Synthesis of boride and nitride ceramics in molten aluminium by reactive infiltration

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The infiltration of solid powder mixtures with molten aluminium has been investigated as a potential route for the synthesis of ceramic/metal composites. Either titanium or tantalum powder was mixed with boron nitride flakes for the reaction powder mixture. The infiltration occurred spontaneously at 1473K for both [Ti + BN] and [Ta + BN] powder mixtures. Owing to reactions between the starting materials, both boride and nitride ceramics were produced in molten aluminium. TiB_2 and AlN were produced from the [Ti + BN] powder mixture, and TaB_2 and AlN were produced from the [Ta + BN] powder mixture. When the [Ti + BN] powder mixture was used, a reaction producing Al_3Ti took place immediately after the infiltration of the molten aluminium, and a subsequent reaction producing TiB_2 and AlN proceeded gradually. The time required to convert BN flakes to TiB_2 and AlN particles at 1473K was in the range of 1800–3600 s. On the other hand, when the [Ta + BN] powder mixture was used, there was an initial incubation period to allow the tantalum and molten aluminium to react with each other. The reaction between tantalum, BN and aluminium took place after this incubation period.

1. Introduction

Ceramic/metal composites have been investigated for more than a decade because of their high modulus, yield stress and creep resistance [1–3]. Several processing routes have been proposed for the fabrication of these materials. The liquid-metal infiltration process has been used industrially for automotive applications [4], however the process would be simpler if the infiltration of powder preforms with molten metals occurred spontaneously. Aghajanian [5] has reported the spontaneous infiltration of Al_2O_3 preforms with liquid aluminium under a nitrogen containing atmosphere. This process employed a combination of Al_2O_3 particles and aluminium alloys, which was not originally wettable. Provided the system is more reactive, the reaction at the interface can induce an increase in the temperature which improves the wettability [6,7]. Kaneda and Choh [8] have reported that the spontaneous infiltration of SiC preforms with molten magnesium occurs provided that a certain amount of SiO_2 particles are added to the powder preform. In this process, an exothermic reaction between magnesium and SiO_2 is reported to contribute to an improvement in the wettability. Among several ceramic/metal combinations, boron nitride (BN) and molten aluminium show a good wettability [9,10] and, therefore, the spontaneous infiltration of a BN powder preform with molten aluminium is expected. Since the BN/Al system is extremely reactive at temperatures greater than 1373 K [9], the decomposition of BN should be taken into account. When titanium or tantalum powder is mixed with BN powder and

reacted with aluminium, the following reactions are expected.

$$Ti + 2BN + 2Al \rightarrow TiB_2 + 2AlN \qquad (1)$$

$$Ta + 2BN + 2Al \rightarrow TaB_2 + 2AlN \qquad (2)$$
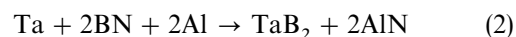
As a result of these reactions, TiB_2, AlN/Al and TaB_2, AlN/Al composites are synthesized. In this work, attempts were made to fabricate ceramic/metal composites by the spontaneous infiltration of BN-based powder mixtures with molten aluminium. Particular attention is focused on the microstructures of the synthesized materials and differences in the *in situ* reactions of the two systems.

2. Experimental procedure
2.1. Spontaneous infiltration process

The starting materials used in this work were titanium powder (99.8%Ti, with a particle size under 44 μm), tantalum powder (99.9% Ta, with a particle size under 44 μm), hcp-BN flakes (99.9% BN, 10 μm in diameter, 1–2 μm in thickness) and a pure aluminium ingot (99.99% Al). The titanium or tantalum powders were mixed with BN flakes (metal:BN mole ratio = 1:2). In the following discussions the powder mixture of titanium and BN with a mole ratio of 1:2 will be denoted as the [Ti + BN] powder mixture. The loose powder mixture (3 g) was placed in the bottom part of an alumina (Al_2O_3) crucible (inner diameter: 13 mm), and an aluminium ingot (15 g) was placed above the loose
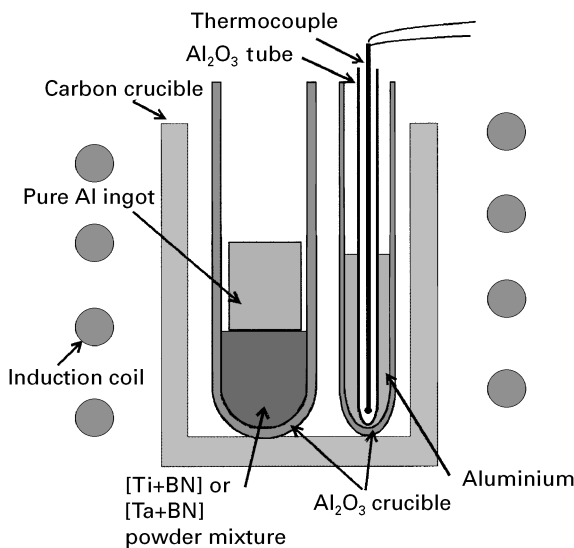
Figure 1 A schematic illustration of the experimental setup.

TABLE 1 Experimental conditions for the spontaneous infiltration

	Powder mixture	Holding time
Specimen 1	[Ti + BN]	3600 s
Specimen 2	[Ti + BN]	1800 s
Specimen 3	[Ti + BN]	300 s
Specimen 4	[Ta + BN]	3600 s
Specimen 5	[Ta + BN]	300 s

TABLE 2 Experimental conditions for the differential thermal analysis

	Components	Mixing ratio
Powder 1	[Ti + BN + Al]	1:2:4
Powder 2	[Ti + Al]	1:4
Powder 3	[Ta + BN + Al]	1:2:4
Powder 4	[Ta + Al]	1:4

microanalysis (EPMA) are shown in Fig. 2. In the X-ray images in Fig. 2, tantalum and boron are present where bright particles are visible in the secondary electron image (SEI). Although it can not be clearly observed in the SEI, there are some regions where X-ray images of nitrogen and aluminium are also detected. Fig. 3 shows an XRD pattern of specimen 4. Strong diffraction peaks that can be assigned to TaB_2 and AlN are detected at appropriate angular positions, whereas diffraction peaks that correspond to BN are rarely detected, indicating that the BN and tantalum were completely converted to TaB_2 and AlN during the 3600 s hold at 1473 K.

Fig. 4 shows the microstructure of specimen 1 in which TiB_2 particles are clearly visible. An XRD pattern of specimen 1 is shown in Fig. 5. It is clear from Figs 4 and 5, that the complete conversion of BN to TiB_2 and AlN occurred.

3.2. The effect of holding time on the microstructure
Fig. 6 (a and b) shows the microstructures of specimens 2 and 3. As indicated in the figures, Al_3Ti and BN are visible in both specimens. The formation site of the TiB_2 particles could be identified as the interface between BN and molten aluminium, although the site of the AlN nucleation could not be clearly identified (Fig. 7). These results indicate that the *in situ* reaction shown as Equation 1 was still in progress after a 1800 s hold. Conversely, specimen 5 showed a complete conversion of the starting materials to TaB_2 and AlN, even with a short 300 s hold.

3.3. Infiltration process
The temperature of the powder phase during the fabrication process was measured by inserting a thermocouple (Pt/6–30% Rh) into the crucible. Fig. 8 shows the temperature of the [Ti + BN] powder mixture as a function of processing time. The temperature increased steadily during the heating process upto 1420 K. The temperature rose sharply at 1420 K and reached a peak value of 1670 K. Although the temperature profile for the [Ta + BN] powder mixture, shown in Fig. 9, was also measured in the same way, the maximum temperature reached by the exothermic reaction could not be measured. In fact we measured a slight fluctuation in the temperature, indicating contact between the thermocouple and the molten
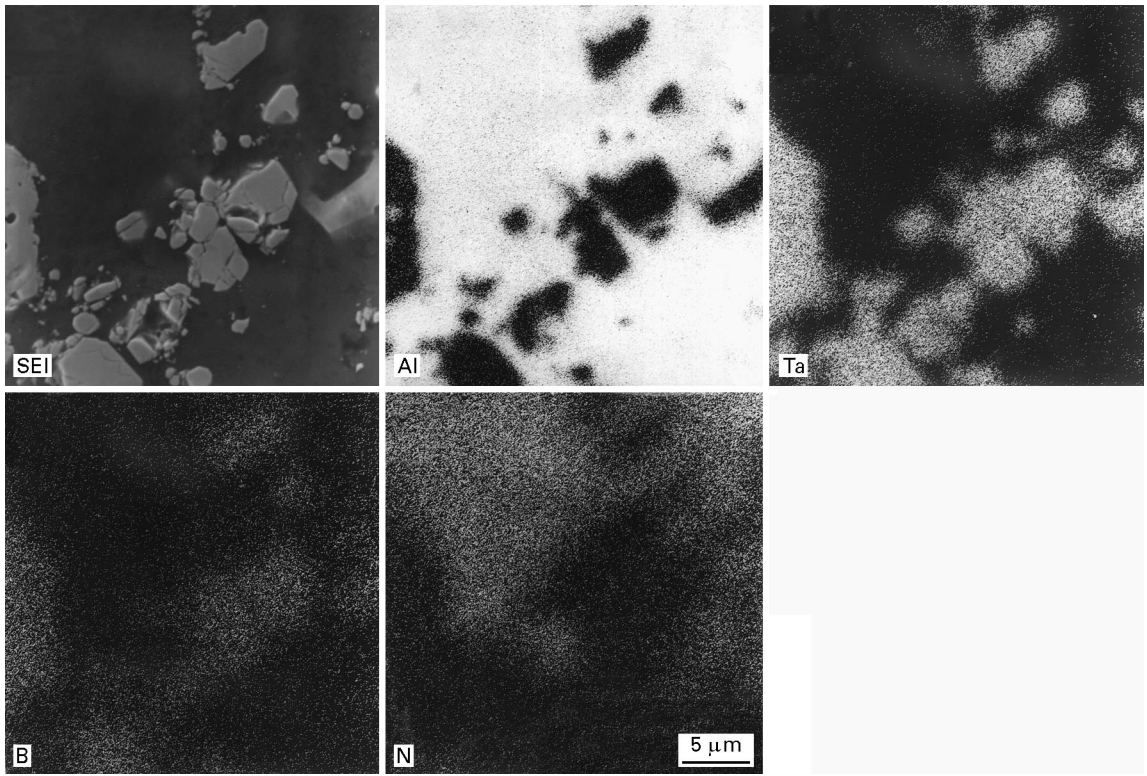
powder mixture as is shown in Fig. 1. The chamber was evacuated using a rotary pump and backfilled with nitrogen gas (99.9% pure). The specimen was then heated to 1473 K in an induction furnace, and held at this temperature for 300–3600 s. After solidification, the specimen was taken out of the crucible, and the vertical cross-section was observed. A qualitative analysis was carried out using X-ray diffraction (XRD) techniques.

Five specimens were prepared for the experiment, and the experimental conditions of the specimens 1 through 5 are listed in Table 1.

2.2. Differential thermal analysis
Four powder mixtures were studied by differential thermal analysis (DTA). The compositions of these powder mixtures are listed in Table II. Specimens were prepared by compressing the powder mixture at a pressure of 1000 MPa. The analysis was carried out in an argon gas atmosphere with a heating rate of $10 \, \mathrm{K \, s^{-1}}$.

3. Results
3.1. Microstructural observations
The molten aluminium completely infiltrated into the powder mixtures of specimens 1 through 5. The microstructures of specimen 4 observed by scanning electron microscopy (SEM) and electron probe X-ray

Figure 2 A secondary electron image and X-ray images of Al, Ta, B and N for specimen 4 ([Ta + BN] powder system).
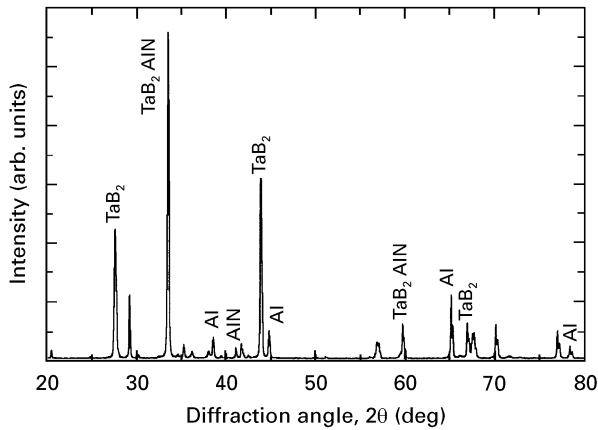

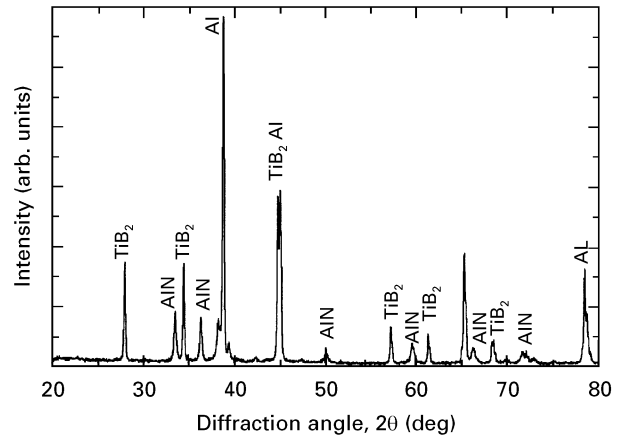*Figure 3* The X-ray diffraction pattern for specimen 4 ([Ta + BN] powder system).

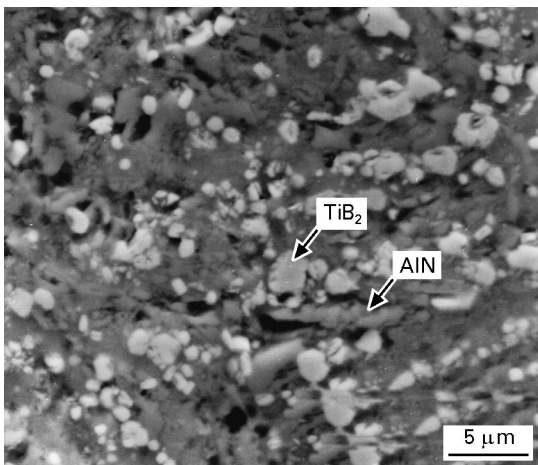*Figure 5* The X-ray diffraction pattern for specimen 1 ([Ti + BN] powder system).

Figure 4 A secondary electron image of the cross-section of specimen 1 ([Ti + BN] powder system).

aluminium. This contact resulted in damage to the thermocouple. The following differences between the two systems are observed: (i) the infiltration and the exothermic reaction take place simultaneously for the [Ti + BN] powder mixture, whereas there is an incubation period for the [Ta + BN] powder mixture. (ii) The peak temperature of the [Ti + BN] powder mixture created by the exothermic reaction is measurable. That of the [Ta + BN] powder mixture is too high to be measured by the Pt/6–30% Rh thermocouple.

3.4. Diffraction thermal analysis
An incubation period between the infiltration and the exothermic reaction was observed only in the case of
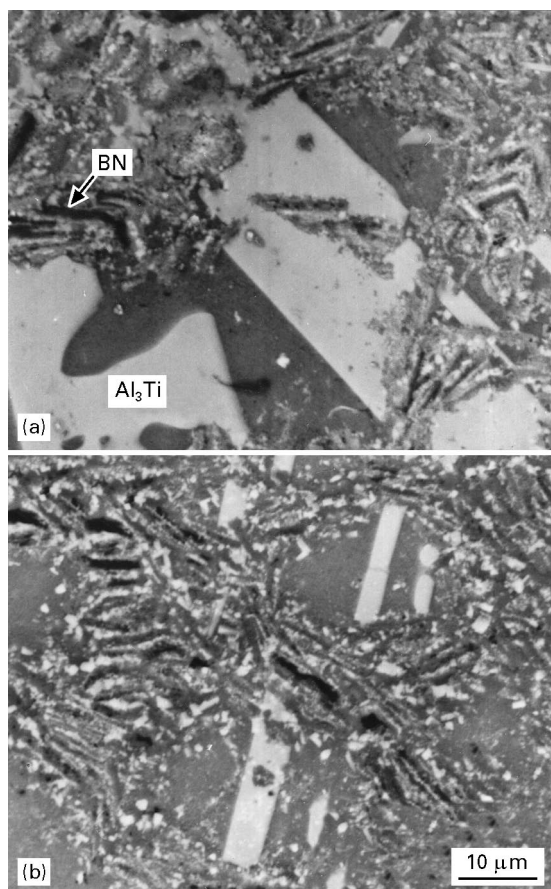
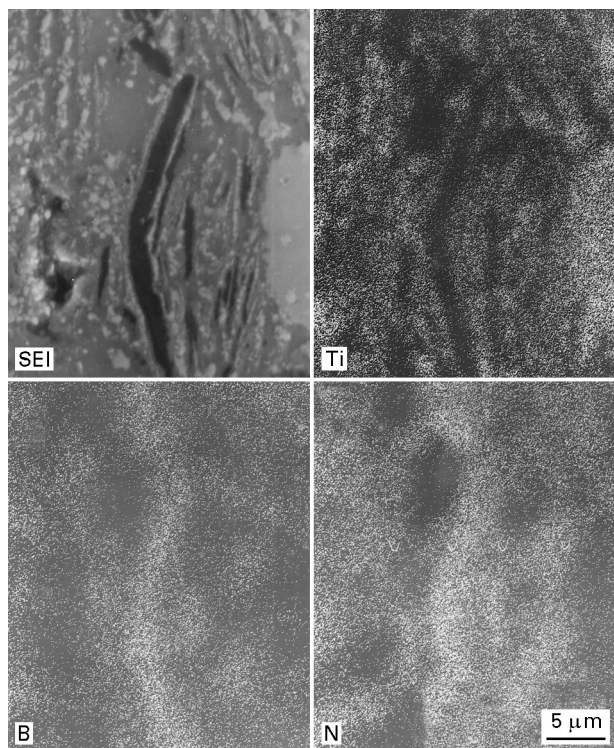Figure 6 Secondary electron images of (a) specimen 2 and (b) specimen 3. ([Ti + BN] powder system).

Figure 7 Secondary electron image and X-ray images of Ti, B and N for specimen 3 ([Ti + BN] powder system).

Figure 8 A schematic representation of the temperature–time curve during the infiltration process for the [Ti + BN] powder system.

Figure 9 A schematic representation of the temperature–time curve during the infiltration process for the [Ta + BN] powder system.

the [Ta + BN] powder mixture. To confirm this, a differential thermal analysis (DTA) was performed for the [Ti + BN + Al], [Ta + BN + Al], [Ti + Al] and [Ta + Al] powder 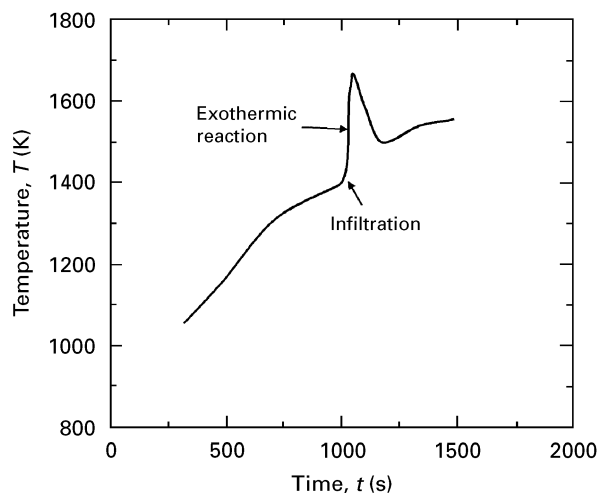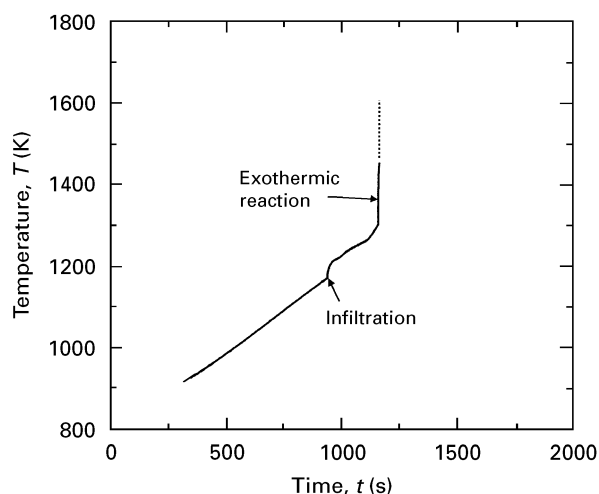mixtures. The DTA curves of the [Ti + BN + Al] and [Ti + Al] powder mixtures are shown in Fig. 10. A strong exothermic peak at 1030 K (peak-B) and a broad peak at around 1300 K (peak C) were detected in the [Ti + BN + Al] powder mixture. A strong exothermic reaction (peak-E) was additionally detected in the [Ti + Al] powder mixture. The endothermic peak-D indicates melting of aluminium and, therefore, the peak-E is regarded as being the formation of titanium aluminides (TiAl, Ti_3Al and/or $TiAl_3$). In contrast to the [Ti + BN + Al] powder mixture, the DTA curves of the [Ta + BN + Al] and [Ta + Al] powder mixtures did not contain the exothermic peak immediately after the fusion of aluminium (Fig. 11), instead an incubation period was observed between peak-F and peak-G. This incubation period is also clearly observed in data for the [Ta + BN] powder mixture. Significant differences between the [Ti + BN + Al] and [Ta + BN + Al] systems observed by differential thermal analysis were observed and included; (i) There are two exothermic peaks (one sharp and one broad) detected from the [Ti + BN + Al] powder mixture, but only one sharp peak is detected from the [Ta + BN + Al] powder
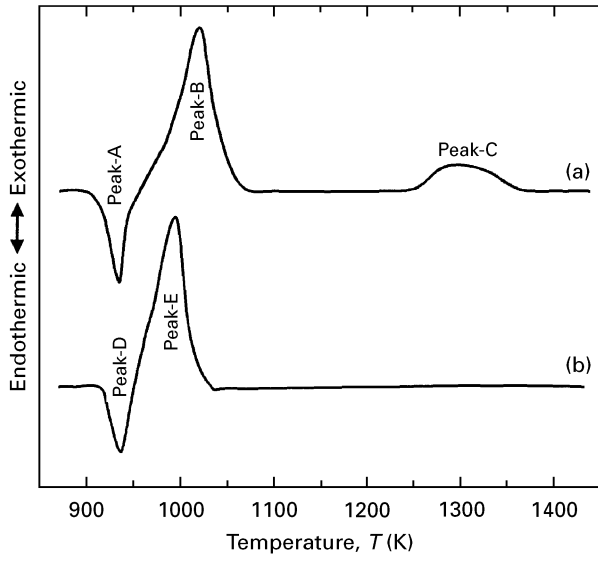
Figure 10 Differential thermal analysis curves obtained from (a) the [Ti + BN + Al] and (b) [Ti + Al] powder mixtures.
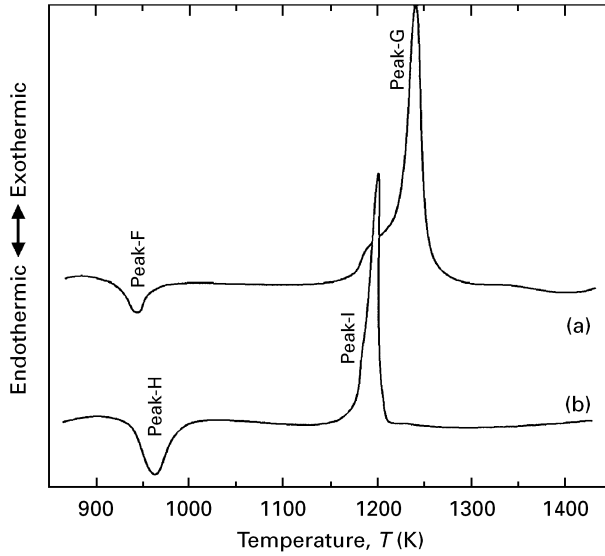

Figure 11 Differential thermal analysis curves obtained from (a) [Ta + BN + Al] and (b) [Ta + Al] powder mixtures.

mixture. (ii) An incubation period to produce tantalum aluminide is observed from the [Ta + Al] powder mixture, although titanium aluminide is produced immediately after the fusion of aluminium in the [Ti + Al] system.

4. Discussion
4.1. Reaction products
From observation of the microstructure of specimen 1 shown in Fig. 2, it is clear that the titanium in the [Ti + BN] powder mixture reacted only with boron. In order to clarify the absence of titanium nitride (TiN), thermodynamic calculations were performed that are discussed below. Since the titanium is in liquid aluminium, the free-energy change of solid titanium into the liquid phase should be taken into account.

$$Ti(solid) \rightarrow Ti(liquid) \qquad (3)$$
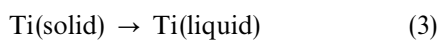
The free-energy change associated with this reaction at 1500 K is calculated to be 4.3 kJ mol^{-1} [11]. The Gibbs energy change and the equilibrium constant (K_N) of the reaction:

$$AlN(s) + Ti(l) \rightarrow TiN(s) + Al(l) \qquad (4)$$
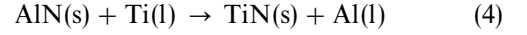
were calculated to be -47.5 kJ and 44.9 [12], respectively. This produces the following equation:

$$\frac{a_{TiN} \, a_{Al}}{a_{AlN} \, a_{Tl}} = 44.9 \qquad (5)$$

Equation 5 can be rewritten assuming that the activities (*a*) of the AlN and TiN can be regarded as 1.0:

$$\frac{(1 - N_{Ti})}{\gamma^0 N_{Ti}} = 44.9 \qquad (6)$$

where N_{Ti} is the mole fraction of titanium in the molten phase and γ^0 is the activity coefficient of titanium dissolved in aluminium. The activity coefficient at 1500 K was taken to be 1.5×10^{-2} from the work of Svendesen and Jarfors [13], which result in an equilibrium mole ratio of titanium of 0.6. This equilibrium mole ratio of titanium apparently exceeds the solubility of titanium in molten aluminium at 1500 K. Hence, it is concluded that AlN is more likely to be present than TiN.

4.2. Adiabatic temperature of the [Ti + BN] powder mixture
The maximum attainable temperature of the [Ti + BN] powder mixture during the infiltration was calculated assuming that the Al$_3$Ti is produced immediately after the infiltration. The constituents of the system change before and after the infiltration as follows:

before infiltration: Ti + 2BN + (3 + x)Al
after infiltration: Al$_3$Ti + 2BN + xAl
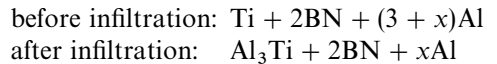
where x is the mole amount of excess aluminium, after the formation of the Al$_3$Ti. Since the porosity of the [Ti + BN] powder mixture was 70 vol %, a value of x was calculated to be 4.7 mol. The adiabatic temperature (T_{ad}) was then calculated using the equation:

$$\Delta H_{f,Al_3Ti} + 4.7 \int_{T_0}^{T_m} C_{P,Al} \, dT + 2 \int_{T_0}^{T_m} C_{P,BN} \, dT$$

$$+ \int_{T_0}^{T_m} C_{P,Al_3Ti} \, dT + V_D \Delta H_{D,Al_3Ti} + 6.7 \int_{T_m}^{T_1} C_{P,Al} \, dT$$

$$+ 2 \int_{T_m}^{T_1} C_{P,BN} \, dT + \int_{T_m}^{T_1} C_{P,TiAl} \, dT = 0 \qquad (7)$$

where ΔH_f is heat of formation, T_0 is the initiation temperature of the reaction, T_m, is the decomposition temperature of Al$_3$Ti (1613 K), C_P is specific heat, V_D is the amount of decomposed Al$_3$Ti at 1613 K and ΔH_D is the enthalpy change of the Al$_3$Ti

decomposition. Since the initiation temperature (T_0) of the reaction is confirmed to be 1420 K from Fig. 8, the adiabatic temperature (T_{ad}) was calculated to be 1660 K. The calculated adiabatic temperature shows a close agreement with the measured maximum temperature (1670 K). This close agreement between the calculated and experimental results indicates that the sharp increase in temperature of [Ti + BN] powder mixture shown in Fig. 8 was caused by the formation of Al_3Ti.

4.3. General discussion of the *in situ* reaction

Fig. 12 shows schematic illustrations of the *in situ* reaction process. When the [Ta + BN] powder mixture was used, the reaction producing Al_3Ta was not observed to occur. However, an over-all-reaction between the tantalum, aluminium and BN occurred after the incubation period. Conversely, when the [Ti + BN] powder mixture was used, the formation of

Al_3Ti occurs immediately after the infiltration. The formation of the TiB_2 particles should occur through the decomposition of Al_3Ti. Therefore, the conversion of BN to TiB_2 and AlN takes a longer time than that of BN to TaB_2 and AlN.

5. Conclusions

Powder mixtures of [Ti + BN] and [Ta + BN] were infiltrated with molten aluminium at 1473 K in order to produce ceramic/metal composites. The results can be summarized as follows.

1. Both [Ti + BN] and [Ta + BN] powder mixtures were completely infiltrated by molten aluminium at 1473 K. TiB_2 and AlN were formed when the [Ti + BN] powder mixture was used, and TaB_2 and AlN were formed when the [Ta + BN] powder mixture was used.
2. According to the differential thermal analysis studies, the [Ti + BN + Al] powder mixture showed two exothermic reactions, whereas the
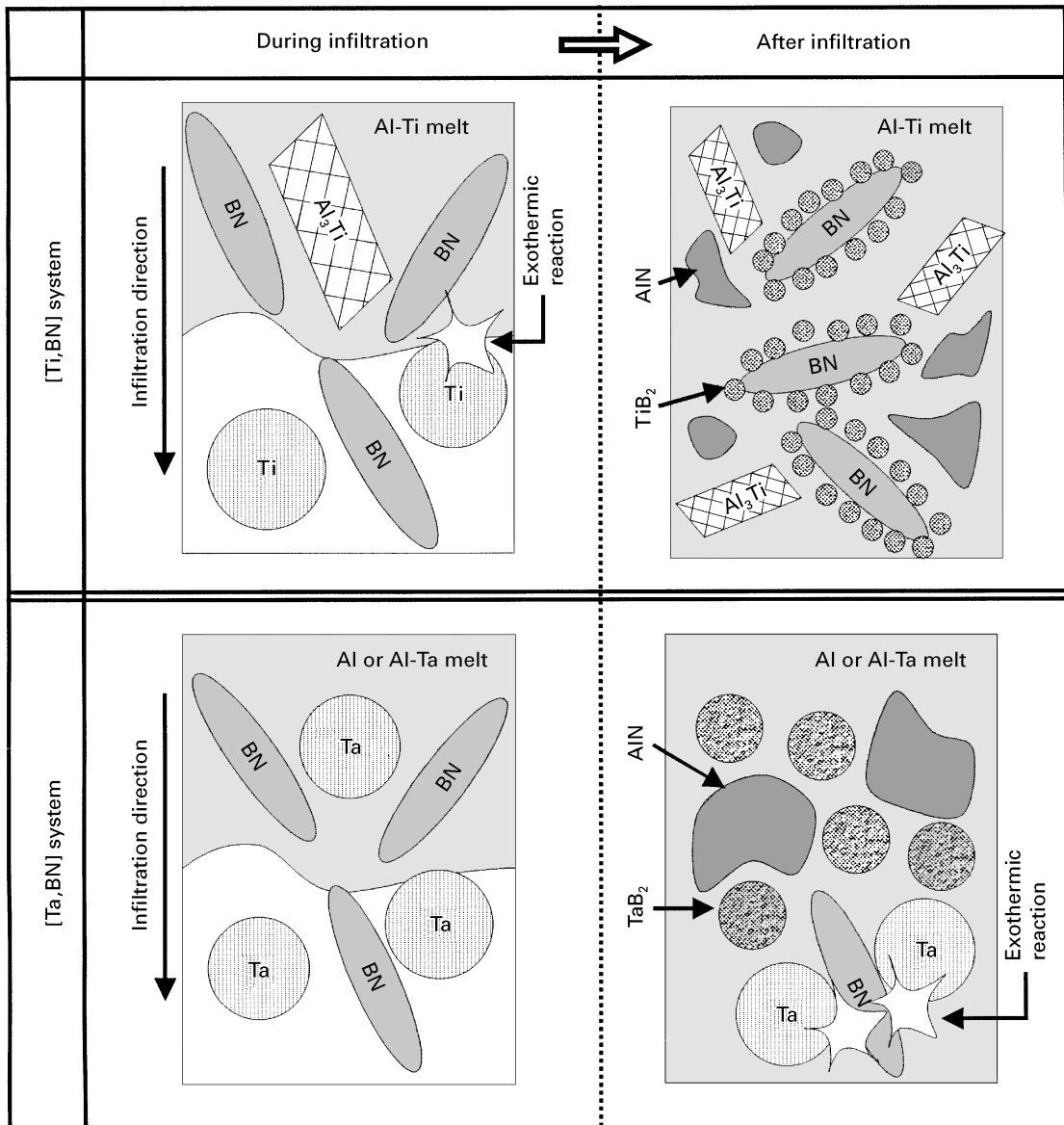

Figure 12 Schematic illustrations of the *in situ* reaction process.

[Ta + BN + Al] powder mixture showed only one exothermic reaction.

3. The reaction to produce Al_3Ti took place immediately after infiltration, but the reaction forming TiB_2 and AlN proceeded gradually. The time required to complete the TiB_2 and AlN formation was in the range of 1800–3600 s.

4. There was an incubation period for tantalum to react with molten aluminium. The over-all reaction between tantalum, aluminium and BN took place after the incubation period. The time required to complete the TiB_2 and AlN formation was less than 300 s.

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