Nitridation of Ti-B-Al-Al₂O₃ Composite Powder

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ABSTRACT

The preparation of Ti-Al-B-N composite ceramic powders from Ti-Al-B composites by nitridation under an ammonia atmosphere has been studied. For obtaining the effects of process parameters such as time and temperature on nitride formation, Ti-Al-B composite powder prepared by thermite ignition was used as a starting material in this work. The reaction products were examined via X-ray diffraction (XRD) and microanalysis using an energy dispersive system attached to a scanning electron microscope (SEM). The X-ray and SEM observations indicate that the nitride formation is confirmed at temperature above 1273 K within 2 hours under a NH₃ gas flow rate of 33 l/h. Although TiN-AlN-BN composite powders were obtained at 1723 K in 6 hours under a NH₃ gas flow rate of 33 l/h, a small amount of intermetallic compound such as AlB₂ and TiB₂ also remains in the product.

Keywords: Ti-Al-B-N composite ceramic powders, nitridation, TiB₂, TiN, AlN, BN.

1. INTRODUCTION

Titanium nitride (TiN), aluminium nitride (AlN), boron nitride (BN), and titanium diboride (TiB₂) are considered advanced ceramic powders showing high

performance properties /1,3/ and are produced via different methods. These ceramic powders can be used alone or in binary or ternary composites to provide materials with enhanced mechanical and high temperature properties. For example, the intermetallic composite consisting of either a binary intermetallic composition of titanium diboride (TiB₂) and boron nitride (BN) or of a ternary composition of titanium diboride (TiB₂), boron nitride (BN) and aluminium nitride (AlN) has been effectively used to produce relatively strong ceramics of high-density such as refractory evaporation boats /4,5/. Titanium diboride (TiB₂) and titanium nitride (TiN) composites having high hardness, good resistance to oxidation and high bending strength are produced by self-propagating high-temperature synthesis (SHS) process /6/. Aluminium nitride-titanium nitride (AlN-TiN) composite obtained by pressureless sintering of aluminium nitride (AlN) and titanium nitride (TiN) powders possess better thermal conductivity /7/. Since titanium nitride (TiN), aluminium nitride (AlN), boron nitride (BN) and titanium diboride (TiB₂) are usually prepared by different production procedures, it is difficult to produce composites possessing particular features found in these respective components in one step.

Many workers have reported that self propagating high-temperature synthesis or thermite process can be used to produce ceramic or cermet composites /8-16/ as well as production of metals and alloys. In this study,

Al-Ti-B-Al₂O₃ [17] powder obtained by thermite ignition was used as a starting material to produce TiN-AlN-BN-TiB₂ composite under ammonia atmosphere. The effects of process parameters such as time and temperature on the production of this particular ceramic composites are studied.

2. EXPERIMENTAL

Ti-Al-B-Al₂O₃ composite powder was prepared by the aluminothermic reduction of TiO₂ and B₂O₃. This composite was subsequently milled in a tungsten carbide mill. The chemical composition, sieve analysis and X-ray diffraction pattern of the raw material are given in Table 1, Table 2 and Figure 1, respectively. X-ray diffraction results indicate that the starting material consists of Ti₂B₅, TiB₂, TiB, AlB₂ and Al₂O₃ components.

The nitridation of the composite was carried out in a horizontal silicon-carbide resistance tube furnace as shown in the schematic diagram of Figure 2. A fused alumina tube with a diameter of 27.5 mm and a length of 900 mm was used as a reaction chamber. The fused

alumina boat containing 3 gram of Ti-Al-B-Al₂O₃ powder was placed in the constant temperature zone of the furnace. The flow rate of NH₃ gas passing through the alumina tube was adjusted by a flowmeter at 331/h. The experiments were conducted with a heating rate of 10 K/min at different temperatures ranging from 673 K to 1723 K for various lengths of time. The soaking time at pre-determined reaction temperature was two hours. The temperature was measured by a 10% PtRh-Pt thermocouple. After cooling, the ceramic composite was milled and examined by X-ray diffraction (Philips instrument) using Cu K α radiation at diffraction angles ranging from 20° to 90°. SEM observations of the powder products were carried out by using JEOL JSM-840.

3. RESULTS AND DISCUSSION

The overall reactions for the production of Ti-Al-B-N ceramic composite by nitridation of milled Ti-Al-B-Al₂O₃ composite may be represented as follows.

Table 1

Chemical analysis of the starting material obtained by aluminothermic reduction.

Element	Al	Al ₂ O ₃	B	Ti
Weight (%)	18.28	26.68	8.92	46.12

Table 2

The sieve analysis of the starting material.

Particle Size (μm)	Weight (%)
-500 + 250	5
-250 + 180	8
-180 + 106	25
-106 + 75	42
- 75 + 38	18
- 38	2
Total	100

Fig. 1: X-ray diffraction pattern of the starting material.

Fig. 2: Schematic illustration of the nitriding system.

The free energy change for reactions of equations (1)~(9) is illustrated in Figure 3 as a function of temperature. As seen in these results, the formation of nitrides from metallic constituents (Ti, Al and B) under ammonia atmosphere is more favourable than the formation of nitrides from borides (AlB_2 , TiB , TiB_2).

Likewise production of these nitrides from their oxides under ammonia atmosphere requires higher temperatures.

The X-ray results of the low temperature experiments, carried out at temperatures between 673-1273 K, are given in Figure 4. Although thermodynamic

Fig. 3: The change of free energy /18/ with temperature for reactions given in equations (1) through (9).

Fig. 4: X-ray diffraction patterns for the low temperature reaction products (673–1273 K).

calculations for equations (1) through (6) show negative free energy of formation below 1273 K, nitride formation is not clearly observed. However, a small amount of Ti_2N was detected at this temperature. The following comment may be worthy of note. Brupbacher *et al.* [19] reported that TiB_2 -Al composite could be nitridised at 823 K within 12 h under 200 MPa nitrogen pressure. Even in this high nitrogen pressure, only the outer surface of the product was found to be nitrided and core of the product remained as TiB_2 -Al.

X-ray diffraction patterns of samples prepared at high temperatures experiments (1473-1723 K) are given in Figure 5. The formation of nitrides, such as TiN , AlN , BN , were observed at temperatures starting from 1473 K. An increase of the nitride content and a decrease of the boride content in the reaction products with increasing temperature could be attributed to the transformation of intermetallic compounds such as AlB_2

and TiB_2 to TiN , AlN and BN . Since equations (1) to (8) give the higher free energy values at higher temperature, the formation of these nitride phases make thermodynamic stability more favourable with increasing temperature.

The effect of time on the nitride formation was also investigated by varying reaction time from 2 to 6 hours at 1723 K. As indicated in Figure 6, a small amount of borides remains in the reaction products even after 6 h at 1723 K. Figure 7 shows SEM micrographs of samples before nitridation (a), nitrided at 1273 K for 2 hours (b), and 1723 K for 4 hours (c). The grain morphology of the sample nitrided at 1273 K containing very little nitride looks similar with the grain morphology of the starting material, while the sample nitrided at 1723 K has a different morphology presumably due to its different composition.

Fig. 5: X-ray diffraction patterns for the high temperature reaction products (1473-1723 K).

Fig. 6: X-ray diffraction patterns for reaction products at 1723 K for different times.

4. CONCLUSIONS

The following two remarks are drawn from the present experimental results;

- 1) A precursor material of Al-Ti-B- Al_2O_3 produced via aluminothermic reduction of TiO_2 and B_2O_3 mixtures can be reacted at high temperatures with NH_3 gas to produce TiN-AlN-BN composite powders. The resultant product however, also contains a small amount of AlB_2 and TiB_2 .
- 2) Nitride formation appears to enhance with increasing reaction temperatures and times, while boride content present in the final product decrease. Nitride formation was not detected at reaction temperature lower than 1273 K, for 2 hours reaction time, under a NH_3 gas flow rate of 33 l/h.

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(a)

(b)

(c)

Fig. 7: SEM micrographs of samples before nitridation (a), nitrided at 1273 K for 2 hours (b), and 1723 K for 4 hours (c).

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