# Designing Superhard Materials: Rhenium Diboride

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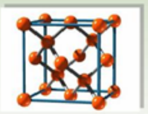
## Abstract

**Superhard materials are useful in many applications such as for refractory and abrasive purposes. Recent work on rhenium diboride has shown the compound's potential as a metallic superhard material. Solid solution and grain size hardening treatments were performed on $ReB_2$. Solid solution hardening was performed on $ReB_2$ by doping with 2%, 4%, and 10% $TiB_2$ as well as 2% Ti. Doping $ReB_2$ with 2% Ti increased the hardness by 14.4% at the lowest applied load of 0.49 N while the addition of 2% $TiB_2$ increased the hardness (6.4% - 26.1%) over a load range of 0.49 to 2.9 N. Higher concentrations of $TiB_2$ showed a minimal increase in hardness compared to pure $ReB_2$. Ball-milling was used to reduce the crystallite size of pure $ReB_2$ for grain size hardening; this method reduced the average crystallite size from approximately 50 nm to 20 nm as shown through peak broadening in x-ray diffraction patterns. Sintering and densification (currently underway) of ball-milled $ReB_2$ crystallites hold potential to dramatically increase the material hardness through grain size refinement.**

## Background

### Hardness

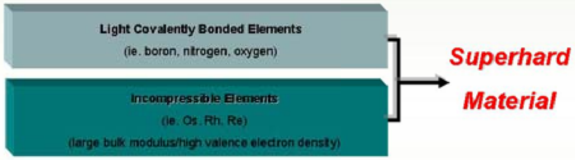


- Resistance to plastic deformation
- Superhard materials: Vicker's Hardness ($H_v$) ≥ 40GPa

  Diamond: 70 – 100 GPa

  c-BN: 45 – 50 GPa

## Material Synthesis



**Light Covalently Bonded Elements**
(ie. boron, nitrogen, oxygen)

**Incompressible Elements**
(ie. Os, Rh, Re)
(large bulk modulus/high valence electron density)

***Superhard Material***

- Light covalently bonded element: **Boron**
- Incompressible element: **Rhenium**
  - Valence electron density of 0.4761 *e-*/Å³ (second highest on the periodic table next to Os)
- Arc-melting synthesis using 50 – 120 Amps of current

  $$Re + 2.5B \rightarrow ReB_2 \text{ (metallic pellet) } + 0.5B$$

- Solid-state furnace reaction

  $$Re + 2B \rightarrow ReB_2 \text{ (powder)}$$

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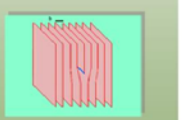
## $ReB_2$ Hardening

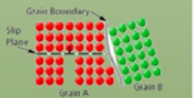
**Must impede the movement of *dislocations (extra "half-planes"* of atoms) throughout the atomic lattice**

### Solid-solution hardening



- Replacement/substitution of atoms
- Titanium – different valence electron density count, atomic radius, and readily forms $TiB_2$ (HCP)
- Arc-melting of Ti or $TiB_2$ with $ReB_2$

### Grain Size Hardening

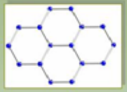


- Grain size reduction localizes the movement of dislocations
- Sintering of ball-milled nanometer sized crystallites of $ReB_2$

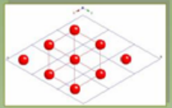
http://en.wikipedia.org/wiki/Dislocation

## $ReB_2$ Structure

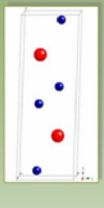
**$ReB_2$**
Hexagonal crystal structure
*a* = *b* = 2.900 Å, *c* = 7.478 Å,
α = β = 90º, γ = 120º
Space group – P63/mmc



Puckered, hexagonal network of B atoms



Hexagonal close-packed network of Re atoms



● Boron
● Rhenium

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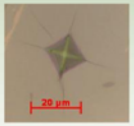
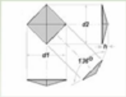
## Analysis

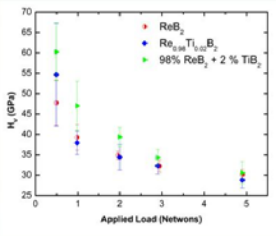


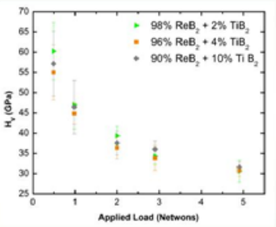


- Hardness measured by microindentation using a pyramidal diamond tip on epoxy cast metallic pellets
- Vicker's hardness ($H_v$) is calculated using the indentation diagonal

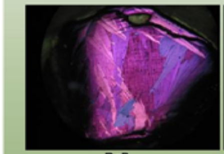
$$H_V = 1854.4\, P/d^2$$

## Solid-Solution Hardening

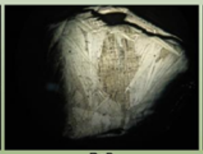




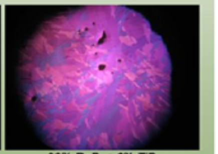
- Increasing hardness with decreasing applied load is a universal phenomena known as the *indentation size effect*
- Addition of 2% $TiB_2$ in $ReB_2$ increased the hardness (6.4% - 26.1%) over a load range of 0.49 to 2.9N.
- $ReB_2$ doped with 2% Ti exhibits an increase at all loads with the highest increase of 14.4% at the lowest applied load (0.49 N)
- Solid-solution hardening with Ti fails to provide a substantial hardness increase at high loads



$ReB_2$
(polarized)



$ReB_2$
(bright field)

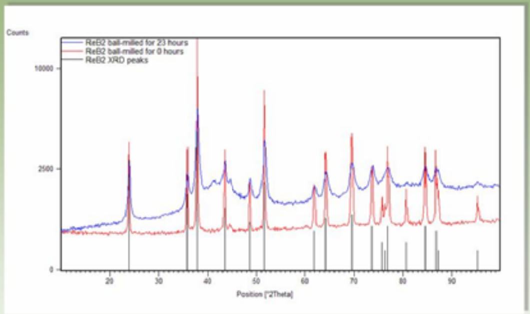


98% $ReB_2$ + 2% $TiB_2$
(polarized)

- Polarized images of arc-synthesized pellets allows the identification of different phases and/or individual grains with differing crystallographic orientations
- Smaller grains apparent in 98% $ReB_2$ + 2% $TiB_2$ due to orientation of the exposed surface and the temperature gradient present during cooling of the arced pellet

## Grain Size Hardening

- $ReB_2$ was ball-milled using a steel vial and steel balls (grinding medium) rotating at 600 RPM for 23 hours
- Crystallite size was determined at 0, 2, 4, 6, 9, 14, and 23 hours

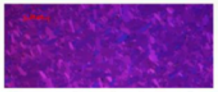


- Crystallite size reduction is observed through peak-broadening in powder X-ray diffraction patterns and is calculated using *Scherrer's Equation*

| Hours | Crystallite Sizes (nm) |
|---|---|
| 0 | 51 |
| 2 | 24 |
| 4 | 23 |
| 6 | 21 |
| 9 | 20 |
| 14 | 20 |
| 23 | 20 |

$$t = \frac{0.9\lambda}{B\cos(\theta)}$$

t = crystallite size
λ = wavelength
B = peak broadening



**Hot pressed pellet using powdered $ReB_2$ produced grain sizes in the range of 2-10 µm. Spark plasma sintering should minimize grain growth**

## Conclusions

Through solid-solution hardening, we are able to increase the hardness of $ReB_2$ at low loads. Hardness increases at higher loads were minimal compared to that of pure $ReB_2$. This may be attributed to non-ideal selection of the dopant. Due to the lower hardness of $TiB_2$ compared to $ReB_2$, formation of precipitates will not impede dislocation movement. However, grain size hardening of $ReB_2$ holds high potential for increasing the hardness of the material through grain size reduction and localization of dislocations.

## Acknowledgements

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