Effect of Sintering Parameters on Room-Temperature Injection Molded, Pressurelessly Sintered Boron Carbide Components

Erich Weaver
NDSEG Research Fellow

Prof. Rodney Trice and Prof. Jeffrey Youngblood

Purdue University, School of Materials Engineering
Boron carbide is highly valued for its extreme hardness and low density

• Favorable properties
  • Density = 2.52 g/cm³
  • Hardness = >30 Gpa Vicker’s
  • Young’s Modulus = 460 GPa
  • Melting Point = ~2450 °C

• Applications
  • Sand-blasting nozzles
  • Grinding and polishing media
  • Lightweight armor

• Excellent properties require full densities; not trivial for B₄C
Ceramic suspensions with controlled rheology can be used to improve upon colloidal processing techniques

- High ceramic (>50%) and low binder (~5%) content (balance = water)
  - Faster burn-out with fewer cracks and bubbles
  - High density after pressureless sintering
- Flowable at room temperature
  - Ability to use low pressure tooling
- Rheology amenable to variety of processing methods including injection molding and additive manufacturing

Colloidal ceramic suspensions solve many of the problems associated with traditional ceramic injection molding

- No need for elevated temperatures during green body forming
- Pressures required to injection mold are very low
Can achieve high densities and hardness values using $Y_2O_3$ and WC as sintering aids

- Found several sintering aid combinations that work well, notably 5 wt. % WC and 10 wt. % $Y_2O_3 + 5$ wt. % WC
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- Achieved relative densities of >95 % and hardness values >3200 Vickers
Success means new equipment! And a good chance to explore sintering parameters in depth

- Purchased a new furnace in order to be able to produce larger parts
- During initial testing, actually managed to exceed results from old furnace
- Decided to thoroughly investigate sintering parameters
Experimental approach

- Sintering aids
  - 5 wt. % WC + 10 wt. % \( Y_2O_3 \)

- Room-temperature injection molding

- Pressureless sintering
  - Temperature (2300, 2350, 2400 °C)
  - Hold Time (1, 2, 4 hours)
  - Ramp Rate (10, 25, 50 °C/min)
  - Atmosphere (Ar, Ar w/ burn-off, Ar w/ vacuum burn-off)
  - Baseline: 2350 °C, 2 hr. hold, 25 °C/min, Ar

- Mechanical testing and microstructure analysis
  - Optical microscopy
  - SEM
  - Archimedes density
  - Vicker’s hardness
Grain pullout is an issue across all sintering parameters

- Weak interfaces between Y phase and $\text{B}_4\text{C}$ make it extremely easy to pull out grains during polishing
- Grain pullout is present in all samples containing $\text{Y}_2\text{O}_3$
Both WC and $Y_2O_3$ react with $B_4C$ during sintering

- WC reacts with $B_4C$ to form $W_2B_5$, occasionally forming platelet structures\(^1\)\(^-\)\(^3\)
- $Y_2O_3$ reduces during sintering to form liquid metal, then forms $YB_6$ when cooled\(^4\)

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Using WC and Y₂O₃ together significantly increases the size of W₂B₅ platelets

- W is soluble in Y metal at sintering temperatures
- Platelets form almost exclusively at the boundary between Y liquid and B₄C
- High aspect ratio due to interface controlled growth

The amount of intragranular carbon inclusion increases at higher temperatures

- Carbon inclusions have been previously observed in $\text{B}_4\text{C}$, authors found that they had no significant effect on mechanical performance\(^6\)
- Reduced grain boundary area could explain higher number of intragranular inclusion at 2375 °C

$\text{Y}_2\text{O}_3$ significantly reduces the amount of carbon inclusions, which could explain hardness increases

- Significantly fewer carbon inclusions when $\text{Y}_2\text{O}_3$ is added as a sintering aid
- Excess C reacts with O during the reduction of $\text{Y}_2\text{O}_3$
Y2O3 significantly reduces the amount of carbon inclusions, which could explain hardness increases.

- Despite having lower densities, Y2O3 consistently has higher hardness values than WC.
- Previous literature performed bulk measurement (Split-Hopkinson Bar), rather than localized measurement like microhardness.

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Quick Reminder of experimental approach

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- Increase in density and hardness as ramp rate increases (up to a point)
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- No significant differences in overall microstructure.
- Maximum density was achieved at 2350 °C.
- Hardness values could not be measured in 2300 or 2400 °C samples due to issues with grain pullout.
Increasing hold time increased density

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- No significant differences in overall microstructure
- Increasing hold time increased density, but with diminishing returns
- Hardness values could not be measured in 1 hr. or 4 hr. samples due to issues with grain pullout
Adding a hold at 1350 °C increased density and hardness

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- No significant differences in overall microstructure
- Well established that a hold between 1300-1500 °C boils off boria\(^4,7\)
- Adding a burn-off step significantly increases density, and the vacuum burn-off also resulted in higher hardness values

Summary

• Pressureless sintering can be used to sinter $B_4C + WC$, $B_4C + Y_2O_3$, and $B_4C + WC + Y_2O_3$ to >95% relative density.

• Best practices for pressureless sintering are to burn off in vacuum at 1350 °C, high ramp rate (>25 °C/min), sinter at 2350 °C for 4 hrs.

• Despite having lower densities compared to WC, adding $Y_2O_3$ consistently demonstrates higher hardness values.

• Ongoing work to determine effects on grain size and to combine best parameters.
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Extra Slides
New stuff to add

• Seemingly no reduction of grain growth due to precipitate drag from carbon inclusions – soluble at high temperatures?

• New story order
  – General microstructure observations as a whole
    • Grain pullout
    • Y2o3 reduction and liquid phase sintering
    • W2b5 platelets
    • Platelets showing up almost exclusively at borders between y liquid and b4c
    • Carbon inclusion
      – Paper claimed no performance on mechanical properties
    • Y2o3 reducing carbon inclusions
      – Could explain hardness benefits
      – Kolsky bar guys claimed no difference, but they were testing sample as a whole rather than a localized area like in hardness testing
  – Benefits from different sintering parameters
Sintering parameters made many small improvements to results, but none large enough to explain the difference.

- Both increasing the heating rate and sintering in vacuum slightly increased density, but not enough to match the old results.
The solution turned out to be increasing the sintering temperature significantly – the old furnace was miscalibrated

- The old Centorr furnace was underreporting temperature due to an error in the e-slope value of the pyrometer
- Increasing the temperature used in the Carbolite furnace increased density even beyond what had been achieved in the Centorr

What if we used all the methods for small improvements again now that we’re at the correct temperature?