation of BO gas must compete with the rate of consumption of BO leading to the formation of TiB_2 phase. The calculation of the free energy change at different temperatures for reactions given by Eq. (5) and (6) show that the equilibrium CO partial pressure for TiB_2 phase is higher than for the stability of TiC or TiOC_{1-x} . It is due to TiC or TiO phase can not co-exist with TiB_2 because the partial pressure of CO is higher. The calculated CO partial pressures are shown in Table 5 below.

Table 6 summarizes the chemical reactions leading to the formation of TiB_2 via Ti_3O_5 and BO (or B_2O_3) phases reduction with carbon. The values of G_0 are derived by using the thermodynamic data compiled by Turkdogan.⁷⁾ Using the equilibrium constant (K) relationship: $K = \exp(-\Delta G^\circ/RT)$, a relationship between the partial pressure of BO, B_2O_3 and CO gases can be established at different temperature. For reaction (d) in Table 6, K_d equals to $P_{\text{CO}} \cdot P_{\text{BO}}^2$ when $P_{\text{B}_2\text{O}_3}$ is 1 atm. At 1673 K, K_d is equal to 2.29×10^{-7} .

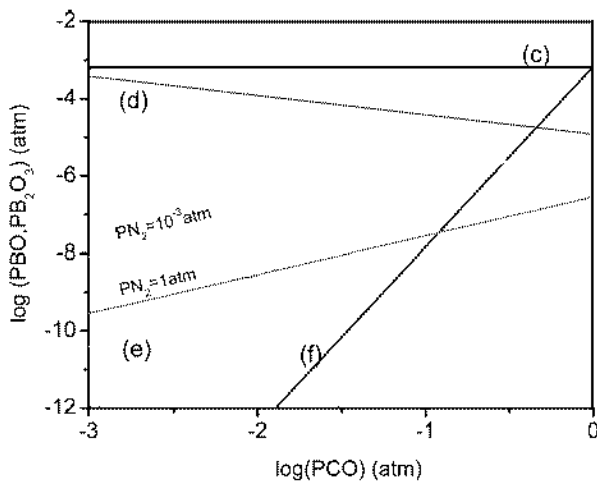
Table 5. The equilibrium partial pressure of CO for various carbothermic reactions.

Reactions	$P_{\text{CO}}(\text{atm})$ at 1573 K
(a) $\text{Ti}_3\text{O}_5 + 2\text{C} = 3\text{TiO} + 2\text{CO}$	4.95×10^{-2}
(b) $\text{Ti}_3\text{O}_5 + 2.3\text{C} = 3\text{Ti}(\text{O}_{0.95}\text{C}_{0.05}) + 2.15\text{CO}$	7.76×10^{-2}
(c) $\text{Ti}(\text{O}_{0.95}\text{C}_{0.05}) + 2\text{BO} + 2.95\text{C} = \text{TiB}_2 + 3\text{CO}$	1.73×10^{10}

Table 6. Standard Gibbs free energy change for various chemical equilibria during the formation of TiB₂.

Reactions	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J)
(a) $3\text{TiO}_2(\text{s}) + \text{C}(\text{s}) = \text{Ti}_3\text{O}_5(\text{s}) + \text{CO}(\text{g})$	273,466 - 198.0T
(b) $\text{B}_2\text{O}_3(\text{l}) + \text{C}(\text{s}) = 2\text{BO}(\text{g}) + \text{CO}(\text{g})$	1,106,844 - 473.4T
(c) $\text{B}_2\text{O}_3(\text{l}) = \text{B}_2\text{O}_3(\text{g})$	362675 - 155.7T
(d) $\text{B}_2\text{O}_3(\text{g}) + \text{C}(\text{s}) = 2\text{BO}(\text{g}) + \text{CO}(\text{g})$	744,169 - 317.7T
(e) $\text{Ti}_3\text{O}_5(\text{s}) + 2\text{BO}(\text{g}) + \frac{11}{3}\text{C}(\text{s}) = \text{TiB}_2(\text{s}) + \frac{11}{3}\text{CO}(\text{g})$	115,358 - 256.6T
(f) $\text{Ti}_3\text{O}_5(\text{s}) + \text{B}_2\text{O}_3(\text{g}) + \frac{14}{3}\text{C}(\text{s}) = \text{TiB}_2(\text{s}) + \frac{14}{3}\text{CO}(\text{g})$	859,527 - 574.3T

Evidently, from the equilibrium constant relationship which is for the formation of BO gas via reaction (d), the partial pressure of BO varies inversely with P_{CO} and, this linear relationship is shown in Fig. 2. A similar algebraic procedure can be demonstrated to establish a graphical relationship between P_{CO} and P_{BO} for reaction (e), which is for the consumption of BO gas. From Fig. 2, it is evident that by fixing the partial pressure of CO gas, P_{BO} can be forced to an invariant value at an isotherm. The difference between the values of equilibrium partial pressure of BO can therefore be fixed, hence permitting the overall chemical reaction to proceed only at a rate proportional to $(P_{\text{BO}}^d - P_{\text{BO}}^e)$. Here the superscripts designate the equilibrium partial pressures for the corresponding reactions in Table 6. If the partial pressure of BO gas falls below the line representing reaction (e), the formation of TiB₂ will cease. Also note that with increasing partial pressure of CO, the BO pressure differential becomes small, leading to a smaller driving force for chemical reaction. Similarly we can consider reactions (c) and (f) for

**Fig. 2.** $P_{\text{B}_2\text{O}_3}$ - P_{CO} / P_{BO} - P_{CO} isotherm diagram at 1673 K.

establishing a relationship between $P_{\text{B}_2\text{O}_3}$ and P_{CO} at a given temperature. These two lines are also shown in Fig. 2.

For the synthesis of composite powder admixture, for example, boron nitride (BN) which can form via $\text{BO}(\text{g}) + \frac{1}{2}\text{N}_2(\text{g}) + \text{C}(\text{s}) = \text{BN}(\text{s}) + \text{CO}(\text{g})$, the equilibrium constant at 1673 K is equal to 3.50×10^6 . In order to establish a P_{BO} - P_{CO} relationship for BN, it is essential to consider the equilibrium between TiB₂, TiN, BN, and N₂ gas given by reaction $\text{TiN} + 2\text{BN} = \text{TiB}_2 + \frac{3}{2}\text{N}_2$. This equilibrium will permit us to establish the minimum partial pressure of N₂ gas in order to form BN via BO gas. By setting the value of partial pressure of N₂ to 1.33×10^{-3} atm at 1673K, which is derived from the equilibrium constant relationship ($K = 4.86 \times 10^{-5}$), the straight line equation for the consumption of BO gas to form BN can be calculated. This line is superimposed in Fig. 2. The BN formation line has a different slope than TiB₂ line (cf. reaction e)). Similarly for P_{N_2} equals to 1 atm, BN line has been drawn and the new BN line lies at lower BO partial pressures. Clearly the reduction-nitridation condition can be selected by predetermining the nitrogen and CO partial pressures in the gas mixture. For example at 1673 K, if P_{N_2} is less than 1.33×10^{-3} atm and the P_{CO} is 0.1 atm, BN phase will not form in the presence of titanium oxide and carbon in the starting mixture. The thermodynamic calculations are in full agreement with the analysis of phases in Table 1, 2 and 5.

An important aspect of Fig. 2 is that it enables us to indirectly estimate the nucleation and the growth rate of ceramic crystals as both processes are dependent on the P_{BO} pressure differential. The larger is the value of the differential, the higher is the nucleation rate. After achieving large nucleation rate, the pressure differential can be changes to allow only a slow rate of growth of ceramic crystals to achieve a better control of microstructure. Therefore we find that the control of vapour phase species is critical not only from the thermodynamic reasons but also for optimising the kinetic conditions.

4.2 The Activation Energy

Using the observed percentage reduction data in the temperature range 1473 K to 1773 K, a relationship between the rate of reduction ($\%R/\Delta t$), and the reciprocal of the absolute temperature was established and this is shown in Fig. 3. This graph enabled to empirically derive the value of overall activation energy barrio for the reduction of TiO₂ and B₂O₃ with carbon to TiB₂ and CO gas. The overall

activation energy for the reduction process is approximately $52 \text{ kJ} \cdot \text{mol}^{-1}$ of $\text{TiO}_2/1.5\text{B}_2\text{O}_3$. The activation energy, however, rises sharply below 1373 K to $150 \text{ kJ} \cdot \text{mol}^{-1}$. The change in the slope the Arrhenius relationship arises due to the rapid transformation of non-stoichiometric oxides of titanium. The experimental results⁶⁾ show that Ti_3O_5 phase forms at the expense of Ti_4O_7 at temperatures above 1373 K. The change in the activation energy can be attributed to the reduction-reaction-induced transformations in the crystalline lattice. At higher temperature above 1573 K, the diffusion of interstitial atoms in these oxides appear to be substantially fast and the enhance chemical reaction yields an activation energy of 52 KJ. The diffusion rate in the oxycarbide lattice rises due to the boron monoxide chemical potential. The low temperature activation energy is within the acceptable value for the nitriding of TiO_2 to TiN . This is also referred in elsewhere⁶⁾.

A detailed investigation on the microstructural aspects of the reduced pellets was undertaken and the average crystallite size was determined by measuring the a-dimension of hexagonal crystallites. The mean value of size in micrometer was plotted against reciprocal temperature. The relationship is compared with the rate of reduction data in Fig. 3 and also with the published results of Baumgartner *et al.*⁶⁾. The derived value of activation energy for grain growth is 160 KJ per mole of TiB_2 in the temperature range 1573 K and 1773 K, and compares reasonably with the low temperature value of activation energy for the grain growth of diboride. The grain growth rate data by Baumgartner indicates that the lattice diffusion dominates above 2373 K, whereas the surface diffusion

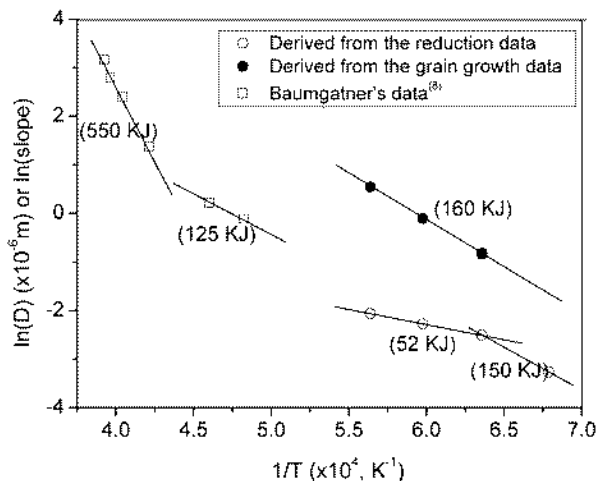
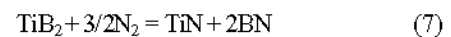


Fig. 3. The activation energy for TiB_2 reaction.

governs only below $0.66 T_m$. The comparison of activation energy for crystal growth rate indicates that the surface diffusion dominates the growth process. This also appears to be true from the micro-structural investigation which shows the presence of spiral and ledge growth. The overall activation energy for chemical reaction on the other hand is almost one third (52 KJ) of the thermal barrier for the grain growth process. This indicates that in the temperature range 1573 K to 1773 K, the overall chemical reaction is not a rate-determining step. For the limited number of reduction experiments below 1573 K, the derived value of activation energy for chemical reaction is 150 KJ and, this clearly indicates a transition in the mechanism of overall chemical reaction.

4.3 The Phase Stability Diagram in Ti-B-N System

After the initial stage, the boride formation progressed via a gas-solid reaction, $2\text{BO} + 1/3\text{Ti}_3\text{O}_5 + 11/3\text{C} = \text{TiB}_2 + 11/3\text{CO}$. When $\text{B}_2\text{O}_3/\text{TiO}_2$ is high, TiC converts into TiB_2 because of the presence of sufficient quantities of BO gas above 1644 K which is the temperature of transformation of TiC to TiB_2 in the presence of B_2O_3 by carbothermic reduction. The ratio of phases produced varied depending upon the composition of starting materials, temperature and reaction time. Therefore it is possible to control the production of ceramic mixtures as well as the volume of constituent phases. Based on the equilibrium phase relationship and Gibbs free energy change data in the presence of nitrogen, we have tentatively constructed a phase equilibrium diagram which identifies the stability range of various phases in the Ti-B-N system, as shown in Fig. 4. Here the two-phase fields surround a three-phase $\text{TiB}_2 + \text{TiN} + \text{BN}$ region in which the degree of freedom is one at a constant pressure. The phase field should reduce to a point at a constant temperature and pressure condition. However this is not the case because the phase equilibrium relationship is a pseudo-equilibrium relationship. This is because we have excluded carbon and oxygen as components in the Gibbs phase relationship. However if CO gas is taken as a component, the degree of freedom is 2 in a 3-condensed phase field. The regions of phase stability are compared with the experimental data. For example by considering the reaction:



At temperature 1773 K, P_{N_2} is 5.95×10^{-3} atm. Below this

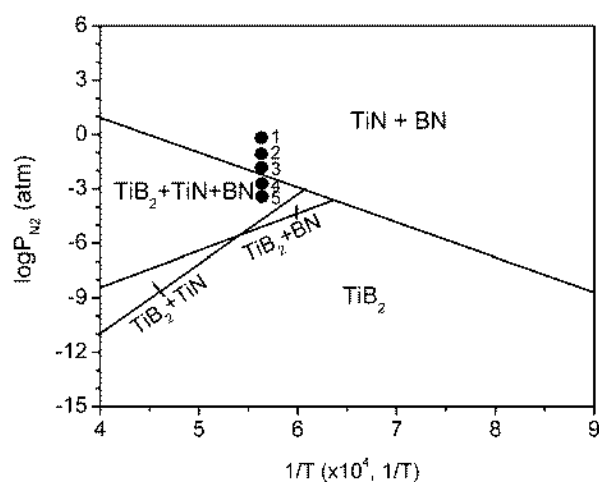


Fig. 4. The stability relationship between condensed phases in Ti-B-N system.

partial pressure of nitrogen, the diboride phase should be more stable. The phase equilibrium, however, in the Ti-B-N system is determined by the combination of univariant lines as indicated in Fig. 4. This is apparent from the experimental results of controlled nitriding of TiB_2 leading to the formation of TiN and BN at 1773 K. Experimental points 1 to 5 in Fig. 4 lie in the TiN+BN and TiB_2 +TiN+BN phase fields. Points 1 to 4 are consistent with the calculated phase diagram for which the number of crystalline phases produced the reduction-nitriding agree with the powder diffraction pattern shown in Table 2. Whereas for the experimental point 5, the BN phase was not identified by X-ray powder diffraction analysis and hence appears to be inconsistent with the calculated phase field. It is also likely that the small quantities of BN might not have been detected by powder diffraction technique.

5. Conclusions

Microcrystallites of titanium diboride (TiB_2) form via a phase reaction between BO or B_2O_3 gas and the solid Ti_3O_5 crystalline phase in a reduction atmosphere. In the TiB_2 synthesis reaction, the metal and boron oxides are mainly reduced via a gas phase reaction. At high temperatures, B_2O_3 produces a vapour phase in a reducing atmosphere, which occurs via $B_2O_3 + C = 2BO + CO$ reaction. The reduction process is sustained by the presence of BO and CO intermediary gaseous products. The overall rate of chemical reaction has activation energy of 52 kJ per mole of TiB_2 in

the temperature range 1573 K to 1773 K.

The produced titanium boride phase has hexagonal platelet morphology and during the reduction reactions, once the crystals nucleated they have a tendency to grow. From the comparison of grain growth rate data, the crystallite of TiB_2 appears to grow via a surface diffusion mechanism. For the production of the composite microstructure, the N_2 partial pressure was found to be the most critical factor. In the composite microstructure, the titanium nitride particle has a submicrometer size whereas the boride particle size is only a few micrometers. The grain growth rate in the temperature range 1573 K to 1773 K indicates that the overall activation energy of grain growth is of the order of $160 \text{ kJ} \cdot \text{mol}^{-1}$ and is significantly higher than the activation energy for the chemical reaction.

The thermodynamic stability of relevant ceramic phases is defined by plotting univariant diagrams from which the condition required to form a multi-phase ceramic microstructure for composite fabrication. The synthesis of TiB_2 /TiN, TiB_2 /TiC, TiB_2 /TiN/BN and mixed diboride composites is possible by employing the reduction route.

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References

1. G. V. Samsonov and I. M. Vinitzkii : "Handbook of Refractory Compounds", IFL/Plenum, NewYork, 1980, p. 40, 441, 442.
2. H. J. Goldschmidt : "Interstitial Alloys", (Butterworth & Co. Ltd., 1967), 255, 225.
3. A. D. McLeod, J. S. Haggerty and D. R. Sadoway, J. Am. Cera. Soc., 67(2), 705-708 (1984).
4. M. A. Janney, Am. Ceram. Soc. Bull., 66(2), 322-324 (1987).
5. C. H. McMurty, W. D. G. Beocker, S. G. Seshadri, J. S. Zhanghi and J. E. Ganier, Am. Ceram. Soc. Bull., 66(2), 325-329 (1987).
6. A. Jha and S. J. Yoon, J. of Materials Sci., 34, 307-322 (1999).
7. E. T. Turkdogan: "Physical Chemistry of High Temperature Technology", (Academic press, New York), pp. 5-26 (1980).
8. H. R. Baumgartner and R. A. Steiger: J. Am. Ceram. Soc. 67(3), 207-12 (1984).