

Oxidation stability of $B_4C-Me_xB_y$ composite materials

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Abstract

The oxidation behaviour of the composite materials B_4C-ZrB_2 , B_4C-CrB_2 and $B_4C-W_2B_5$ is investigated. The samples are obtained by activated sintering at 2150–2250 °C in argon. The experiments are carried out in dry air or oxygen up to 1300 °C. The behaviour of the sintered materials is very similar to that of non-porous samples of B_4C obtained by hot pressing. The results obtained show that $B_4C-Me_xB_y$ possess higher oxidation stability than hot-pressed boron carbide samples. The possibility of producing a wide range of composite materials based on B_4C by activated sintering is shown.

1. Introduction

Boron carbide has a number of important properties which make it suitable for a variety of high performance applications in modern technology. It is a typical representative of primarily covalently bonded non-metallic refractory compounds. The existence of strong directed bonds in the lattice of boron carbide hinders diffusion processes during its high temperature compacting as a polycrystalline material. Because of its poor sinterability, dense boron carbide products are obtained by hot pressing. This method ensures a high density of the materials but has a number of disadvantages that reduce its efficiency and make it expensive.

We have previously developed a method of activated sintering of dense boron carbide products [1]. Various carbides of the group IV–VI transition metals are suitable as additives to activate the sintering processes of boron carbide. The reaction



proceeds between the boron and metal carbides during sintering. The transformation of the metal carbide into the corresponding boride and the formation of active carbon according to reaction (1) cause the occurrence of diffusion processes in the bulk and along the grain boundaries of the available phases. The appearance of eutectic phases in $B_4C-Me_xB_y$ systems [2] at temperatures above 2200 °C (close to the temperature of intense compacting of B_4C during sintering) intensifies the dissolution and recrystallization processes, which favours the formation of a dense structure of the sintered composite material [3, 4]. The formation of metal borides

such as ZrB_2 , CrB_2 and W_2B_5 considerably enhances the hardness of the composite material [5].

In 1899 Moissan established that powdery boron carbide is oxidized at 500 °C to B_2O_3 and CO_2 [6]. Since then, the oxidation stability of this material has been investigated many times under different conditions [7, 8]. It is established that the oxidation of hot-pressed boron carbide begins at 630 °C, the porosity being decisive with respect to the material stability [9]. Among the group IV–VI transition metal borides, an especially high stability has been exhibited by ZrB_2 and CrB_2 . These borides are applied in compositions of various heat-resistant materials. Investigations on the high temperature oxidation of hot-pressed samples of individual borides in oxygen and dry air have shown that visible oxidation of ZrB_2 begins at 1100 °C [10], a layer with pronounced protective properties being formed [11]. Hot-pressed CrB_2 samples are found to be affected by oxidation at temperatures higher than 1100 °C [12, 13]. The data in the literature concerning the oxidation stability of tungsten borides are scarce and contradictory. At oxidation temperatures of 1200–1300 °C hot-pressed W_2B_5 samples exceed CrB_2 in stability [14].

The purpose of the present work is to study the stability towards high temperature oxidation of B_4C-ZrB_2 , B_4C-CrB_2 and $B_4C-W_2B_5$ composite materials obtained by activated sintering.

2. Experimental details

The high temperature oxidation tests were carried out on composite material samples prepared by the

sintering of boron carbide with ZrC , Cr_3C_2 and WC additives (up to 40 wt.%). Powdery boron carbide (Ventron) containing 77.54 wt.% boron and 21.70 wt.% total carbon was used. The grain size of the main (above 90%) fraction was 40–63 μm . Homogenization and wet grinding (acetone) in a Fritsch planetary mill were performed. Automatic electron microscope analysis of the ground powders showed a size of 0.18–0.48 μm for 90% of the particles. The specific surface area of the ground boron carbide powder determined by the Brunauer–Emmett–Teller (BET) method using nitrogen at $-196^\circ C$ was $18.0\text{ m}^2\text{ g}^{-1}$. The boron carbide powders mixed with the additives, plastified with paraffin (3–7 wt.%) and granulated were subjected to double-ended cold moulding in steel dies under a pressure of 78 MPa. The sintering of the samples proceeded in a Degussa vacuum furnace at 2150–2250 $^\circ C$ under argon. To compare the properties of the composite materials, practically non-porous boron carbide samples were prepared by hot pressing at 2220 $^\circ C$ under a pressure of 25 MPa. The structure and properties of the sintered samples were investigated by X-ray, metallographic and thermogravimetric analyses. Oxidation of the samples occurred within the temperature range 600–1300 $^\circ C$ in both the static and dynamic regimes in oxygen or air.

3. Experimental results and discussion

Figure 1 presents a characteristic microstructure of B_4C-ZrB_2 composite material. The metal boride phase (that with the light colour) is distributed uniformly among the crystallites of boron carbide. An analogous microstructure is shown by the B_4C-CrB_2 and $B_4C-W_2B_5$ activated sintered composite materials. The grain size

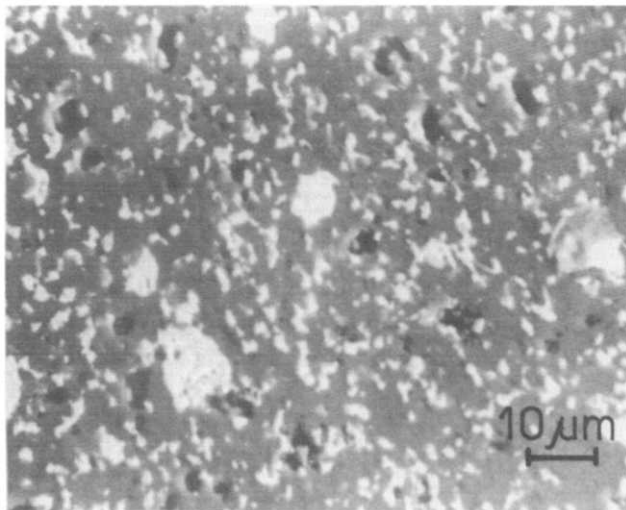


Fig. 1. Microstructure of sintered composite material $B_4C-11\text{wt.}\%ZrB_2$.

of the main boron carbide phase is 8–15 μm , while that of the metal borides is 2–5 μm . The dependence of the oxidation stability of $B_4C-W_2B_5$ composites on the amount of the second phase is shown in Fig. 2. To eliminate the effect of porosity, samples with closely related densities (90.0%–91.5% of the theoretical values) have been chosen. For comparison, the curve showing the oxidation stability of hot-pressed boron carbide (with zero porosity) is also given. Evidently, an enhanced amount of tungsten boride in the composite material leads to a rise in the temperature at which the sample exhibits a pronounced weight change. In the presence of 43.2 wt.% W_2B_5 the increase in temperature exceeds 100 $^\circ C$. The weight loss at 300–600 $^\circ C$ is due to evaporation and oxidation of the carbon in the samples to CO_2 .

To establish the joint effect of the second phase (W_2B_5) and the density of the composite material on the oxidation stability, isothermal oxidation at 750 $^\circ C$ in oxygen was carried out. The kinetic curves of the sintered boron carbide samples containing various amounts of W_2B_5 are given in Fig. 3.

A glassy B_2O_3 layer (the linear parts of the curves) is formed at the above temperature which preserves the samples from intense oxidation. A monotonously parabolic increase in the $\Delta G/S$ ratio is observed in the diffusion region. This increase is most abrupt in the case of the boron carbide sample sintered without an activating additive (relative density 90.5%). On increasing the amount of activating additive to 10 wt.%, the relative density (γ) of the composite material increases to 97.0% of the theoretical value (2.68 g cm^{-3}). The amounts and kinds of phases existing after sintering are taken into consideration in the calculation of the densities. Thus, when activation is performed with 20

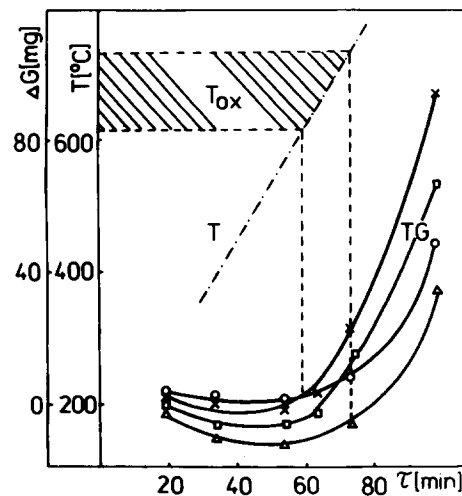


Fig. 2. Oxidation stability of sintered composite materials $B_4C-X\text{wt.}\%W_2B_5$: \times , $X=10.8$; \square , $X=21.6$; \triangle , $X=43.2$; \circ , B_4C-HP .

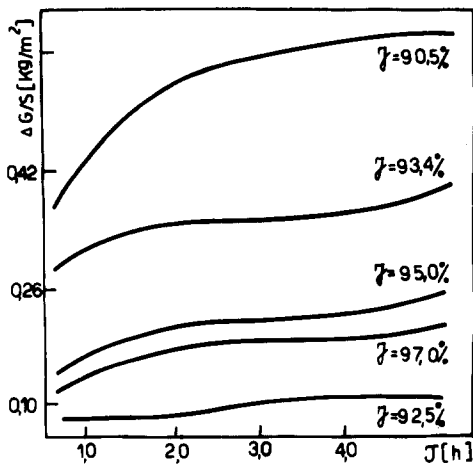


Fig. 3. Effect of amount of W_2B_5 and density on the weight gain of sintered $B_4C-W_2B_5$ composite materials.

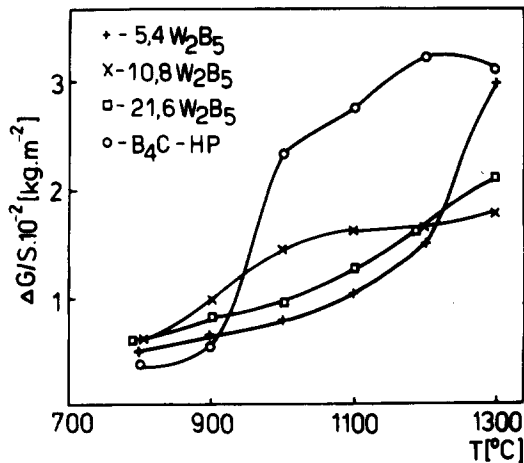


Fig. 4. Oxidation behaviour of sintered $B_4C-W_2B_5$ composites and hot-pressed B_4C in dry air.

wt.% WC, 21.6 wt.% W_2B_5 is present in the sintered sample and the density reaches 2.87 g cm^{-3} , which corresponds to 95.0% relative density.

In the presence of 43.2 wt.% W_2B_5 in the composite material the oxidation stability is higher than that of the other samples despite the fall in density to 92.5% of the theoretical value and the formation of a significant amount of free carbon. This is due to the blocking of part of the surface of the material under investigation by unoxidized W_2B_5 .

Owing to the strong effect of the density on the physicochemical and mechanical characteristics of the $B_4C-Me_xB_5$ composite materials, samples with maximum relative densities are oxidized in the further investigations.

Figure 4 presents data on the weight changes at 800–1300 °C of $B_4C-W_2B_5$ composite materials with relative densities of 95.0%–97.0%. Heating has been performed in air, increasing the temperature at a rate of 15 °C min^{-1} .

Boron carbide compacted by hot pressing (B_4C-HP) has been used for comparison. The data show that the W_2B_5 -containing samples are stable towards oxidation over the temperature range 1000–1200 °C, which is in agreement with data from the literature on the properties of the individual borides. The protective layer formed on the sample surfaces consists of glassy B_2O_3 with WO_3 inclusions. At the above temperatures the $B_4C-W_2B_5$ composite materials have an oxidation stability of about twice that of hot-pressed boron carbide.

The weight changes found during the isothermal (1000 °C) oxidation in air of the B_4C-ZrB_2 (5 and 20 wt.%) and B_4C-CrB_2 (5 and 20 wt.%) composite materials are given in Table 1.

The results obtained show that the composite material containing 5 wt.% ZrB_2 has after 60 min oxidation a protective layer which prevents further intense oxidation.

It is known that at temperatures above 1000 °C the evaporation of B_2O_3 drastically changes the oxidation kinetics of boron carbide materials. To investigate this, B_4C-ZrB_2 (10 wt.%), B_4C-CrB_2 (10 wt.%), $B_4C-W_2B_5$ (10 wt.%) and hot-pressed boron carbide samples were subjected to oxidation at 1100 and 1200 °C for 5 h. The evaporation was accelerated by blowing dry air at a rate of 20 l min^{-1} through the reaction space. The results obtained are included in Table 2.

The intense evaporation of B_2O_3 during the oxidation of hot-pressed B_4C samples leads to an essential change in their weight, while the metal borides in the composite materials form borate (of the type $CrBO_3$) layers with

TABLE 1. Weight increases of $B_4C-x\text{wt.}\%ZrB_2$, $B_4C-x\text{wt.}\%CrB_2$ and B_4C samples during oxidation at 1000 °C

Time (min)	Weight increase ($10^{-2} \text{ kg m}^{-2}$)				
	$B_4C-5ZrB_2$	$B_4C-20ZrB_2$	$B_4C-5CrB_2$	$B_4C-20CrB_2$	B_4C-HP
5	1.12	2.71	1.71	0.54	1.37
15	1.27	2.49	1.89	1.28	0.49
30	1.07	2.35	2.11	1.53	0.05
45	1.20	4.33	7.69	6.09	1.80
60	0.06	6.35	8.31	8.03	2.18

TABLE 2. Evaporation rates for B_4C-HP and $B_4C-x\text{wt.}\%Me_xB_5$ materials at two oxidation temperatures

Material	Evaporation rate ($10^{-2} \text{ kg m}^{-2} \text{ h}^{-1}$)	
	Oxidation temperature	
	1100 °C	1200 °C
$B_4C-10ZrB_2$	0.76	1.22
$B_4C-10CrB_2$	1.45	1.85
$B_4C-10W_2B_5$	1.25	1.77
B_4C-HP	1.80	3.42

pronounced protective properties. Under the above conditions the highest stability is again shown by the B_4C-ZrB_2 composite material.

4. Conclusions

$B_4C-Me_xB_y$ sintered materials surpass hot-pressed boron carbide in their oxidation stability.

The possibility of obtaining a wide range of dense $B_4C-Me_xB_y$ composite materials in order to broaden, on the basis of their physicochemical properties, the application of boron carbide products is shown.

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