

Synthesis of Titanium Diboride and Composites by Carbothermic Reduction of Titanium Oxide and Boric Oxide

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The formation of titanium diboride (TiB_2) via the reduction of TiO_2 with boric oxide and carbon was studied in a partially reducing atmosphere of argon mixed with 4 vol.% H_2 . The effect of reaction time, temperature, partial pressure of nitrogen and TiO_2/B_2O_3 stoichiometric ratio on the reducibility of oxides has been studied. The phases formed were analysed by using X-ray powder diffraction and scanning electron microscopic techniques. In this paper, we also investigated the presence of CaC_2 as a reducing agent on the reducibility of oxide mixtures and on the Ti-B-C-Ca-O phase equilibria. The morphology of TiB_2 formed in the presence of CaC_2 is compared with the microstructure of TiB_2 formed as a consequence of carbothermic reduction. The observed variation in TiB_2 crystals formed is also explained.

Key words : Titanium diboride, Composite, Synthesis, Carbothermic reduction, Morphology, Gas-solid reaction

I. Introduction

The selection of engineering ceramics is determined by their properties. Metal diborides are one such material and titanium diboride falls in this category. The properties of borides are intimately associated with the electronic structure of the metallic components. On this basis, the borides constitute a group of ceramic materials with attractive and unusual properties. Titanium diboride is a unique material because it combines many properties typical of metals and ceramics. In addition to its high melting point and hardness, the ceramic crystal structure has low electrical resistivities¹⁾ and metal-like thermal conductivity. Titanium diboride products are among the more expensive engineering materials. Firstly, it is difficult to synthesise these materials economically in a pure form. Secondly, the material characteristics of TiB_2 such as its hardness, inevitably lead to high manufacturing costs. At present there are several methods for the preparation of diborides and these are briefly described below.

① High-temperature reduction of the metal oxide by boron carbide (or titanium carbide²⁾) and carbon. ② Reaction of the metal halide with BH_3 in a plasma arc^{3,4)} yields TiB_2 , HCl and H_2 gas mixture. ③ The reductive dehalogenation of halide with sodium metals as a low temperature route to boride and carbide precursors.⁵⁾ ④ Similarly the hydrogen plasma arc process has been employed to carry out the reduction of the metal and boron oxides.⁶⁾ ⑤ TiB_2 powders with sub-borides of Ti have also been synthesised by solid state reactions of metallic titanium and amorphous boron powder⁷⁾ and is an exothermic reaction, also known as the SHS reaction. ⑥ The decomposition of

metal borohydrides⁸⁾ can also yield TiB_2 powder. ⑦ The final category of synthesis reaction is called the carbothermic reduction of oxides.

Amongst all the above processing techniques, the carbothermic reduction process is by far the cheapest because it relies on the supply of inexpensive raw materials. Also for each mole of TiB_2 produced, the process generates CO which will release a energy when burnt with a oxygen. The heat released could therefore be utilised to meet a part of the total energy requirement of the materials fabrication process. The economic benefits are also potentially realizable for the production of pure TiB_2 powders, mixed diborides and composite materials. In particular the diborides can be formed in the partially-densified geometries by adding suitable sintering agents such as high-melting point alloy phase that not only provides adequate bonding but also is expected to improve toughness of the composite materials. This is important for the fabrication of cutting tool inserts. Some powder synthesis routes are rather expensive and also produce pyrophoric powders. The reducing atmosphere maintained in the carbothermic reduction process reduced the surface contamination of the titanium diboride powders.

In this investigation, an attempt has been made to establish the kinetic and thermodynamic aspects of boride synthesis. The mechanism of growth of TiB_2 particulates also explored and the effect of gaseous atmosphere on the morphological modification is discussed. Furthermore, the phase equilibria have been established for the synthesis of TiB_2/TiN , TiB_2/TiC , $TiB_2/TiN/BN$ composite materials and a few phase fields have been empirically verified.

Thermodynamics of the synthesis reaction: The

Table 1. The Values of $-RT\ln PCO$ (KJ) for Various Carbo-thermic Reactions in the Ti-C-B-O-N System

Reactions	$-RT\ln PCO$ (KJ)	Teq. (K)
(a) $TiO_2+B_2O_3+5C=TiB_2+5CO$	267.483-0.166T	1613
(b) $TiO_2+2C+N_2=TiN+2CO$	187.945-0.128T	1469
(c) $TiO_2+3C=TiC+2CO$	263.717-0.168T	1567
(d) $B_2O_3+3C+N_2=2BN+3CO$	136.161-0.108T	1255
(e) $2B_2O_3+7C=B_4C+6CO$	296.325-0.166T	1786
(f) $TiN+B_2O_3+3C=TiB_2+3CO+N_2$	320.508-0.191T	1677
(g) $TiC+B_2O_3+2C=TiB_2+3CO$	269.994-0.164T	1644
(h) $2BN+TiO_2+2C=TiB_2+2CO+N_2$	484.466-0.252T	1844
(i) $B_4C+2TiO_2+3C=2TiB_2+4CO$	224.221-0.166T	1353

compiled thermodynamic data⁹ were used to predict the phase stability of titanium boride and titanium and boron nitride in equilibrium with a gas phase as a function of the temperature. The thermodynamic feasibility of the formation of titanium diboride and nitride phases via the reduction of oxides in the presence of carbon is considered. For the synthesis of TiB_2 , we can write



From the Le Chatelier principle, the removal of CO gas from the reaction chamber by purging argon gas will ensure a shift in the equilibrium of reaction (1) in the forward direction, otherwise the backward equilibrium will dominate.

For the formation of titanium diboride (TiB_2), nitride (TiN), carbide (TiC), boron nitride (BN) and carbide (B_4C) phases, the relevant reactions are summarised in Table 1. For example, it is evident that TiB_2 is the most stable high temperature ceramic phase whereas BN is the stablest phase in the temperature range 1255 to 1844 K. Similar deductions concerning the stability relationship between other phases can also be established. The proximity of ΔG° values of TiC and TiN phases is indicative of the fact that the two crystalline phases are likely to be similar in their chemical and structural characteristics.

II. Experimental Procedure

Pigment grade titanium oxide (TiO_2), boron oxide (B_2O_3) and carbon were the starting materials for the synthesis of pure and mixed ceramic phases. The stoichiometric proportions of TiO_2 , B_2O_3 and carbon were weighed. The weighed materials were thoroughly dry-mixed, ground in agate mortar and pressed in a steel die to form cylindrical shape pellets. The compacted pellets were heated in the temperature 1173-1823 K range. The pressed samples were transferred inside a graphite crucible and heated in the isothermally-maintained zone of the resistance furnace. Each pellet took approximately a few minutes to reach the selected isotherm. In most mixtures, more than the stoichiometric amount of boron oxide and carbon was added for the completion of the reduction reaction. Two

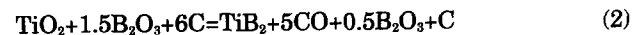
different kinds of carbon were used namely graphite and activated charcoal. Depending upon the composition of the synthesised product, the gas mixture was selected. For example, TiB_2 was synthesised by flushing the reaction chamber with argon (Ar) gas whereas a stream of N_2 was maintained when nitrides were synthesised. A typical gas flow rate was 500 ml/min. After reaction, the pellets were weighed for the calculation of percentage reduction. The phases present in the reacted pellets were determined by x-ray powder diffraction technique using $Cu-K\alpha_1$ radiation (0.15406 nm). The reaction products were also examined by scanning electron microscopic technique.

III. Results and Discussion

1. The synthesis of titanium diboride

1.1 The extent of reduction of titanium and boron oxides

The percentage reduction of titanium and boron oxide with carbon was investigated by measuring the weight of sample before and after reaction at the selected reaction temperature and time. The degree of reduction (%R) was calculated from the stoichiometry of reaction shown below in equation (2):



$$\text{Percentage reduction (\%R)}=(\Delta W/W_o) \times 100 \quad (3)$$

where ΔW is the observed percentage weight loss in a pellet during the course of reaction at any arbitrarily chosen time 't' from the starting time $t=0$, and W_o is the maximum expected stoichiometric percentage weight loss. Total weight of the reactant is 256.4 gram, while that of the product should be 116.3 gram, from which a maximum weight loss of 140.1 gram is expected. This means that the theoretical maximum W_o is 54.62%. B_2O_3 , however, is easily volatilised as a BO (or B_2O_3) gas. Therefore, it is reasonable to assume that there is no B_2O_3 remaining in the product after reaction, and in this case theoretical maximum W_o is 68.20%. The reaction occurred rapidly leading to formation of TiB_2 crystals. For example, in 10 minutes reaction, more than 80%R was obtained of which TiB_2 was the main phase with small amount of TiC . The reduction was complete within 30 minutes below 1773 K and no further change in weight was observed even after 24 hours.

1.2 The effect of reaction temperature and time

When pellets with $TiO_2+B_2O_3$ in the mixture were reduced with carbon at 1573 K in an argon atmosphere, the boride (TiB_2) phase formed. At short reaction time, the formation of $Ti_{1-x}C_x$ phase was noticeable, but with prolonged reaction time, the $Ti_{1-x}C_x$ phase became less stable. Table 2 summarises phases produced as a consequence of co-reduction of titanium and boron oxides. For the synthesis of TiB_2 by carbothermic reaction, $TiO_2+B_2O_3+5C=TiB_2+5CO$, the equilibrium temperature is 1613 K. From the Le Chatelier principle, the removal of CO gas

Table 2. Summary of Phases Produced a Consequence of Co-reduction of Oxides

Starting Materials	Gas	Temp (K)	Time (hr)	Phase
TiO ₂ +1.5B ₂ O ₃ +6C	Ar	1473	0.17	Ti ₃ O ₅ , TiC _x O _y
		1573	0.17	TiB ₂ , TiC
			0.5	TiB ₂ , TiC
		1673	0.17	TiB ₂ , TiC
			0.5	TiB ₂ , B ₄ C
			1.0	TiB ₂ , B ₄ C*
			4.0	TiB ₂
8.0	TiB ₂			
24.0	TiB ₂			
1773	0.17	TiB ₂		

1) carbon source: activated charcoal, 2) *: very small trace, 3) gas flow rate=0.5 l·min⁻¹.

from the reaction chamber by purging argon carrier gas shifts the equilibrium reaction in the forward direction, so that TiB₂ phase can be produced below the equilibrium temperature. Ti₃O₅ was the intermediate phase for the formation of titanium diboride at 1473 K. TiB₂ was the main phase along with TiC or B₄C in the samples reduced above 1573 K for 10 minutes reaction. At relatively low temperature, titanium carbide formed via titanium oxycarbide phase. The formation of TiC via Ti₃O₅ → Ti_{1-x}C_x is expected and is thermodynamically feasible. The formation of the boron monoxide gas or B₂O₃ gas is expected above 1373 K. In the presence of excess unreacted carbon, the formation of carbide of boron is expected via:



Either Ti₃O₅ or TiC_{1-x}O_x could then possibly react with either B₂O₃ or BO gas at higher temperatures to form TiB₂. A selected few X-ray powder diffraction patterns of the reduced pellets are shown in Fig. 1. From this the relative intensities of various phases can be compared.

1.3. The effect of composition

The effect of composition of starting materials, especially B₂O₃/TiO₂ ratio was investigated. At short reaction time, titanium oxide reduced to suboxide (eg. 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, but as the amount of B₂O₃ was raised from the molar ratio of 1 to 2, the Ti_{1-x}C_x phase became less stable. It was observed from the powder diffraction pattern that the molar ratio of TiO₂:B₂O₃=1 is sufficient for the synthesis of TiB₂+Ti_{1-x}C_x phase mixture. Table 3 summarises the experimental condition for the formation of two or more refractory phases mixture. The observations are consistent with the overall stoichiometry of the reduction reaction which is a major

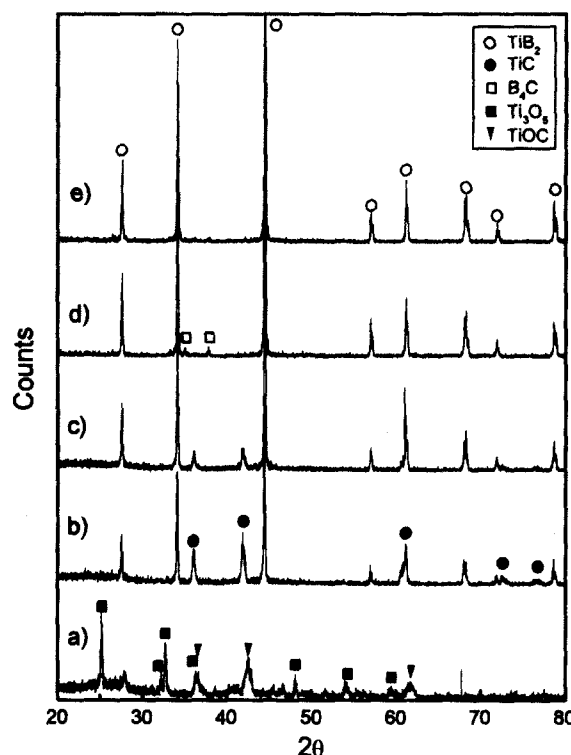


Fig. 1. X-ray diffraction patterns of the reduced samples at (a) 1473 K, 10 min, (b) 1573 K, 10 min, (c) 1573 K, 30 min, (d) 1673 K, 10 min and (e) 1773 K, 10 min in Ar gas (0.5 l·min⁻¹).

Table 3. Produced Phases According to Composition of Starting Materials

Starting Materials	Gas	Temp (K)	Time (hr)	Phases
TiO ₂ +2B ₂ O ₃ +8C*	Ar	1773	24.0	TiB ₂ , C
TiO ₂ +1.5B ₂ O ₃ +6C**		1673	24.0	TiB ₂
TiO ₂ +B ₂ O ₃ +5C**		1673	24.0	TiC, TiB ₂
TiO ₂ +B ₂ O ₃ +6.5C*		1773	24.0	TiB ₂ , C
2TiO ₂ +0.5B ₂ O ₃ +5.52C*		1673	18.0	TiC, TiB ₂

*: 50% graphite/50% activated charcoal, **: 100% activated charcoal

subject of discussion.

1.4 The effect of partial pressure of nitrogen

The results of several phase mixtures formed via the reduction route are summarised in Table 4. The nitrides, TiN and BN, are evidently the dominant phase produced in the nitrogen atmosphere via carbothermic reduction. But in the inert gas atmosphere, titanium diboride (TiB₂) phase formed with titanium carbide (TiC). X-ray powder diffraction patterns of phases produced are shown in Fig. 2.

Titanium nitride (TiN) phase easily formed by carbothermic reaction of TiO₂ in the nitrogen atmosphere as shown in elsewhere,¹⁰ for example, TiN phase formed with titanium suboxide, Ti₃O₅, 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

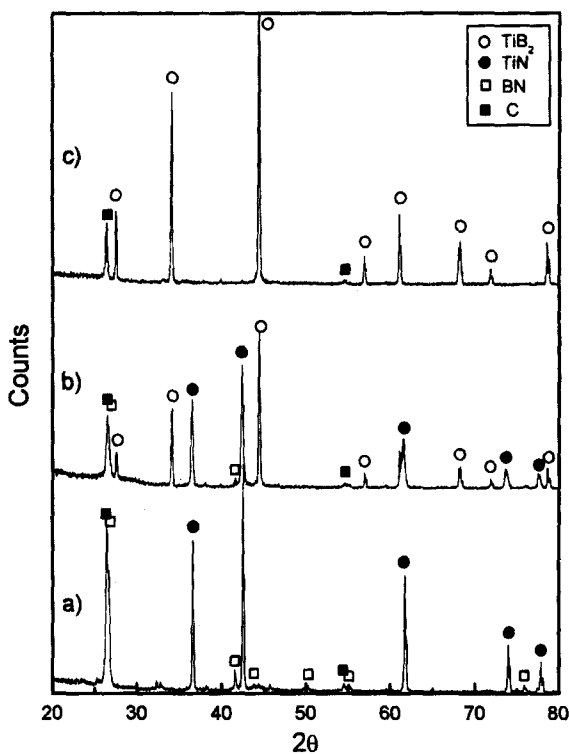
Table 4. Produced Phases According to Partial Pressure of Nitrogen (graphite : activated charcoal=1 : 1)

Starting Materials	Temp (K)	Time (hr)	PN ₂	Produced Phases
TiO ₂ +2B ₂ O ₃ +8C	1773	24	1	TiCN, BN, C
			0.1	TiCN, BN, C
			0.02	TiCN, BN, C
			0.002	TiB ₂ , TiCN, BN, C
			0.0005	TiB ₂ , TiCN, C
			0 (P _{Ar} =1)	TiB ₂ , C

Table 5. Summary of Phases Produced by Carbide Reduction

Starting Materials	Gas	Temp (K)	Time (hr)	Phases
TiO ₂ +B ₂ O ₃ +3CaC ₂	Ar/ H ₂ (4%)	1523	0.5	TiB ₂ , X, Y
TiO ₂ +B ₂ O ₃ +3CaC ₂		1673	0.25	TiB ₂ , X, Y
TiO ₂ +B ₂ O ₃ +3CaC ₂		1673	0.75	TiB ₂ , Y
TiO ₂ +B ₂ O ₃ +2CaC ₂ +C		1673	24.0	TiB ₂ , Y
TiO ₂ +B ₂ O ₃ +2CaC ₂ +C		1773	0.5	TiB ₂ , Y

1) carbon source: activated charcoal, 2) X: borate, Y: Ca-Ti-O phase

**Fig. 2.** X-ray diffraction patterns of the reduced samples (PN₂=(a) 0.05, (b) 0.002 and (c) 0 atm at 1773 K after 24 hrs) (Ar+N₂ flow rate: 0.5 l·min⁻¹).

at 1573 K. It is understood that because of the formation of BO gas, the reduction of titanium oxide was retarded.

1.5 The synthesis of TiB₂ with calcium carbide

As a part of the carbothermic reduction reaction of titania and boric oxide (B₂O₃) for the formation of titanium diboride crystalline phase, we have also carried out a limited number of experiments with CaC₂ as a reducing agent. The reduction with calcium carbide facilitates study that of the aspects of both carbothermic and calciothermic reduction reaction mechanisms. The synthesis of titanium diboride from calcium carbide reduction is defined below:



The standard Gibbs free energy change is equal to 406.39-

0.388T kJ·mol⁻¹. The equilibrium of this reaction shifts to the right hand side above 1047 K. TiO₂ and B₂O₃ were mixed with CaC₂ in the above stoichiometric ratio and pelletized. The cylindrical pellets were heated inside the radio frequency induction coil. The temperature of the pellet was raised above 1273 K over a period of 5 minutes at which a minor pyro-activity was observed inside the crucible. The inert gas was purged through the reaction chamber while the pellet was reduced. The ignition was spontaneous and localized that lasted a few seconds. The ignition front, unlike aluminothermic reduction, did not propagate right through the pellet. The pyroactivity was more violent when calcium carbide was replaced by metallic calcium. After the ignition phase, no further activity was observed. The pellet temperature was then raised to an isotherm 1773 K at which it was held for a fixed period of time. After the isothermal hold period, the radio frequency coil supply power was turned-off and the sample was allowed to cool in the stream of the argon gas.

Using this method, several pellets were reduced in this way. The reduction was only partially possible in a few samples. However, further isothermal annealing at 1773 K resulted in a higher extent of conversion. The reduction, however, was never complete because of the presence of impurity lime in commercially available calcium carbide. The presence of impurity lime slows the conversion rate by forming an unknown complex borate which appeared to be amorphous. This was verified from X-ray powder diffraction patterns in which the extent of crystalline phase and their relative intensities significantly changed as the extent of boride conversion increased. The complex borate phase, however, was found to be unstable above 1673 K. The results of the carbide reduction are summarised in Table 5. When laboratory synthesized calcium carbide was substituted for commercially-available calcium carbide, the reduction reaction reached completion at 1773 K.

2. Microstructure of TiB₂

The synthesised titanium diboride powder had a hexagonal platelet morphology with layers parallel to the (001) basal plane. The microstructure indicated that the TiB₂ crystals are likely to grow by condensation of the vapour phase. It is well known that in some crystals de-

posited from the vapour phase, thin plates are often formed, and it is probable that these are separated by faulted layers.¹¹ In other cases where the crystals have a large structure, it is possible for irregularities in structure to occur as the result of stacking faults which ex-

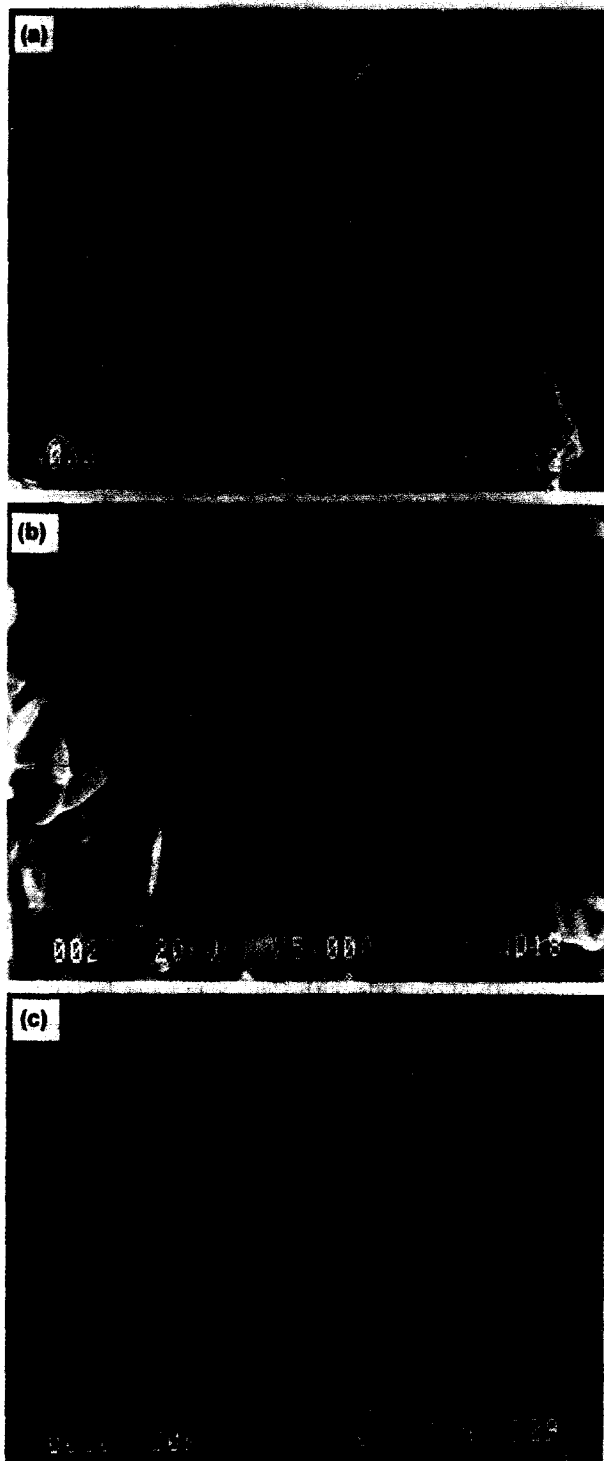


Fig. 3. Scanning electron micrograph of titanium diboride produced at (a) 1573 K, (b) 1673 K and (c) 1773 K after 10 minutes of reduction in a flowing stream of argon gas (flow rate: $0.5 \text{ l} \cdot \text{min}^{-1}$, starting material: $\text{TiO}_2 + 1.5\text{B}_2\text{O}_3 + 8\text{C}$).

tend across the entire crystal. The grain size of TiB_2 was strongly affected by reaction temperature. It grew up to $10 \mu\text{m}$ diameter at 1773 K in 10 minutes. Grain growth occurred mainly along the basal plane direction. Fig. 3 showed the morphology of TiB_2 for 10 minute reaction. At 1573 K, grains were growing from the reduced oxide matrix, even though not many TiB_2 crystals formed under this condition. TiC phase co-existed along with TiB_2 phase. As the temperature rose, more TiB_2 grains formed and the large grain growth of TiB_2 was observed at 1773 K.

At lower reaction temperature, however, irrespective of the reduction time, the grain growth rate of TiB_2 seem to be insignificant. For example, at 1673 K, the change in the average size or crystals with increasing reaction time was not noticeable. After 10 minutes of reduction, TiB_2 phase nucleated from the matrix which appears to be sintered and TiB_2 forms a wetted interface with the matrix, i.e. the interface between the crystal and matrix is rather poorly defined. However after 1 hour, the matrix phase completely disappeared. The nucleation and crystal growth from the micrographic analysis appears to be a time-dependent process which might have a classical incubation period, a period of sustained nucleation and then the growth of existing nuclei. Both nucleation and growth steps are dependent upon the mass transport. The crystallite size of TiB_2 formed in this way is between $0.3 \mu\text{m}$ and $4.5 \mu\text{m}$. This is shown in Fig. 4. The variation of crystalline size with time at 1673 K is apparent from the micrograph. After 8 hours, the average crystallite size did not vary significantly. This indicates that the major growth of crystals occur between 1 hr and 8 hrs.

The average size of titanium diboride crystals obtained from the reaction between the oxides and calcium carbide was much larger than with the carbothermic reduction process and up to $35 \mu\text{m}$ diameter. This can be seen from the comparison of micrographs in Fig. 5 with Photo 1 or 2. In the carbide reduction process, the average crystal diameter size of $30 \mu\text{m}$ sharply contrasts with the 2 to $4 \mu\text{m}$ diameter size crystals produced from carbothermic reduction at the same temperature ($T=1773 \text{ K}$). The growth of crystals in the carbothermic reduction process took place over a period of 24 hours, whereas the growth during the reduction with CaC_2 was only 30 minutes at 1773 K. Under the above two reduction conditions, the average measured thickness of the crystals were $1.75 \mu\text{m}$ and $3.52 \mu\text{m}$, respectively. From the measured dimensions of the TiB_2 crystals, it is apparent that the planar growth rate along the a-axis of the hexagonal lattice appears to be faster than the growth rate in c-direction.

IV. Conclusions

Titanium boride powder was produced by the reduction of a mixture of titanium and boron oxides with carbon via

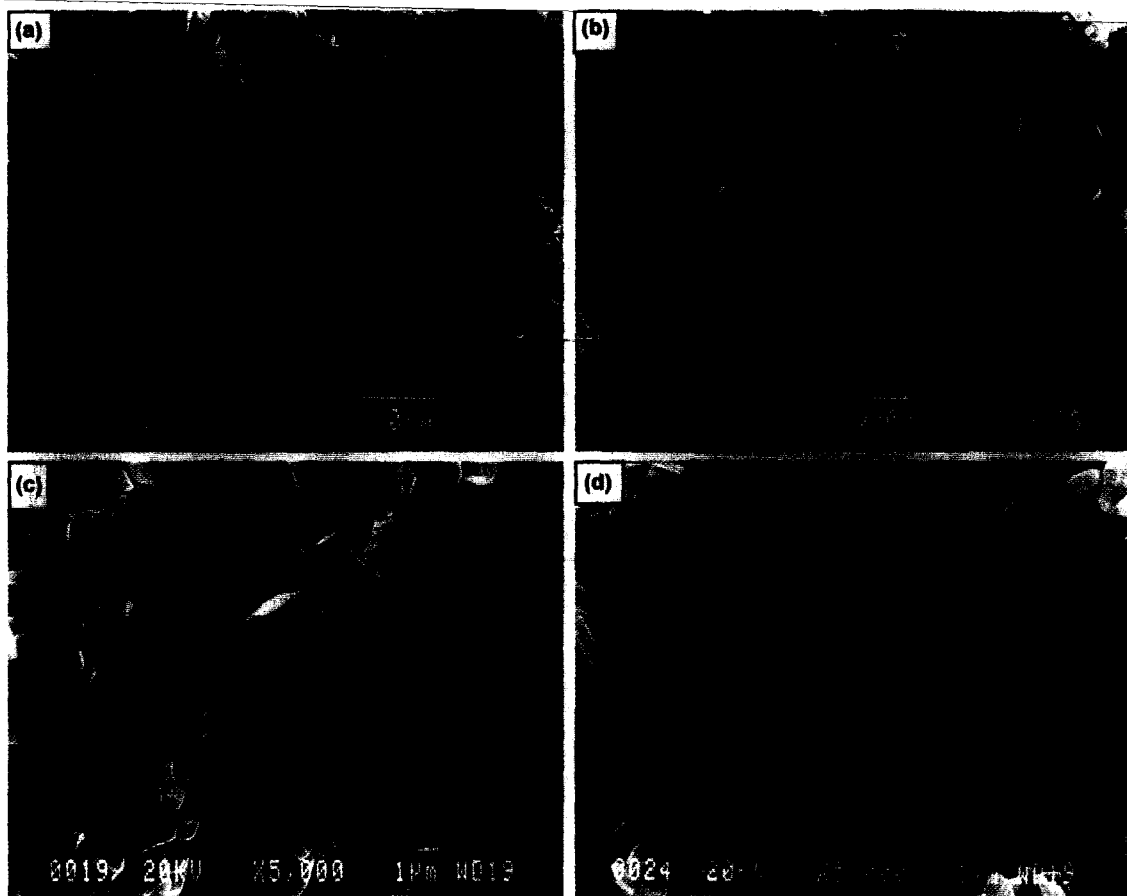


Fig. 4. Scanning electron micrograph of titanium diboride produced after (a) 10 min, (b) 30 min, (c) 8 hrs and (d) 24 hrs of reduction at 1673 K in a flowing stream of argon gas (flow rate: $0.5 \text{ l} \cdot \text{min}^{-1}$, starting material: $\text{TiO}_2 + 1.5\text{B}_2\text{O}_3 + 8\text{C}$).

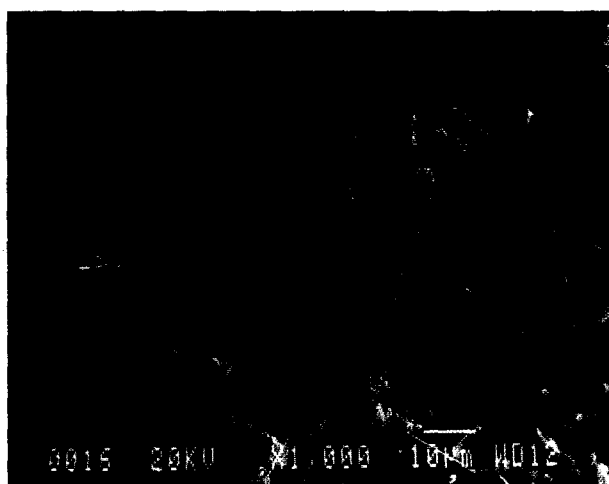


Fig. 5. Scanning electron micrograph of titanium diboride produced by carbide reduction after 30 min at 1773 K (flow rate: $0.5 \text{ l} \cdot \text{min}^{-1}$, starting material: $\text{TiO}_2 + \text{B}_2\text{O}_3 + \text{CaC}_2 + 2\text{C}$).

a gas-solid phase reaction. The titanium boride (TiB_2) phase produced by carbothermic reduction has a hexagonal platelet morphology and during the reduction reactions, once the crystals nucleate they have a tendency to grow.

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 growth of crystals with CaC_2 was more faster than with carbon and the average measured thickness of the crystals were $3.52 \mu\text{m}$ and $1.75 \mu\text{m}$, respectively. From the measured dimensions of the TiB_2 crystals, it is apparent that the planar growth rate along the a-axis of the hexagonal lattice appears to be faster than the growth rate in c-direction.

The carbothermic reaction process of TiO_2 and B_2O_3 in the presence of N_2 atmosphere leads to the formation of ceramic phase mixtures ideal for designing composite materials. The investigation also shows that production of the composite powder mixture via the oxide co-reduction technique is available. The synthesis of TiB_2/TiN , TiB_2/TiC , $\text{TiB}_2/\text{TiN}/\text{BN}$ and mixed diboride composites is possible by employing the reduction route.

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