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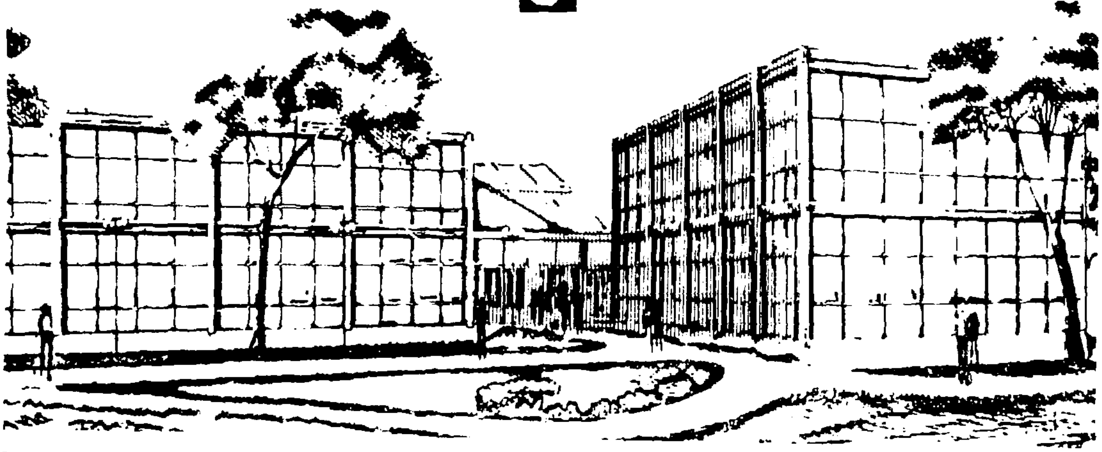

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SINTERING KINETICS OF PURE AND DOPED BORON CARBIDE

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ABSTRACT

The sintering of pure and doped boron carbide was investigated over the temperature range 1898 to 2380 K and at additive levels ranging from 0.75 to 10.0%. The addition of 0.75 and 3.8 wt% of AlF_3, Ni, Fe, and Cu deactivated the sintering of B_4C at all temperatures. In contrast, the addition of 10.0 wt% these additives resulted in enhanced shrinkage in B_4C for the temperatures 1898 and 2133 K. At the highest temperature, 2380 K, the addition of 10.0 wt% AlF_3 was the only case where enhanced shrinkage was observed. In this case, x-ray analysis showed the formation of a $B_{12}C_2Al$ compound and the release of fluorine. These results are interpreted in terms of a grain-boundary diffusion process for pure and doped B_4C.

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INTRODUCTION

Interest in using covalently bonded solids in a variety of high- temperature applications has recently refocused attention on their sintering behavior. Materials such as SiC, Si_3N_4, and B_4C have been considered for application as high-stress components in gas turbines, as Lysholm-expander blades in topping cycles, and as materials in nuclear reactors.[1,2] In contrast to metallic substances, covalent solids are not easily sintered. Various proposals have been advanced to explain this phenomenon and numerous attempts have been made to sinter these materials by altering their chemical and physical characteristics.

Proposals for explaining the low densification associated with the sintering of covalent solids have included the role of grain-boundary energy[3] and point-defect formation and migration.[4-6] The latter proposal is explained in terms of high activation energy for self-diffusion in the highly directional bond structures of covalent solids.

Relatively little work has been done on the sintering of B_4C. The latest and most extensive research is that of Borchert and Kerler,[7] who measured shrinkage in B_4C as a function of temperature, particle size, and green density. Their results showed that the sintering process for B_4C consists of two early stages, a middle stage, and a late stage, which are differentiated by the different transport mechanisms that take place.

EXPERIMENTAL MATERIALS AND METHODS

Materials

In our measurements to determine the sintering kinetics of B_4C, we used high-purity powders produced by the Ceradyne Chemical Company and Callery Chemical Company.* These powders had particle sizes of 2 to 5μm (high-purity Ceradyne powder) and approximately 0.03μm (Callery powder) and were used in a mixture of 25 to 75 wt%, respectively. A typical impurity analysis showed them to contain Fe, Ti, and Zn in the range 150-200 ppm and others elements (Ca, Al, Si) at considerably lower concentration (50 ppm).

We investigated the effect of activators on the sintering kinetics of B_4C by mixing different percentages of various additives into the base material.

Sample Preparation

The mixture of 25 wt% high-purity Ceradyne powder and 75 wt% Callery powder were blended with approximately 2.7 wt% polyethylene glycol (carbo-wax 6000) in toluene at a volume ratio of 1:3, respectively. The blending was done in plastic bottles. The glycol was used as a binder to help in the pressing of the powder compacts.

Pellets were pressed in a tool-steel dye employing a double piston action. Compacting was accomplished with a pressure of 800 MPa (117 ksi). This pressure resulted in pellets with green densities in the range 42-46% of the theoretical value, depending on the amount of additive present in the powder mixture. Each pellet required two pressings: After the first pressing, the pellets were broken up and then repressed. This produced crack-free pellets, which were then measured with a micrometer to an accuracy of ±2.5μm and weighed with an accuracy of ±10μg.

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*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be available.

Equipment and Procedure

The system used for all sintering runs consisted of a top-loading vacuum chamber with a tungsten-mesh heating element capable of attaining a maximum temperature of approximately 3000 K. The system was evacuated to a minimum pressure of 13.3 mPa, flooded with argon to approximately 50.5 kPa and then re-evacuated with sorption pumps to a pressure of 66.5 Pa. The argon atmosphere was maintained at this level throughout the sintering run by use of the sorption pumps whenever needed. A heating rate of 20 K/min was used to obtain a temperature of 1373 K. The pellets were allowed to outgas at this temperature for 30 min to drive off any remaining volatiles. Then the heating was resumed at an increased rate of 40 K/min until the sintering temperature was obtained. All sintering was isothermal. Three sintering temperatures--1898, 2133, and 2380 K--were used. These corresponded to 0.66, 0.76, and 0.86, respectively, of the melting point of pure B_4C. Three sintering times (60, 120, and 240 min) were used at each temperature.

RESULTS

The change in the linear shrinkage of sintered B_4C pellets with the isothermal sintering time is shown as a log-log plot in Fig. 1 for the three sintering temperatures. From the slopes of these lines, the characteristic exponent N of the mechanism was calculated to be 6.4, 6.3, and 6.2 for the temperatures 1898, 2133, and 2380 K, respectively. The linear shrinkage is plotted against the inverse of the sintering temperature in Fig. 2 for the three sintering times. The experimentally obtained values for the activation energy for the sintering of B_4C compacts for 60-, 120-, 240-min sintering times are 162.0, 160.7, and 164.9 kJ/mol, respectively, with an average value of 162.4 ± 2.1 kJ/mol.

Figures 3 and 4 show the variation in linear shrinkage with sintering time for B_4C with AlF_3, Ni, Fe, and Cu additives, where the sintering was done in argon at 1898 K. The plots at the sintering temperatures 2133 K and 2380 K are similar for B_4C with these additives.

For these doped B_4C powders sintered in argon for 60 min, we used plots of linear shrinkage vs the inverse of sintering temperature to calculate activation energies. The results, presented in Table 1, show the dramatic influence of the impurities on the sintering of B_4C. Additions of approximately 0.75 and 3.8 wt% of AlF_3, Ni, Fe, or Cu reduced the

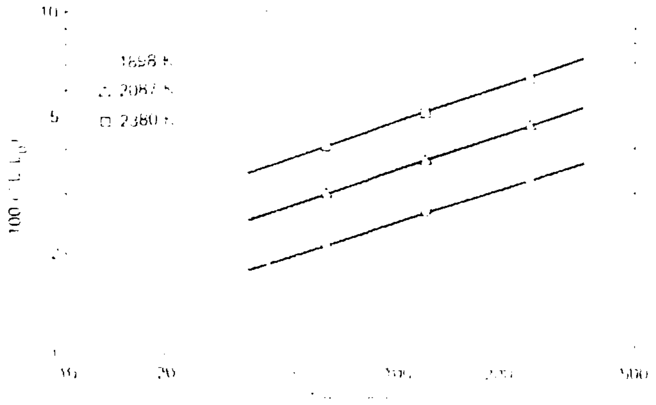

Fig. 1. Variation in linear shrinkage (ΔL) with sintering time for B_4C powders sintered in Ar at various temperatures.

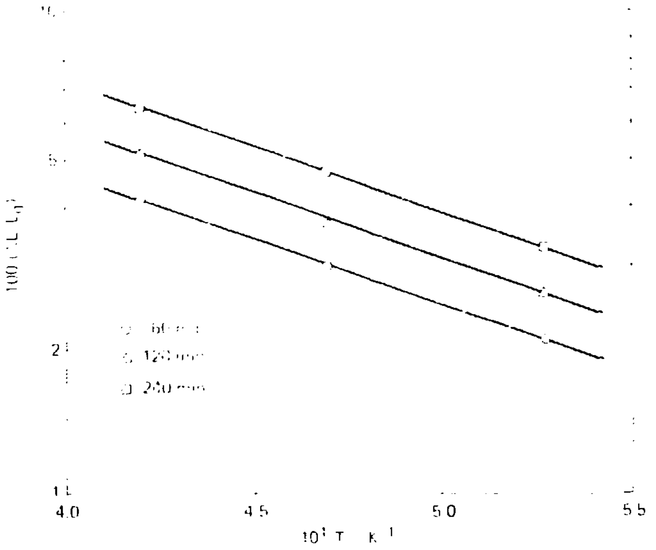

Fig. 2. Temperature dependence of linear shrinkage for B_4C powders sintered in Ar for various times.

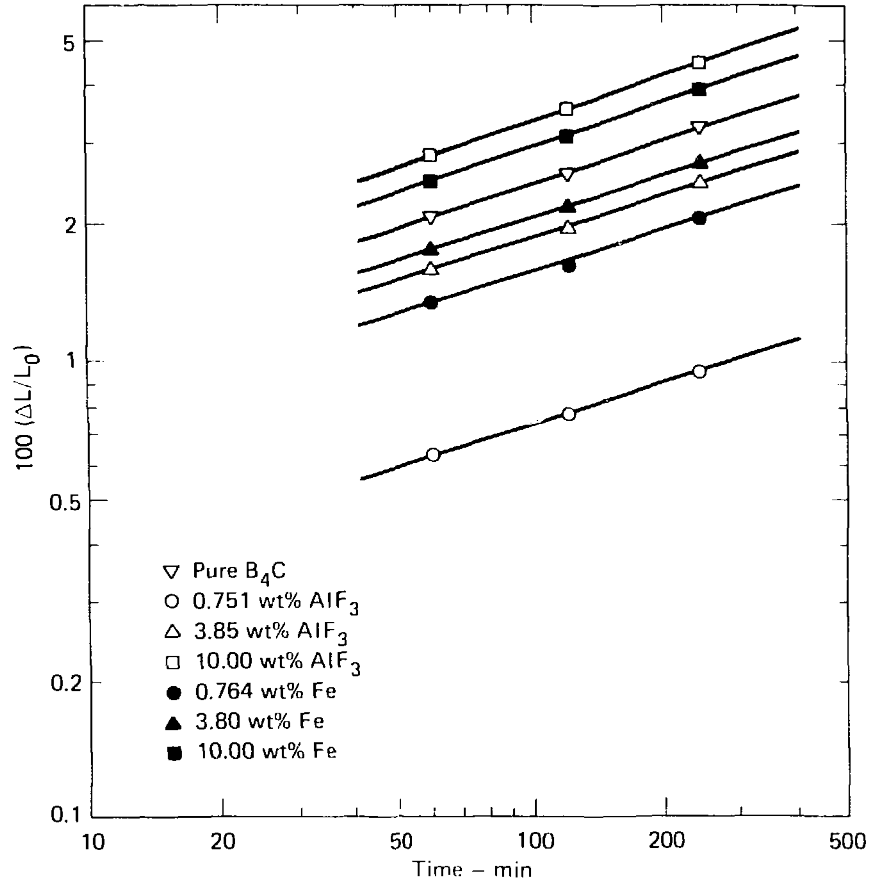

Fig. 3. Effect of AlF_3 and Fe additives on the variation in linear shrinkage with sintering time for B_4C powders sintered in Ar at 1898 K.

linear shrinkage, i.e., deactivated the sintering process, of B_4C for all the temperatures and times under investigation. Also, additions of 10 wt% of AlF_3, Ni, Fe, or Cu increased the linear shrinkage, i.e., activated the sintering process, of B_4C at the temperatures of 1898 and 2133 K. Only the addition of 10 wt% AlF_3 activated the sintering process at the highest temperature (2380 K).

Table 1 shows definite trends for the effect of sintering additives on the activation energy Q and the characteristic

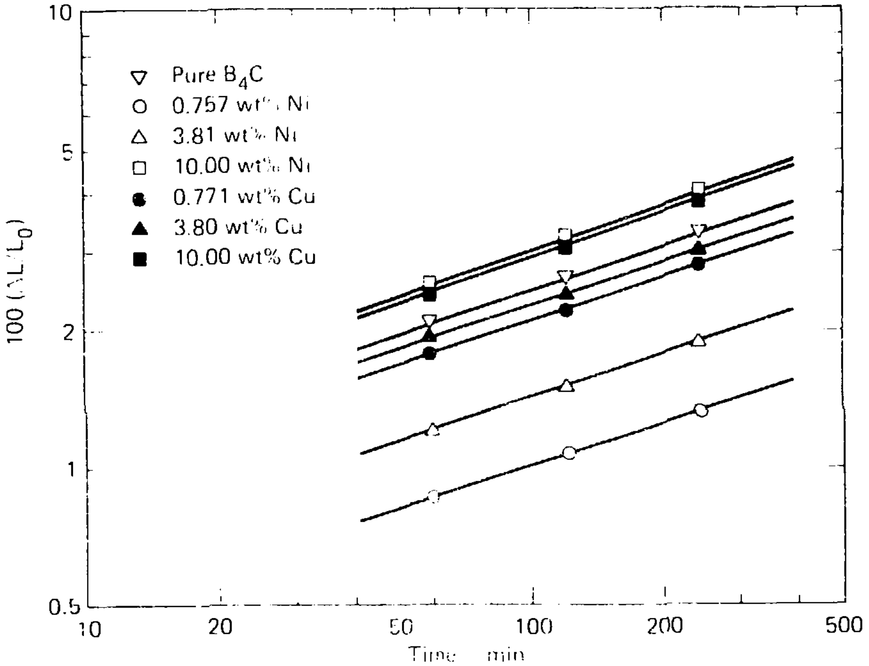

Fig. 4. Effect of Ni and Cu additives on the variation in linear shrinkage with sintering time for B_4C powders sintered in Ar at 1898 K.

exponent N. For the cases where the sintering process was deactivated, the activation energies for sintering the doped material generally nearly equal or exceed the activation energy for the sintering of pure B_4C. For the cases where the sintering process was activated, the activation energies are significantly lower. Generally, the characteristic exponent N decreased with increasing amounts of additives.

Analyses of surfaces of B_4C with additions of AlF_3, Ni, Fe, and Cu were made by means of electron-microprobe techniques. These analyses indicated the presence of a significant amount of aluminum and the absence of fluorine in the B_4C matrix. This suggests that AlF_3 completely dissociates during sintering. Results on the B_4C pellets that had 10 wt% Ni and were sintered for 120 min at 1898 and 2380 K indicated that Ni remains in the B_4C at the lower sintering temperature but is totally absent from B_4C sintered at the higher temperature. Similar results were obtained with 10% Fe additions. In the case of 10% Cu additions, the microprobe analyses on the samples sintered at 1898 and 2380 K for 120 min indicated the absence of Cu.

DISCUSSION

Of major interest in this work is the role of the various additives in the sintering of B_4C. The elemental analyses conducted with the electron microprobe, and diffractometer scans of pure B_4C and of B_4C with 10.0 wt% AlF_3, provided an interesting insight into the method by which sintering can be enhanced, or activated, through the addition of impurities. It was first believed that additions of AlF_3 provided a thin layer of AlF_3 on the B_4C particles and that this thin layer would enhance grain-boundary diffusion and thus produce an increase in the sintering rate. It was also thought that the additive would sublime in sintering, leaving behind a pure, dense compact of B_4C. However, in the present study we found that a considerable amount of Al was incorporated into the B_4C matrix but the F was fugitive. X-ray-diffraction scans of samples with AlF_3 indicated a consistent downward shift in the peak locations, compared with those of pure B_4C. These peak

Table 1. Calculated Average Values of N and Q for the Sintering of Boron Carbide Powders in Argon with Additions of AlF_3, Ni, Fe, and Cu

Material	Additive, wt%	Average N	Average Q, kJ/mol
B_4C	0.00	6.3 ± 0.1	162.4 ± 2.2
B_4C + AlF_3	0.751	6.4 ± .7	180 ± 24
	3.850	6.1 ± .6	163 ± 12
	10.000	5.97 ± .01	105.0 ± 1.2
F_4C + Ni	0.757	6.5 ± .1	188 ± 4
	3.810	6.2 ± .3	159 ± 12
	10.000	6.02 ± .04	105.1 ± 0.8
B_4C + Fe	0.764	6.6 ± .4	163 ± 16
	3.800	6.1 ± .4	134 ± 20
	10.000	6.00 ± 0.03	104.2 ± 2.3
B_4C + Cu	0.771	6.1 ± 0.3	167 ± 16
	3.800	6.2 ± 0.3	163 ± 8
	10.000	5.97 ± 0.04	105.5 ± 1.2

shifts provide strong evidence that Al is substitutionally incorporated into the B_4C lattice, resulting in a slight expansion of the unit cell. Some formation of a $B_{12}C_2Al$-type structure is probably occurring. In support of these conclusions, it is noted that the strongest new B_4C peaks correspond closely to the strongest peaks of $B_{12}C_2Al$ as reported by Lipp and Roder.[8] These observations also agree with previous work on hot-pressed B_4C containing additions of AlF_3.[9]

The incorporation of Al into the B_4C lattice provides an explanation for the observed loss of F. Carbon and fluorine can combine to form CF_x gas, most likely CF_3 or CF_4 or a mixture of both. Therefore, it is quite likely that B_4C reacts with AlF_3 in the following manner:

$$3B_4C(s) + AlF_3(s) = B_{12}C_2Al(s) + CF_3(g) \quad .$$

The absence of thermodynamic data for the compound $B_{12}C_2Al$ makes the assessment of the energetics for this reaction impossible. We conclude that additions of 10 wt% AlF_3 in B_4C activate the sintering process by lowering the diffusion energy barrier for the dominant transport mechanism of grain-boundary diffusion by altering the chemical nature of the grain-boundary layer. As stated earlier, the calculated activation energy for the sintering of pure B_4C decreased from 162.4 to 105.0 ± 1.3 kJ/mol as a result of the addition of 10.0 wt% AlF_3.

The other additives that activated the sintering process of B_4C were Ni, Fe, and Cu for the 10.0 wt% level at the lower two temperatures. The difference between these additions and AlF_3 is that they also deactivated the sintering of B_4C at 2380 K. Electron-microprobe and x-ray-diffraction analyses of B_4C containing these additives offer interesting contrasts. For the additives of Ni and Fe the electron-microprobe analyses showed the presence of Ni and Fe precipitates at 1898 K but not at 2380 K, but the microprobe analyses of samples with Cu additives showed no Cu at either temperature. Furthermore, the x-ray-diffraction scans indicated possible compound formations of Fe with carbon and boron at 1898 K.

These results indicate that additions of 10.0 wt% Ni, Fe, and Cu to B_4C will activate the sintering process at 1898 and 2133 K by possibly the same mechanism as that proposed for AlF_3. For these three additives, the activation energies for the sintering of pure B_4C decreased from 162.4 to 105.1 ± 0.8, 104.2 ± 2.3, and 105.5 ± 1.2 kJ/mol as a result of the additions of 10.0 wt% Ni, Fe, and Cu, respectively. The apparent deactivation of B_4C sintering in the presence of 10.0 wt% Ni, Fe, and Cu at sintering in the presence of 10.0 wt% Ni, Fe, and Cu at 2380 K is explained by the relatively high vapor pressures of these elements at this temperature. It is believed that at this temperature the additives sublimate and leave the compacts before sintering can take place. Furthermore, the rapid sublimation of these additives at the higher temperature may cause gases to be trapped in closed pores and thus reduce shrinkage. This loss of additive is supported by results obtained in the electron-microprobe and x-ray-diffraction analyses.

The addition of about 0.75 wt% and 3.8 wt% AlF_3, Ni, Fe, and Cu is believed to be insufficient to provide the compacts with an evenly distributed layer of the additive on the B_4C particles. The compacts with approximately 0.75-wt% additions provide a layer of only 0.03 nm thick; the compacts with approximately 3.8 wt% additions, a layer of approximately 0.16 nm thick. Therefore, the additive is likely to occur in isolated islands throughout the powder, and such islands would act as either obstacles or sinks for the migration of vacancies along the grain boundaries. Rapid sublimation of these additives can also produce entrapped gases in closed pores. Because the calculated activation energies for the sintering of B_4C with approximately 0.75-wt% and 3.8-wt% additions of AlF_3, Ni, Fe, and Cu are nearly equal to the activation energy for the sintering of pure B_4C, another mechanism, e.g., surface diffusion, must be contributing to the sintering process. This would explain the observations that even though the shrinkage was reduced the activation energy for the overall process did not increase.

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