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B_4C/metal boride composites derived from B_4C/metal oxide mixtures

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Abstract

This study examines the reactions occurring from room temperature to 2180 °C during the heating under argon of mixtures of B_4C and metal oxides, as well as the properties of the ceramic composites prepared by these reactions. The cations of the oxides investigated, belonged to the transition metal and to the lanthanide groups. The mixtures underwent solid-state reactions in the range between 1100 and 1900 °C. These reactions resulted in composites in which the metal borides and B_4C are the majority phases. The boron carbide/metal boride(s) mixtures resulted from these reactions exhibited a sintering aptitude significantly higher than that of pure boron carbide. The improvement in the sintering aptitude was proportional to the oxide content present in the initial mixture, up to an upper limit. B_4C/boride(s)-type composites, exhibiting bulk densities $\geq 97\%$ TD, could be prepared for certain compositions by *pressureless* heating at 2180 °C. The ceramic parts prepared under these conditions are characterized by strength and hardness values similar to those determined for pure boron carbide.

Keywords: Sintering; Composites; Carbides

1. Introduction

Monolithic B_4C is a useful structural material characterized by high hardness, low density and high strength.[1–3] Its main drawbacks are the low fracture toughness of the fully sintered ceramic and the low sintering aptitude of the powdered material.[4,5] The commercial powders can be fully and reproducibly densified only by hot pressing (HP) at temperatures ranging between 1950 and 2200 °C.[1,2,6–9]

Densification – by pressureless sintering (carbon powders as sintering aid) of commercial powders in 2–10 μm particle size – is also feasible, but it requires higher temperatures, usually above 2200 °C for ceramics with bulk densities (BD_R) above 97% theoretical density (TD), which is the range required for most practical uses.[2] Such densities can be achieved also at lower temperatures (2120–2150 °C) but only by sintering submicronic powders.[10] The use of carbon powder additive as a sintering aid, requires a highly uniform dispersion of the additive, which is difficult to achieve in practice.[11] This route leads to a high incidence of defects in the sintered ceramic parts.

These considerations underlie the sustained interest in the development of alternative materials which, ideally, should preserve the valuable characteristics of the B_4C, like fracture toughness and strength, but which can be reliably densified by *pressureless* sintering at "low" temperatures (below 2200 °C).

A step ahead in this context was provided by the observation that some B_4C/TrB mixtures (TrB stands for transition metal borides) exhibit an increased sintering aptitude compared to a pure B_4C matrix.[11–14] Besides easier densification, such composites exhibit the additional advantage of a toughness higher than that of pure B_4C.[4,11–20] Crack deflection, associated with crack bridging and (in special cases) even controlled microcracking, contribute to the toughening of such composites.[13,14,18] However, pressureless sintering of such composites could not yield BD_R values higher than 95% TD.

An interesting fabrication approach, for B_4C/TiB_2 composites – was proposed by Skorokhod et al.[4] in B_4C/TiO_2 mixtures – subjected to pressureless heating under argon, in the temperature range between 1950 and 2050 °C, yield fully densified B_4C/TiB_2 in situ composites. The sintering aptitude of such materials was higher than that of composites derived from initial mixtures of B_4C and TiB_2. The sintering aptitude did not appear to have a strong dependence on the initial ratio B_4C/TiO_2. These authors suggested that a high sintering aptitude can be achieved even for mixtures containing less than 10 vol.% TiO_2. More recent work on the $B_4C + TiO_2$ system, by Levin et al.,[5] indicated that the sintering aptitude of the powders – which result from the reaction of the components – is a strong function of the amount

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of oxide present in the initial mixture.[5] Only mixtures including more than 22 vol.% TiO_2 could be brought to a BD_R above 95% TD. The temperatures required for achieving good sintering were in the 2180–2200 °C range, higher than indicated by Skorokhod et al.[4]

In the earlier works[4,5] the prevailing opinion was that the behavior described above is specific to the B_4C/TiO_2 system. In the present paper, we examine the behavior of other composites derived from B_4C + refractory metal oxide (MeO) mixtures regarding their reactivity, sintering aptitude and mechanical properties, and compare it to the case of the $B_4C + TiO_2$ system. The behavior of $B_4C + TiO_2$ composites was also re-examined in order to further clarify the differences between.[4,5]

2. Experimental

The raw material used for most of the samples was grade B_4C_{HS} supplied by H.C. Starck (Goslar, Germany). The powder has a B:C ratio of ∼3.9, an average particles size of 1.6 μm and an oxygen content of 1.7%. The round shaped particles are aggregated in relatively soft agglomerates. A coarser (average size ∼6 μm) powder-based on plate shaped, non-agglomerated particles-labeled B_4C_{Ch}, was also used. The sources of oxide were micron and submicron high purity powders supplied by DKKK (ZrO_2), H.C. Starck (Y_2O_3), Merck (Cr_2O_3, V_2O_5) and Fluka (La_2O_3).

The powders were suspended in isopropanol and mixed for 30 min at 700 rpm in an attrition mill.

Green specimens of various shape (disc, plate, cylinder) and size (20–50 mm) were formed via isostatic pressing (200–250 MPa). Their green density (BD_g) varied between 50 and 54% TD.

Differential thermal analysis was used to determine reaction temperature ranges. The tests were done in a Setaram machine (Multisystem 92.14–18).

Firing was performed under argon, in an Astro 1000 type furnace (TTI, Santa Rosa, CA). A 30 min dwell was maintained at 1650 °C, and sintering was accomplished at 2180 °C/120 min for all the mixtures studied.

The fired state bulk density (BD_f) was determined by the Archimedes technique and the BD_R was then calculated by comparison with the TD. The phase composition was determined from the XRD patterns (Siemens D-5000).

The amount of Zr in green fired specimens was determined by gravimetry (phosphate precipitation).

The microstructure was visualized by SEM (JEOL SM 5000) on polished specimens (BEI COMPO image type).

The Vickers hardness (H_v) was measured under a load of 1 kg (15 s). The modulus of rupture (MOR) was derived from four point bending tests effectuated on 45 mm × 4 mm × 3 mm polished bars (Instron model 8800R).

3. Results and discussion

3.1. Selection of the $B_4C + MeO$ systems

A set of refractory oxides was selected for study. Each oxide, of the set, exhibits some specific features.

For reaction sintering to occur, it is necessary that the cation present in an oxide can generate refractory borides with a melting point high enough to prevent massive loss by vaporization during sintering. Due to this, the cations examined in this study belonged to the group of transition metals, or to the lanthanides. A number of oxides with variable cation to oxide ion ratios and characterized by different oxidation states of the cation were considered. For a given ratio cation/oxide anion, systems generating borides with different metal/boride anion ratios were selected. We examined whether these characteristics of the oxide exert an influence on the behavior of the $B_4C + MeO$ mixture during firing. The oxides investigated included: TiO_2, ZrO_2, V_2O_5, Cr_2O_3, Y_2O_3 and La_2O_3.

3.2. Phase transformations and sintering

Preliminary sintering tests in the range between 2100 and 2250 °C, indicated that the lowest temperature leading to an acceptable densification level is 2160 °C.[21] Therefore, all the specimens discussed below were fired at 2180 °C for 120 min.

The first solid-state reactions in the $B_4C + MeO$ mixtures start around ∼1100 °C. In the case of TiO_2, V_2O_5, ZrO_2 and Cr_2O_3, the reactions in a rapid heating regime were complete at a temperature below 1600 °C. In the case of Y_2O_3 and La_2O_3, this limit was around 1900 °C.

In Fig. 1, examples of the XRD pattern of the sintered specimens, derived from $B_4C + Cr_2O_3$ and $B_4C + La_2O_3 + ZrO_2$, are shown. The final phase composition of the sintered specimens belonging to all the examined systems is shown in Table 1.

The data in this table show that the $O^{\delta-}$ ion, present in oxides, interacts with the carbon of B_4C, triggering "low" temperature (1100–1900 °C) reactions, which generate *solid* and gaseous products.

Table 1
Phase composition of specimens – derived from B_4C/MeO mixtures – fired at 2180 °C/2 h (Ar)

Oxide(s) in raw materials mixture	Fired specimens phase composition	Known borides of oxide cation
TiO_2	$B_4C + TiB_2$	Ti_2B, Ti_2B_5, TiB, TiB_2
ZrO_2	$B_4C + ZrB_2$	ZrB, ZrB_2, ZrB_{12}
V_2O_5	$B_4C + VB_2$, VB	VB, VB_2
Cr_2O_3	$B_4C + CrB_2$	Cr_2B, CrB, CrB_2, Cr_3B_2, Cr_3B_4
Y_2O_3	$B_4C + YB_2 + YB_4 + YB_2C + YB_2C_2$	YB_2, YB_4, YB_6
La_2O_3	$B_4C + LaB_6 + LaBO_3$	LaB_4, LaB_6
$La_2O_3 + ZrO_2$	$B_4C + LaB_6 + LaBO_3 + ZrB_2$	

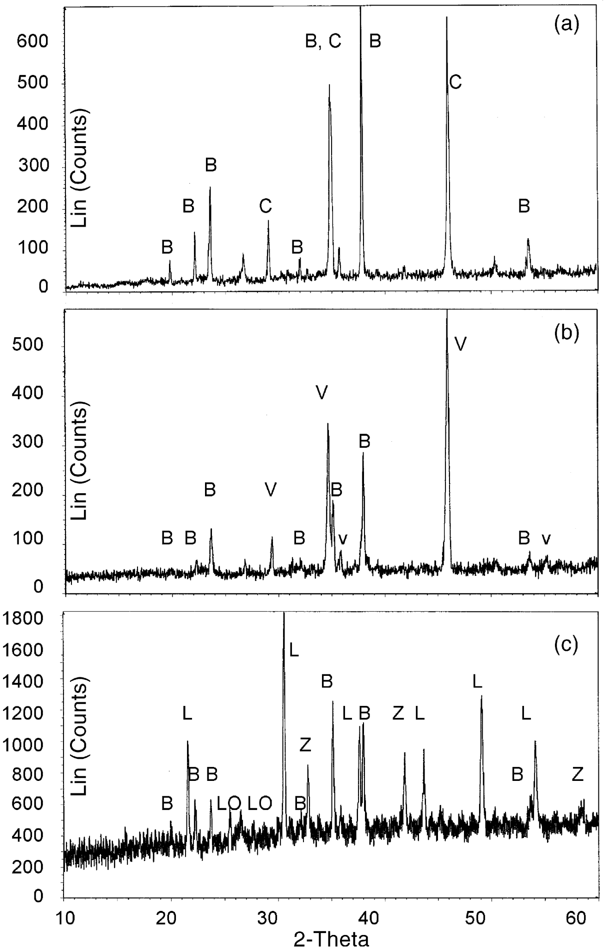

Fig. 1. XRD patterns, showing phase composition, of sintered specimens (2180 °C/2 h) derived from some of the $B_4C + MeO$ systems investigated. (a) B_4C + 18 vol.% Cr_2O_3, B: B_4C; C: CrB_2; (b) B_4C + 26 vol.% V_2O_5, B: B_4C; v: VB; V: VB_2; (c) B_4C + 10 vol.% La_2O_3 + 8 vol.% ZrO_2, B: B_4C; L: LaB_6; LO: $LaBO_3$; Z: ZrB_2.

The main solid reaction products are borides. In most cases, they are the only products. In the case of Y_2O_3 and La_2O_3, other boron-containing compounds are also among the products. When La_2O_3 and ZrO_2 were both added to the initial mixture, each reacted as if it were alone.

The carbide/boride powder compacts resulted from the reactions, underwent advanced sintering during the dwell time at the peak firing temperature. The final level of densification reached by a specimen increased with the amount of oxide in the initial mixture in all the systems that were investigated.

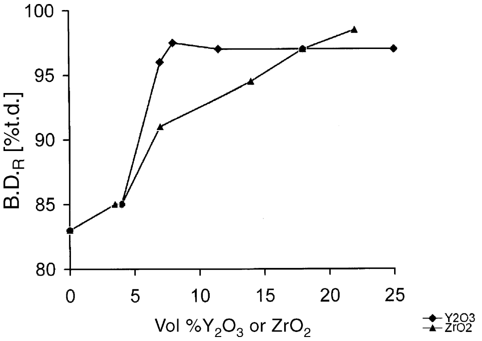

Fig. 2. Bulk density of sintered (2180 °C/2 h) specimens – derived from $B_4C + Y_2O_3$ and $B_4C + ZrO_2$ systems – as a function of MeO vol.% in the initial mixture.

The amount of oxide required to reach a certain BD_R value, varied markedly from system to system. The lowest amount of oxide for preparing sintered composites exhibiting a $BD_R \geq 95\%$ TD is shown in Table 2. In the case of the $B_4C + TiO_2$, our results were quite similar to those given in ref.[5] In order to obtain composites with a $BD_R \geq 98\%$ TD, oxide amounts ≥28 vol.% were needed in the initial mixture. The oxide amounts needed for advanced sintering were significantly higher than those suggested by Skorokhod et al.[4] In Fig. 2, the dependence of BD_R on the initial oxide concentration is illustrated for the case of $B_4C + Y_2O_3$ and $B_4C + ZrO_2$ systems. The former system requires no more than 8 vol.% of MeO to generate composites with a $BD_R \geq 98\%$ TD, while the latter needs some 22 vol.% for a similar result.

As the data in Fig. 2 and Table 2 indicate, the sintering aptitude of B_4C/MeB mixtures was significantly higher than that of monolithic B_4C ($BD_R \sim 83\%$ TD).

The high sintering aptitude of B_4C/MeB (in situ) powder compacts does not depend on either initial oxides or the stoichiometry of the borides resulted from the reaction. The lanthanide oxides Y_2O_3 and La_2O_3 (LnO's) are more effective than the transition metal oxides (TmO's) in promoting sinterability.

It is not yet clear which is/are the mechanism(s) responsible for the observed high sintering aptitude of the B_4C/MeB (in situ) mixtures. In ref.[4] the participation of liquid TiO_2 (melting point at ∼1900 °C) was postulated, as an explanation of the high sintering aptitude of such compositions. The presence of a liquid oxide phase cannot be assumed for other $B_4C + MeO$ systems, like $B_4C + ZrO_2$. In fact, even in the $B_4C + TiO_2$ system there is no liquid TiO_2 at any time, because the oxide is completely consumed under 1900 °C by reaction with the B_4C. So the mechanism proposed in ref.[4] is not plausible.

Table 2
Minimal oxide content (in the initial B_4C/MeO mixture) required for the obtainment (by firing at 2180 °C/2 h) of B_4C/MeB type composites exhibiting a $BD_R \approx 95\%$ TD

	Composite type					
	B_4C/TiB_2	B_4C/ZrB_2	$B_4C/VB_2 + VB$	B_4C/CrB_2	B_4C/Y-B + Y-B-C	$B_4C/LaB_6 + LaBO_3$
Oxide in initial mixture	TiO_2	ZrO_2	V_2O_5	Cr_2O_3	Y_2O_3	La_2O_3
Vol.%	24	18	24	18	6	10

An alternate explanation for the enhanced sintering aptitude observed in the case of B_4C/TiB_2 (in situ) composites was given by Levin et al.[5] It was suggested there that the carbide/oxide reactions taking place have a stoichiometry conducive to the formation of B_4C_{1-x} ($x \in 0.6$). The boron rich solid solutions would sinter more easily than B_4C. It seems reasonable to expect an increased sintering aptitude from such boron carbides. In such materials some of the chain-located carbon atoms (structure given in ref.[22]) are removed. Therefore, the diffusion in the distorted lattices is enhanced. In fact, Ekbom and Amundin have shown that $B_{13}C_2$ is more sinterable than B_4C.[23] The problem is that such a mechanism does not explain the increased sintering aptitude shown also by B_4C/MeB systems in which the boride is added from the start (not formed in situ by carbide/oxide reaction). In such systems, no boron rich solid solution is produced by reaction of the initial components and, despite that, increased sinterability was observed by others[11–14] and by us (the B_4C/ZrB_2 system). In the case of the latter system, the sintering aptitude was a function of the ZrB_2 content. It has to be noted that for a given amount of ZrB_2, the sintering aptitude of a B_4C/ZrB_2 (in situ) material was higher than that of a carbide/boride mixture in which the boride is present from the start. For instance, for a mixture containing 24 vol.% ZrB_2, the in situ boride containing composites could be densified to a $BD_R = 98.0\%$ TD, while the mixture including ZrB_2 from the start reached only 94% TD.

For composites derived from initial B_4C/MeB mixtures, the improved sintering aptitude was linked, by some authors, to a B_4C grain growth reduction caused by the MeB particles.[11]

It is possible that in the case of the materials derived from B_4C + MeO mixtures, both the mechanisms proposed in refs.[5,11] are operational.

3.3. Microstructure

The microstructure of monolithic B_4C, and that of a pair of B_4C/Y-B-C type composites, is shown in Fig. 3.

The microstructure of materials derived from the B_4C/V_2O_5 and B_4C/Cr_2O_3 systems is presented in Fig. 4.

The metal boride(s) phases appear as multigrain aggregates (strings, platelets). These aggregates delimit boron carbide zones, the average size of which varies with the amount of metal borides. A similar pattern is exhibited by all the B_4C/MeB composites. The shapes and sizes of the boride aggregates vary from system to system and are a function of the MeB content.

3.4. Mechanical properties

In Table 3 selected mechanical properties, of materials which could be sintered to a $BD_R \geq 97\%$ TD, are given. The hardness of the composites is close or similar to that of the monolithic B_4C. The strength of the composites is similar to that of B_4C, except for the materials derived from the B_4C/Y_2O_3 system, which are noticeably weaker. From a practical point of view, an interesting material is that derived from B_4C/8 vol.% Y_2O_3. The resulting composite has a picnometric density (PD) of 2.7 g/cm^3 (the PD ≈ TD). It is, to the best of our knowledge, the most lightweight B_4C containing ceramic which can be densified to $BD_R = 97.5\%$ TD by pressureless sintering. Considering the H_v exhibited by well densified parts, this material may find use as lightweight ceramic armor.

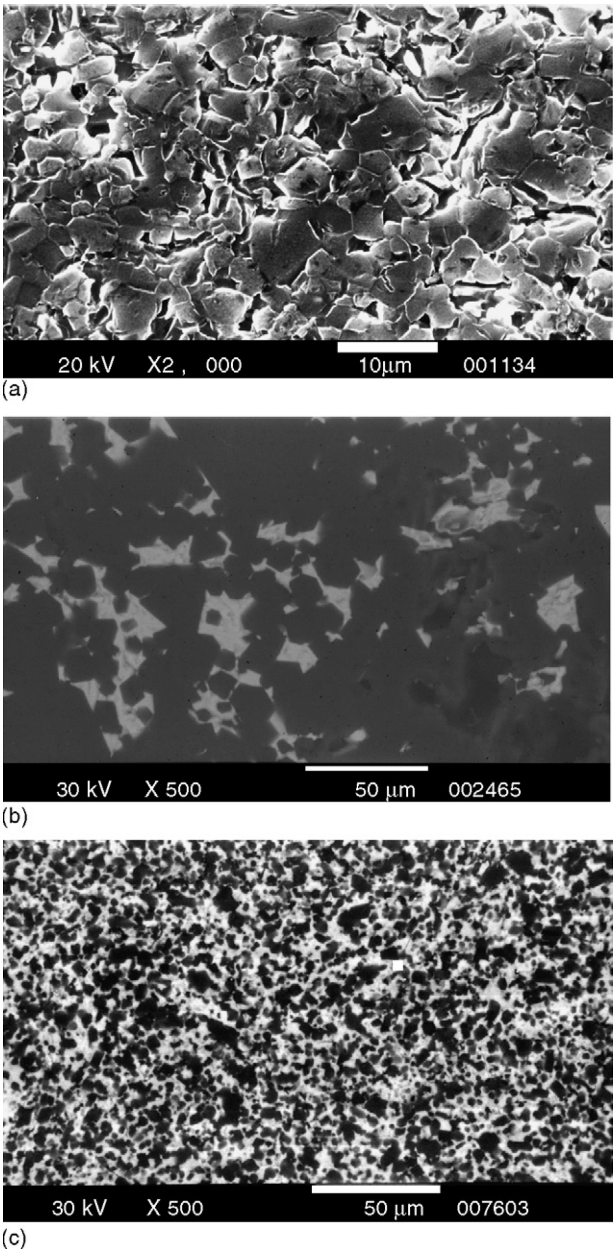

Fig. 3. Microstructure of dense specimens, derived from B_4C, B_4C/8 vol.% Y_2O_3 and B_4C/26 vol.% Y_2O_3. SEM (BEI-COMPO); on polished specimens (white zones = Y containing phases). (a) Pure B_4C (electrochemical etching); (b) B_4C/8 vol.% Y_2O_3 initial mixture; (c) B_4C/26 vol.% Y_2O_3 initial mixture.

3.5. Processing

The sintering aptitude of the B_4C/MeB (in situ) powders is strongly dependent on the characteristics of the carbide powders used in their synthesis.

The BD_R values for some composites derived from the two powders, B_4C_{HS} and B_4C_{Ch} are shown in Table 4. The BD_g of

Table 3
Mechanical properties of some well densified ($BD_R \geq 97\%$ TD) B_4C/MeB (in situ) composites

Initial composition B_4C/MeO	BD_F (g/cm^3)	BD_R (% TD)	H_v (GPa)	MOR (MPa)
B_4C (HPed; reference)	2.50	99.0	32–34	310–350
B_4C/8 vol.% Y_2O_3	2.63	97.5	27–30	160–200
B_4C/22 vol.% ZrO_2	3.28	98.5	27–31	320–370
B_4C/28 vol.% TiO_2	2.95	98.5	28–33	360–390

BD_F: Bulk density after firing.

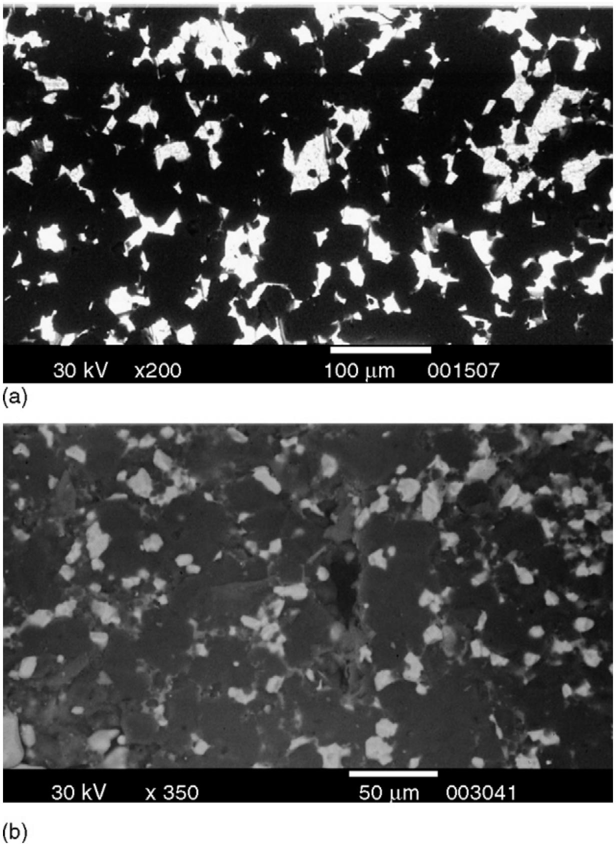

Fig. 4. Microstructure of dense specimens derived from B_4C + 18 vol.% Cr_2O_3 and B_4C + 24 vol.% V_2O_5 initial mixtures. SEM (BEI-COMPO). (a) B_4C/18 vol.% Cr_2O_3; (b) B_4C/24 vol.% V_2O_5.

the specimens derived from both powder types was similar. The final densification level – attained by the specimens based on the coarse B_4C_{Ch} raw material – is nevertheless significantly lower than that of the ones derived from B_4C_{HS}. This result is probably due to the fact that the fine oxide particles were located within the "cages" generated by the B_4C_{Ch} platelets. The carbide/oxide interface area is therefore smaller than in the specimens including B_4C_{HS}.

Table 4
BD_R of B_4C/MeB type specimens derived from B_4C_{HS} (fine) and, respectively, B_4C_{Ch} (coarse) raw material grades

Composition of initial B_4C/MeO mixture	BD_R (% TD)	
	B_4C_{HS}	B_4C_{Ch}
B_4C/28 vol.% TiO_2	98.0	90.0
B_4C/22 vol.% ZrO_2	98.0	93.0
B_4C/8 vol.% Y_2O_3	97.5	87.0
B_4C 100 vol.%	83.0	71.0

4. Conclusions

The reaction under argon of certain transition oxides (TmO) and lanthanide metal oxides (LnO) with B_4C at temperatures between 1100 and 1900 °C, leads to composites of the B_4C/MeB (in situ) form. Such composites exhibit a sintering aptitude higher than that of monolithic B_4C. The sintering aptitude increases with the amount of metal oxide in the initial mixture. The profile of this dependence varies from oxide to oxide. The LnO's Y_2O_3 and La_2O_3 are required in lower amounts than TmO's, for the ceramic material to reach a given level of densification. While monolithic B_4C reaches a BD_R = 83% TD, after sintering at 2180 °C, the composites attain levels of 95–98.5% TD in the same firing conditions. The boron carbide/oxide pressureless firing may be used as a fairly low-cost technology for the production of dense hard materials. In the case of the B_4C/Y_2O_3 system, a BD_R = 98.5% TD can be reached starting from a composition which includes no more than 8 vol.% of oxide. The TD of such a composite is remarkably low, close to that of pure B_4C. The hardness and strength of the composites are in the range of the values measured for hot pressed B_4C.

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