Dense, amorphous B and B_4C coatings through vacuum arc deposition from non-metal, sintered cathodes: ExtreMat applications

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Vacuum arc deposited B and B_4C coatings

- B and B_4C are both high temperature materials (mp >2000°C) and maintain high hardness at high temperatures
- Both resist attack from almost all corrosive agents
- Energetic deposition using cathodic arc technology allows the production of amorphous coatings from B and B_4C with hardness approaching that of crystalline material but with much lower elastic modulus -> H ~28GPa, E ~280GPa
- The tendency of B to form stable compounds with most transition metals allows for strong adhesion to commercial substrates.
- Energetic deposition enables break up of surface oxides as well as surface mixing to encourage compound formation
- Deposition rates of up to 30nm/sec (unfiltered) and up to 5nm/sec (filtered) with novel filter compared to <5nm/min with best sputter process.

Enabled by robust cathode technologies, substrate biasing techniques and a novel debris filter, this emerging coating technology has great promise for extreme environment applications.

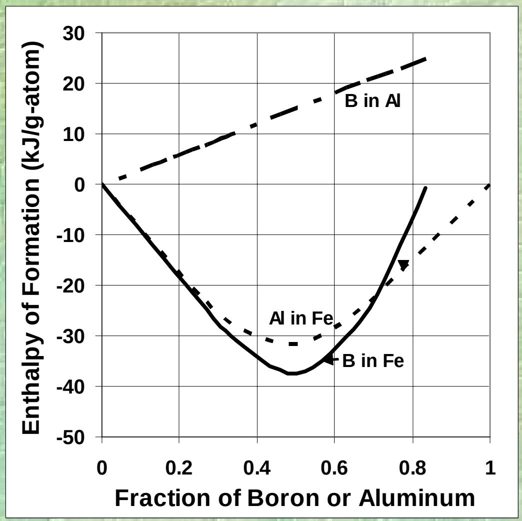
Key Extreme-Environment Materials ("ExtreMat") Applications

Aluminum Die casting	• Preliminary data obtained in Pure Al (see below)
Corrosion protection for steels	• Tests of B coated 52100 steel in brine solution showed no corrosion
Erosion protection for fusion plasma facing components	• B_4C well known for very low erosion rate[1] • B_4C coatings produced so far are amorphous and are limited in thermal conductivity • Methods to induce crystallinity are being sought
Sand Erosion Protection	• Boron is 3 times as hard as sand • Current project exploring sand erosion protection for Ti turbine blades. • Good adhesion to Ti demonstrated. • Dense B_4C already shown to be ideal for sand erosion protection[2]
Chlorine-Ion resistance and bio-compatiblity	• Strong corrosion resistance was found in long term wear tests under high-load conditions against UHMWPE in concentrated saline solution
Automotive Applications	• Components: Ti poppet valves, Fuel injector plungers, piston rings • Useful properties: High temp corrosion resistance, lubricity in presence of water[3,4], hardness, not combustible

1. O.I. Buzhinskij, Yu.M. Semenets, "Thick boron carbide coatings for protection of tokamak first wall and divertor," *Fusion Engineering and Design*, **45**, 4, p. 343-60 (1999).
2. R.J.K. Wood, "The sand erosion performance of coatings," Materials and Design 20, 179 (1999).
3. Erdemir, A., Fenske, G.R., and Erck, R.A., "A Study of the Formation and Self Lubrication Mechanisms of Boric Acid Films on Boric Oxide Coatings," *Surf. Coat. Technol.*, Vol. 43/44 (1990), pp.588-596.
4. J.M. Williams, C.C. Klepper, R.C. Hazelton, and M.D. Keitz, J.E. Lemons, et. al., "Boron and Boron-based Coatings as Deposited by the Cathodic Arc Technique", to appear in Proceedings of the ISEC-SMT St. Paul, MN 2005

Aluminum Die-casting Applications

- **Lifetime of H13 steel dies is limited by aluminum soldering (Al sticking to dies) requiring replacement of dies ($$$)**
- **Mold releases are used to mitigate this problem but present environmental, health and cost issues.**
- **B is predicted to adhere to steel and not aluminum.**
- **Initial results substantiate this prediction**
- **Single application eliminates manufacturing steps in casting**

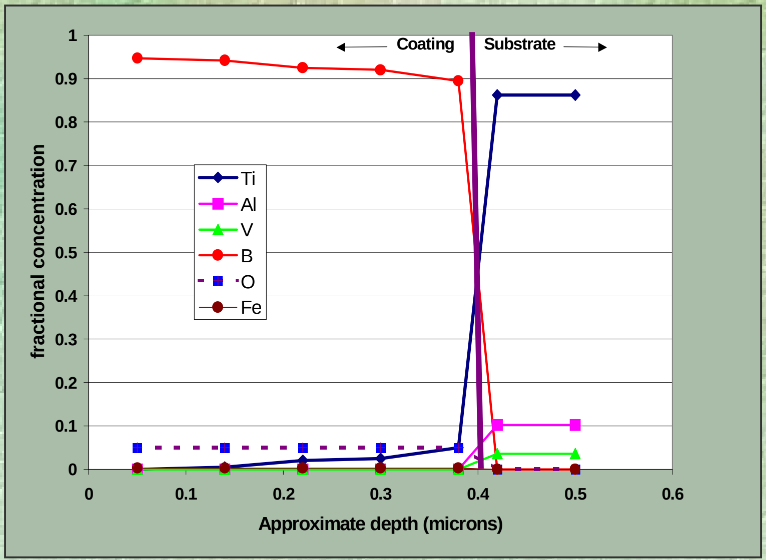


Thermodynamic calculations of the heats of formation show a repulsive interaction between B and Al while strong bonding between B and Fe is favored.

- **Dipping test into molten Al (pure) at 700°C, until Al solders to the steel pin:**
  - **Uncoated H13 Steel - one cycle**
  - **Boron Coated H13 steel - >51 cycles**
- Relative to the casting application, this is regarded as a severe environment because of the higher temperature and aggressive reactivity of the pure Al, in comparison with the liquidus temperature and composition of the hypereutectic Al-Si alloy used for many automotive applications. *Thus the test can be regarded as accelerated.*

Improved Adhesion

- Energetic deposition and small atomic size promotes better adhesion by diffusing the coating into the substrate.
- Depending on substrate, the B coatings can diffuse up to 500nm into substrate.
- Strong chemical reactivity also promotes adhesion but can limit diffusion.



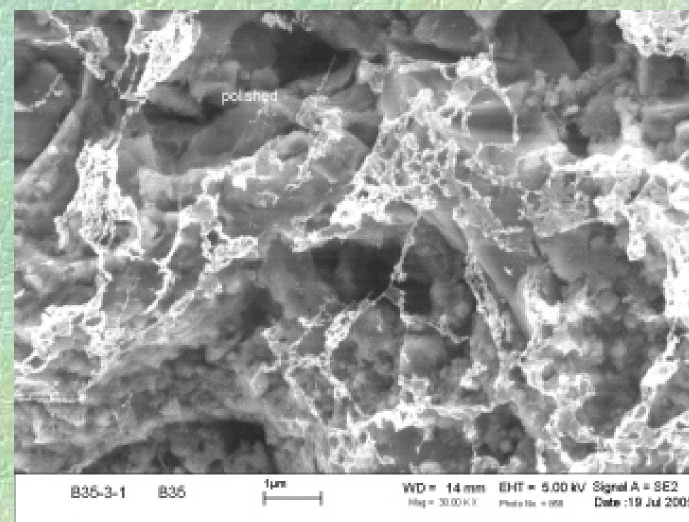
← RBS analysis of a ~1µm B coating on Ti-6Al-4V. In this case the small (barely resolvable) in-diffusion of boron into the Ti-alloy may be a result of the stronger Ti-B reaction. However, the Ti is reacting deep into the boron coating. Finally, the oxygen level is at about 5-6%, which is ideal for forming boron sub-oxides. (The thin, vertical line defines the coating-substrate divide in the simulation)

Robust Cathodes

A pure boron cathode after exposure to cathodic arc electrical discharge for a number of coating runs.

This was not possible with commercially available, consolidated B (e.g. materials sold as sputter targets will shatter under the stress of the arc current).

- **Open-pore microstructure** is typical successful cathode material
  - Will not trap gases that lead to failure in high thermal stress environments
- *Highest densification for pure boron (70%) ever achieved*



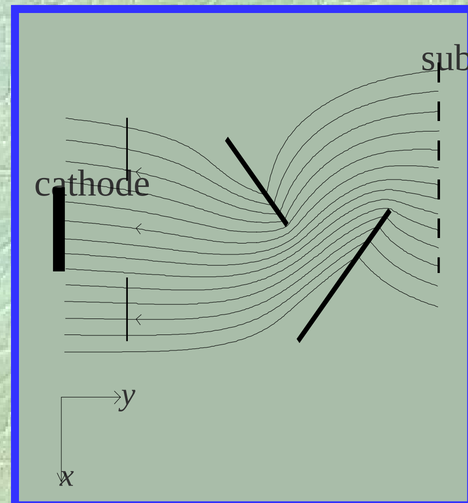
Use of microwave sintering has been a key ingredient in the processing of successful cathodes, both for B and for B_4C

Novel macroparticle filter that works with B and B_4C cathodes

Modified version of Ryabchikov's blade style macroparticle filter[1] has been developed to work with non-metal/sintered cathodes

Modified Blade Filter -
Some deflected macro-particles still reach the substrate by reflection of the anode and the walls.

Modified Blade Filter with traps -
Nearly all deflected macro-particles are contained with particle traps.



Typical magnetic field geometry -

- Unlike the original filter in [1], external field coils are also required to make this modified version work.
- The filter in [1], which has a "Venetian blind configuration for the blades, works for metal macroparticles, which are mostly molten drops and will stick to the blades.
- Like graphite, B and B_4C macroparticles are solid fragments of the cathode and are also highly elastic (the can undergo multiple bounces).

Filter Performance
2 particles/cm^2/100nm thickness

B on CoCrMo - Unfiltered

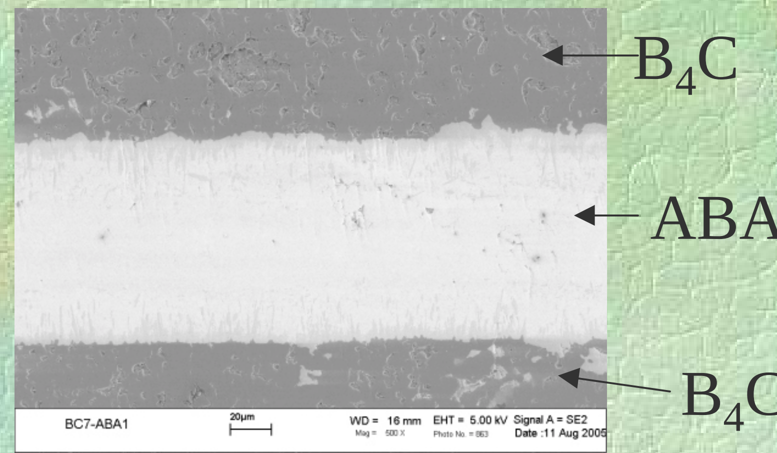
B on CoCrMo - Filtered

Squiggly features in both images are part of substrate, not macros

[1] A.I. Ryabchikov, *Surface and Coatings Technology* **96** (1997) pp 9-15.

Fusion PFC applications for Cathode Materials (Sintered B_4C, B)

- Sintered B_4C can be brazed to itself or other metals (Stainless Steel, Ti, Cu) using Active Brazing Alloys (ABAs)
- Net shape casting techniques allow construction of complex structural geometries
- Much lower chemical and high temperature erosion rate than graphite
- Only low Z erosion products
- Thermal conductivity can exceed stainless steel



- Using laser flash technique according to *M.V. Krishnaiah et al., Rev. Sci. Instrum. 73 (9) 3353-3357, 2002* the thermal diffusivity can be measured
- **Result:** ***20 W m^{-1} K^{-1}*** **for 80% dense B_4C samples**
  Compare to ~*20 W m^{-1} K^{-1}* for steel
  Compare to ~*30 W m^{-1} K^{-1}* for solid B_4C
- Porosity can be customized to near solid B_4C (~*30 W m^{-1} K^{-1})*

Plasma Facing Components (PFC) applications possible such as armor for RF antenna Faraday shields

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