

Advances in pressureless densification of boron carbide

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The coarsening processes which occur concurrently with the sintering of B_4C were deduced using differential dilatometry, weight loss and grain size measurements. B_2O_3 coatings on B_4C particles stalled the onset of densification until these coatings decomposed away at $1840^\circ C$. Oxide gaseous species formed in this process were postulated to be one conduit of particle coarsening. At higher temperatures, the volatilization of B_4C itself were interpreted to be the second vapor phase coarsening mechanism, starting at temperatures above $2000^\circ C$. Carbon additions or soaking the compact in a hydrogen-containing atmosphere at $1350^\circ C$ removed the oxide coatings at temperatures below those in which sintering or coarsening occurred. Accelerating densification above $2130^\circ C$ was attributed to nonstoichiometric volatilization, leaving carbon behind to facilitate activated sintering.

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1. Introduction

Boron carbide is the third hardest material next to diamond and cubic boron nitride, having a Vickers hardness of 3770 kg/mm^2 [1]. Combined with its low density (2.52 g/cm^3), it is the premier material for personal armor—typically in the form of front and back inserts into flack jackets in which B_4C plates are bonded to a polymer backing. B_4C is also used for nuclear shielding applications based on boron's high neutron absorption cross section. It is used in particulate form as an abrasive, and as a nozzle material for slurry pumping and grit blasting because of its excellent abrasion resistance.

Boron carbide exists as a solid solution in the range of 8.8 to 20 mol% carbon. Its crystal structure is complex owing to the highly covalent nature of interatomic cohesion. Twelve atom boron-rich icosahedra reside at the corners of a rhombohedron, and each icosahedron is bonded to six others via direct bonds, and three-atom inter-icosahedral chains reside between the icosahedra [2].

When a high-velocity projectile impacts the surface of a ballistic material such as B_4C , a compressive shock wave extends hemispherically from the impact point, generating tensile tangential stresses, in turn forming radial cracks with emanate from the point of contact. These tangential stresses tear open cracks, preferentially at the site of pores and fissures. As a result, ballistic performance improves with decreasing porosity, i.e., with increasing fired density. Pressureless sintering of B_4C to high density, however, has proven difficult. Achieving near-theoretical density (TD) has re-

quired gang-hot pressing (stacked parts under pressure) which precludes the formation of complex shapes. Additives such as SiC, Al_2O_3 , TiB_2 , AlF_3 and W_2B_5 have been used as sintering aids to increase pressureless sintered density [3–6], but the second phases formed often have deleterious effects on mechanical behavior [1]. The best known additive for B_4C is carbon, most successfully added in the form of phenolic resin, which distributes carbon around the B_4C particles, and also serves as a pressing agent. Up to 98% of TD has been obtained using this additive [7]. In our recent work [8, 9], the reasons for limited densification have been investigated, and methods for circumventing them have been developed. In this paper, these results are summarized.

2. Experimental procedure

Commercially available B_4C powders (Grade HS, H. C. Starck, Berlin, Germany) were used in the as-received state. Table I shows the characteristics of the powder based on the manufacturer's data. Fig. 1 depicts the wide particle size distribution. Powder compacts of B_4C powder were prepared by placing loose powder in a die and punch assembly and pressing at 200 MPa. For carbon-doped specimens, B_4C powder was mixed with phenolic resin (SP6877, Schenectady International, Schenectady, NY) dissolved in acetone to yield 3 wt% carbon additions. The densification process was monitored by a differential dilatometer, in which the dilation/contraction of the B_4C specimen was measured

ULTRA-HIGH TEMPERATURE CERAMICS

TABLE I B₄C powder characteristics

Surface area	18.8 m ² /g
Particle size	90% of particles ≤ 2.99 μm 50% of particles ≤ 0.84 μm 10% of particles ≤ 0.24 μm
Impurity levels	1.50 wt% O 0.41 wt% N 0.022 wt% Fe 0.055 wt% Si 0.003 wt% Al 0.23 wt% Other
Total boron	75.39 wt%
Total carbon	22.26 wt%
B/C molar ratio	3.76

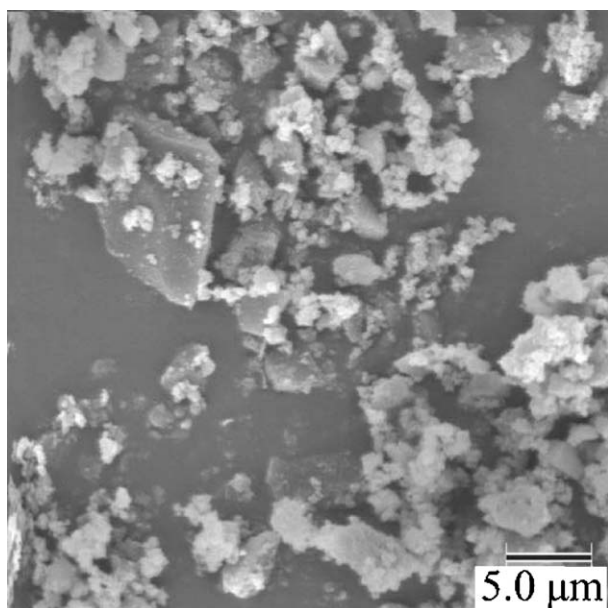


Figure 1 SEM micrograph of as-received B₄C powder particles.

relative to a graphite (Poco Graphite, Decatur, TX) reference. Specimen sizes were 6.4 mm in diameter and ~5 mm in height. Displacement was measured using a linear variable differential transformer (Theta Industries, Port Washington, NY) measuring the relative displacements of graphite pushrods in contact with the sample and reference, which in turn rested on a graphite dilatometer casing. The specimen pushrod was counterweighed to apply a minimum of force (3.5 kPa). The furnace consisted of a cylindrical graphite bayonet surrounded by graphite felt insulation, inside a water-cooled aluminum furnace housing. Atmospheres were formed in the furnace chamber by evacuation (mechanical pump) followed by backfilling from compressed gas cylinders, repeated two times. Helium and hydrogen/helium gas streams were used, with mixture and flow rates maintained via mass-flow controllers. The total gas flow rates during heating and soaking were ~0.5 liters/min (furnace vessel interior volume: 3 liters). Temperature was monitored using an infrared pyrometer (Model MA15C, Raytek Co., Santa Cruz, CA), viewing through a fused silica window to sight on to the cut open cavity of the dilatometer casing. A previously calibrated power profile was programmed into the furnace to generate at heating rate of ~50°C/min

up to 800°C, above which the infrared pyrometer was within its measuring range, and proportional-integral-derivative feedback control of temperature took over.

A thermogravimetric analyzer (TGS-2 analyzer and balance control unit, Perkin-Elmer, Norwalk, CT) was used to monitor low-temperature weight loss, and weight loss after higher temperature heat-treatments in the dilatometer was measured using an analytical balance. Average particle/grain sizes were measured from scanning electron microscopy (SEM, 500S, Hitachi, San Diego, CA) micrographs of fractured surfaces using the linear intercept method (1000 measured intercept lengths). These results are only useful for relative comparisons since fired densities were too low to obtain polished surfaces. Densities of fired specimens, relative to TD, were measured using the Archimedes method. Phase analysis was performed using X-ray diffraction (Philips, Mahwah, NJ).

3. Results and discussion

Fig. 2 shows the TG results for a B₄C compact heated to a maximum of 380°C, while Fig. 3 shows the results of heating B₄C compacts in the dilatometer furnace to more elevated temperatures in flowing He, followed by furnace cooling. These specimens were immediately weighed and then weighed again after 24 h in room air. Both figures point toward the presence of B₂O₃ coatings on the B₄C particles. B₂O₃ is highly hygroscopic, forming, for example H₃BO₃ (orthoboric acid). In the TG, the moisture was volatilized during heating and carried away with the flowing Ar atmosphere. During cooling in Ar, and subsequent soaking at room temperature in dry air, no moisture was available, and no change in weight was recorded. After heating in the dilatometer furnace to temperatures up to 1200°C, specimens lost weight associated with removal of moisture, but regained more than that weight after exposure to room moisture for a day. Between 1200 and 1600°C,

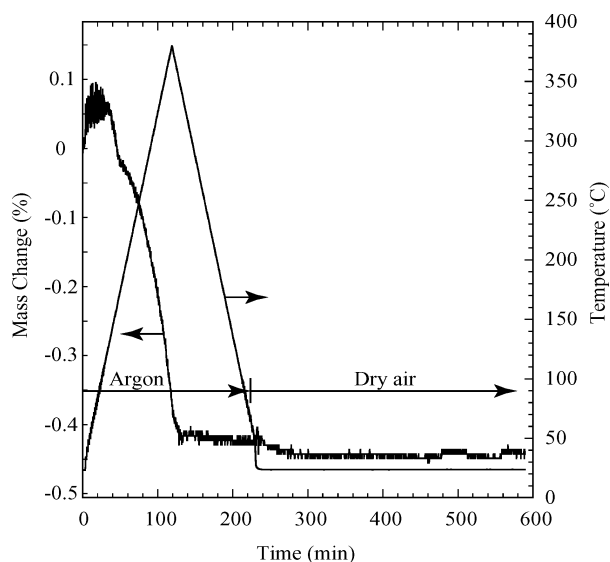


Figure 2 Thermogravimetry trace of B₄C powder in flowing Ar or dry air under heating and cooling rates of 4°C/min. Original specimen mass: 14.522 mg.

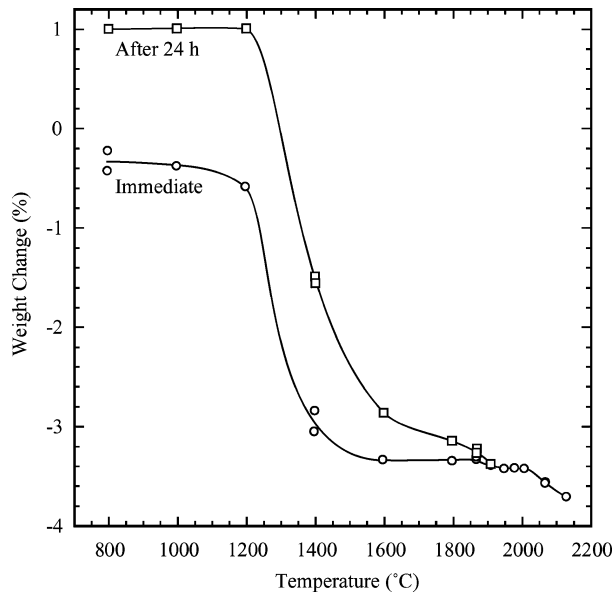


Figure 3 Weight changes in pressed B₄C pellets after heating to various temperatures at 50°C/min up to 1800°C, and 5°C/min above this temperature, under flowing He. Specimens were cooled in the furnace, with the power turned off, under flowing He. Measurements were made immediately after removal from the furnace, and again after exposure to room air for one day. Pellets were exposed to room air prior to heat treatments.

the vapor pressure of B₂O₃ became substantial and the elimination of B₂O₃ resulted in permanent weight loss. Above ~1800°C, the B₂O₃ coatings were fully eliminated, as indicated by no weight recovery after exposing the samples to room temperature moisture for 24 h. Based on an average spherical particle diameter of 1 μm and a measured weight loss of 2.9%, the average B₂O₃ coating thickness was 4.8 nm. The weight loss appearing above 2000°C is associated with the increasing vapor pressure of B₄C (or molecular fragments) itself.

Fig. 4 shows the effect of different heating rates on the densification of undoped B₄C, while Fig. 5 shows the effect of heating rates on the densification of C-doped

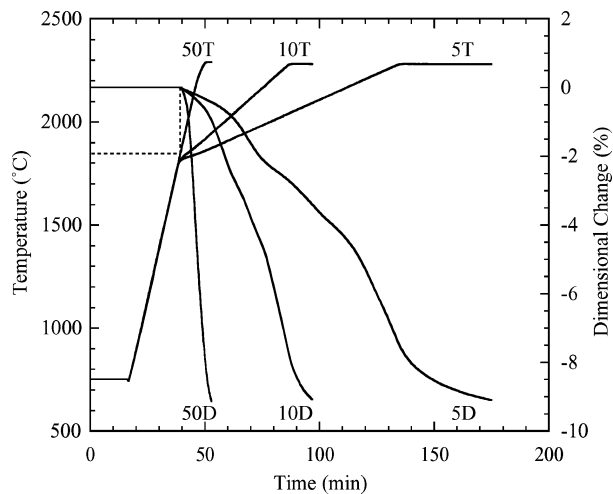


Figure 4 Temperature (T) and (CTE-corrected) dimension change (D) traces of undoped samples under varying TCS heating rates. All samples were quickly cooled when the corrected contraction reached 9.1% (90% of TD). The numbers on the figure indicate heating rates (°C/min).

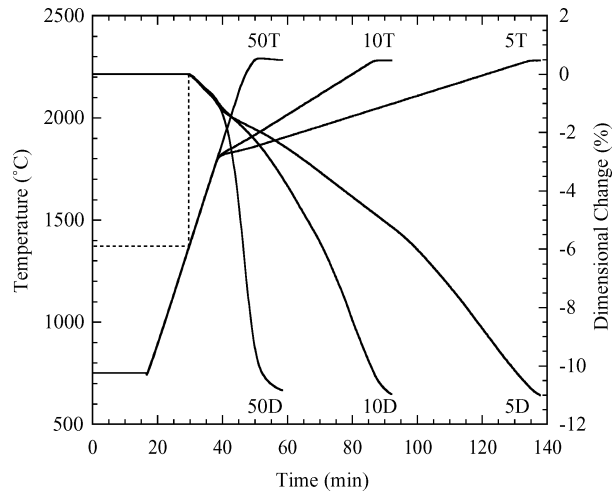


Figure 5 Temperature (T) and (CTE-corrected) dimension change (D) traces of carbon-doped samples with different heating rates. All samples were quickly cooled when the corrected contraction reached 11.0% (97% of TD).

B₄C. In both cases, specimens were heated to 2280°C and soaked until a specified density was reached; 90% of TD for undoped and 97% of TD for C-doped B₄C. Of note is the substantially lower sintering onset temperature for the C-doped samples, 1380°C, as compared to 1840°C for undoped ones. Carbon reacted with the B₂O₃ coatings; in a local environment rich in the reducing species, the reaction products would likely be B₄C and CO gas. This would allow uncoated B₄C to B₄C particle contact, in turn permitting sintering to initiate at a lower temperature. With faster heating rates for C-doped specimens, less time was permitted for sintering during the heating ramp, so that more time was required during the soak to reach the specified density. This is an expected result; however, the opposite trend occurred for the undoped specimens. As discussed further in following paragraphs, for these samples, particle coarsening simultaneous with sintering was more substantial with slow heating rates. Such coarsening lowered the driving force for densification, so that more time was required at the soaking temperature with slower heating rates to reach the same final density.

Fig. 6 shows dimensional change and temperature derivative dimensional change plots superimposed on mass loss and particle/grain size plots for undoped specimens. A surge in densification rate occurred starting at 1870°C, slowing by 2000°C. This is attributed to the volatilization of remaining B₂O₃ coatings, removing the barrier to direct B₄C particle contact and subsequent sintering. A surge in particle size leading up to the maximum sintering rate in this temperature range is interpreted to be via the formation of oxide vapors (e.g., BO and CO), which preferentially evaporated from small particles and deposited on large particles [10], though the mechanism details have not been established. Starting at 2000°C, a second surge in weight loss initiated, which is interpreted as attributable to the increasing vapor pressure of B₄C or fragments of this molecule. Evaporation from small particles and vapor deposition on large particles would then be the second mechanism of coarsening which occurred at and

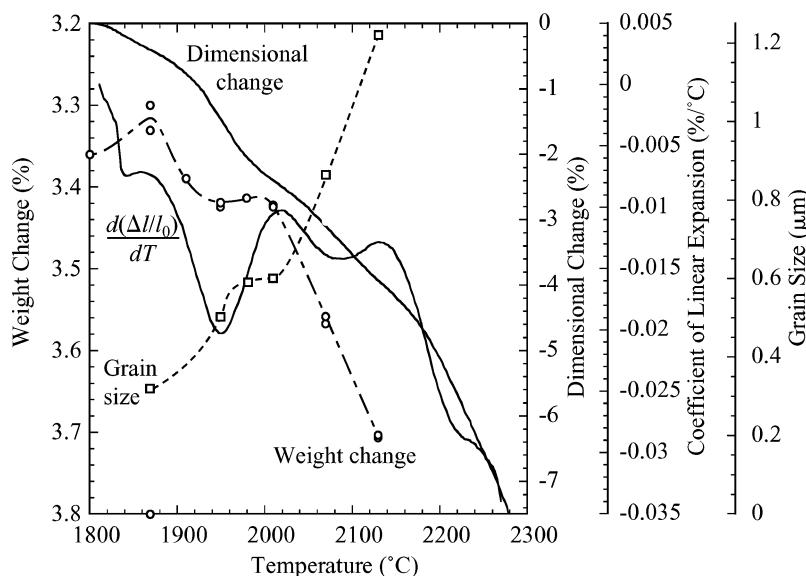


Figure 6 Trends in particle/grain size and weight change of undoped samples after heating at 5°C/min up to specific maximum temperatures and then cooling with no soaking. Temperature derivatives of dimensional change ($d(\Delta/l_0)/dT$) were calculated based on slopes of least-squares lines fit to 25 points (12 points on either side of and including a center point to which the calculated slope was assigned) in a dimensional change data set (also shown) containing 194 points.

above this temperature. The sintering rate accelerated substantially at and above 2130°C. It is believed that non-stoichiometric volatilization of B_4C in this temperature range, leaving residual carbon behind, facilitated enhanced diffusion via an activated sintering process [11].

To decrease the amount of time spent in the temperature range above which B_4C volatilization-induced coarsening was active but below which activated sintering began, the effect of faster heating rates was evaluated. Specimens were heated at various rates to 2250°C and soaked until the contraction rate was 0.00%. Densities increased from 91.33 ± 0.42 percent of TD to 92.76 ± 0.27 percent of TD, in changing the heating rate from 10°C/min to 100°C/min.

In attempt to eliminate the B_2O_3 coatings from the B_4C particles before the onset of sintering, compacts were soaked at various temperatures in flowing H_2 -He mixtures, so that the hydrogen would react with B_2O_3 to form B_2O_2 and H_2O gases. After evaluating a matrix of soak temperatures and H_2 -He mixtures, it was found that a maximum density of 93.8 ± 0.4 percent of TD was obtained by soaking at 1350°C in a mixture of 10 vol% H_2 -He (then switching to flowing He, heating at 30°C/min to 2230°C and soaking for 30 min). Lower temperature soaks were not effective at removing the oxide coatings, and higher temperature soaks permitted coarsening to occur prior to reaching the soaking temperature. Higher concentrations of H_2 at 1350°C had the benefit of more efficient removal of B_2O_3 , but as can be seen from Fig. 7, resulted in slowed densification in the latter stages of sintering. It is interpreted that hydrogen entered B_4C in the form of interstitials, which acted to increase the vapor pressure of B_4C at more elevated temperatures, facilitating coarsening. When a 1350°C soak in a 50-50 volume percentage H_2 -He mixture was followed by a 2 h soak at 1350°C under flowing He (to draw out residual hydrogen) prior to subsequent

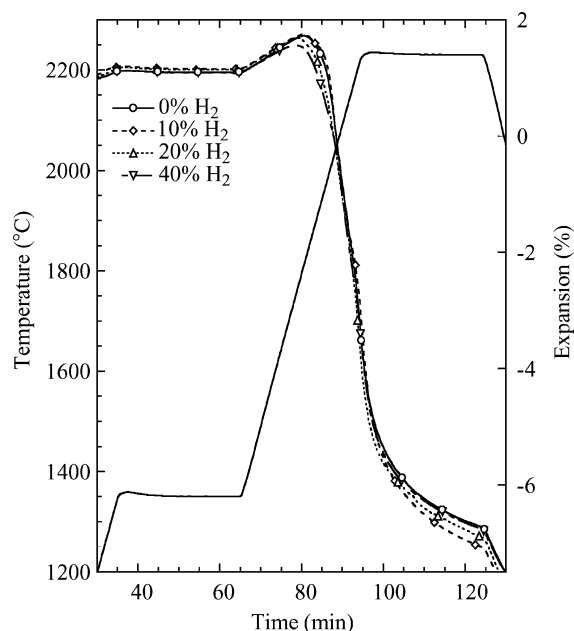


Figure 7 Contraction profiles from specimens sintered with a 30 min soak at 1350°C under different mixtures of flowing He/H_2 . Heating rates before and after the soak were 30°C/min. The atmosphere was changed to pure He after the 30 min soak at 1350°C. Markers in this figure are used to identify traces, and do not represent data points.

heat treatment, a fired density of 94.7% of TD was achieved.

4. Conclusions

Key considerations in improving the pressureless-sintered density of B_4C are related to the coarsening processes which occur during heat treatment. H_2 gas treatments at 1350°C were effective at removing B_2O_3 particle coatings which otherwise were interpreted to facilitate coarsening and stalled the onset of sintering. Rapid heating to a 2230°C soak temperature minimized

the time for coarsening via B₄C volatilization, and quickly brought the compact into a temperature regime in which sintering was rapid.

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