Ultra-high temperature ceramics with exceptional strength at elevated temperature

Laura Silvestroni
Nicola Gilli
Diletta Sciti
Jeremy Watts
William Fahrenholtz

Follow this and additional works at: https://dc.engconfintl.org/uhtc_v
ULTRA-HIGH TEMPERATURE CERAMICS WITH EXCEPTIONAL STRENGTH AT ELEVATED TEMPERATURE

Laura Silvestroni\textsuperscript{1}, Nicola Gilli\textsuperscript{1}, Diletta Sciti\textsuperscript{1}, Jeremy Watts\textsuperscript{2}, Greg Hilmas\textsuperscript{2}, William Fahrenholtz\textsuperscript{2}

\textsuperscript{1}CNR-ISTEC, Institute of Science and Technology for Ceramics, Via Granarolo 64, I-48018 Faenza, Italy
\textsuperscript{2}Dep. of Materials Science & Eng., Missouri University of Science and Technology, MO 65409 Rolla, USA
Goal & Approach

1. Understanding basic phenomena
   - CORE-SHELL formation by addition of transition metal (TM)
   - How to SUPER-SATURATE the shell to precipitate nano-inclusions within \( \mu \)m-sized grain

2. Custom-making nano UHTC composites
   - PHASE STABILITY DIAGRAMS define the partial pressure conditions within the sintering chamber that drive precipitation of nano-inclusions of variable nature.

Materials:
- \( \text{ZrB}_2 \): refractoriness & ablation resistance
- SiC or Silicide: formation of SiO\(_2\)
- TM-compound: densification, refractoriness, oxidation & shell formation

\( W \): Low Solubility within \( \text{ZrB}_2 \) (~4 at%)
\( Ta \): High Solubility within \( \text{ZrB}_2 \) (~15 at%)
ZrB$_2$ – 3 SiC – 5 WC:

- Epitaxial (Zr,W)B$_2$ solid solution
- Dislocation accumulation at core/shell interface
- WC → WB
- Clean grain boundaries

$\sigma > 600$ MPa up to 2100°C
• Increased dislocations activity
• PDW at & across the core/shell boundary: grains refinement 2 μm → 50 nm
**ZSW upon σ1800, Ar: core - shell**

- Clean boride/boride interfaces
- Dislocations activity & crew
- W ppt at the core/shell boundary
- Bright W ppt on the fracture
ZSW upon $\sigma$1800, Ar: grain boundaries

- Clean boride/boride interface
- Clean boride/SiC interface
ZSW upon $\sigma_{1800}$, Ar: second phases

- SiC, WB with stacking faults $\rightarrow$ pull-out, crack deflection
ZSW upon $\sigma1800$, Ar: second phases

- Wetted SiC/SiC interfaces $\rightarrow$ softening
Strengthening at UHT

- Refractory phases ---- ZrB$_2$
- MGS preserved ---- grain refinement: dislocation movement and intersection, Petch-Hall hardening
- Clean grain boundaries --- WC
- Formation of a healing glassy layer --- test in Ar
- Reinforcing phases --- precipitation hardening & metal toughening (W is ductile and tough at HT)

$\sigma = \frac{K_{Ic}}{Y \sqrt{a}}$
Local toughening at UHT

- SiC, WB platelets pull-out
- W precipitation from the (Zr,W)B₂ solid solution
- W is ductile and tough at HT and absorbs fracture energy
- M.g.s. is retained, but the shell region is enlarged
- Toughening at nano-scale by twins and stacking faults

\[ \sigma = \frac{K_{lc}}{Y} \sqrt{a} \]
ZrB$_2$ - TaSi$_2$

- Formation of (Zr,Ta)B$_2$ shell (~40 vol%)
- Residual TaSi$_2$ and SiOC

- Expansion of the shell (~60 vol%)
- SiOC conversion to SiC
ZBT-ann

- (Zr,Ta)C second phase
- Smooth fracture in the core
- Zig-Zag fracture & nano-sized bright ppt in the shell

• (Zr,Ta)C second phase
• Smooth fracture in the core
• Zig-Zag fracture & nano-sized bright ppt in the shell
ZBT-ann: boride matrix

- Epitaxy between core and shell
- Intricate core-shell dislocation network
- Sharp core/shell interface, no clear definition between shell 1&2
- Dark inclusion at the core/shell interface
ZBT-ann: interfaces

- Clean shell/shell gb
- Unclear core/shell boundary
- No clear ppt

(Zr,Ta)B$_2$

(Zr,Ta)B$_2$

(Zr,Ta)B$_2$

ZrB$_2$

5 nm

300 nm

5 nm

3 nm
ZBT-ann: finally precipitates!

• Needles at core/shell interface
ZBT-ann: TaC needles

![Image of TaC needles](image1)

![Image of TaC needles](image2)

![Image of TaC needles](image3)

![Image of TaC needles](image4)

![Image of TaC needles](image5)

- Counts (a.u.)
- 200 nm
- 100 nm
- (Zr,Ta)B$_2$
- TaC
- TaC [2,1,1]
- TaC [1,1,0]
- Zr, Ta
- 3 nm
- ECI: UHTCs V, June 8 2022
Nature of the precipitates

- ZBW → (Zr,W)B₂ + rounded metallic W nano-precipitates
- ZBT → (Zr,Ta)B₂ + elongated needle-like shaped TaC precipitates

Nature of the ppt dictated by HP CO/O₂ partial pressure

- By changing the sintering atmosphere (CO-rich or vacuum) we might tune the nature of the ppt
TM-C-O phase stability diagrams

- Metal: Mo, Re, Os, Ir
- Carbide: Ti, Hf, Nb, Cr, V
Shape & location of the precipitate

- Interface properties of solid solution and ppt
- Wettability between solid solution and ppt
- Plasticity of the novel formed phase
- Cooling rate?

**Sphere**: isotropic energy, low wettability

**Needle**: anisotropic energy, growth rate controlled by mobility

- Local TM enrichment / supersaturation
- Low energy sites with enhanced mobility for atomic attachment and precipitate growth (dislocations at the core-shell interface)
Amount of ppt

• Solubility of the guest TM in the boride cell
  ➢ High solubility: Ta up to 15 at% → high amount of TM-additive to super-saturate the boride solid solution
  ➢ Low solubility: W up to 4 at% → low amount of TM-additive to super-saturate the boride solid solution

• Shell thickness
  ➢ can be manipulated by changing the T & t of the heat treatment
  ➢ Is formation of a **homogeneous solid solution** desirable?
    ‒ elimination of one hierarchy grade
    Dislocations at the core-shell interface useful for:
    - grain refinement down to 30-50 nm
    - increased plasticity @UHT

• How to quantify the ppt?
  ➢ Ppt are difficult to image in TEM specimens
  ➢ can only be observed on fracture surfaces by SEM
  ➢ FIB slice and view ongoing
Mostly pure ZrB$_2$ mgs: 5-20 μm
**ZBW-ann**

- Nanotexturing coarsening
- Dislocation structure relieve?

**ZrB$_2$ + WC + SiC**
2.1 ± 0.8 µm
Core/shell
little WB

σ$_{RT}$: ~630 MPa
σ$_{1800^\circ C}$: ~600 MPa

(As-sintered material
σ$_{1800^\circ C}$: ~800 MPa)

- microbands, nano-twins, stacking faults...
- protruding elongated particles: HT toughening?
UHT strength vs ductility

- Ductility of WB phase
- Approach to eutectic temperatures in the Zr–W–B–C system

ZrB$_2$ + 15 vol% WC
1.6 ± 0.4 µm
Core/shell
Residual WB

σ1800°C: ~1 GPa
σ1900°C: ~830 MPa
σ2000°C: bending
Conclusions

• **ZrB$_2$** ceramics hot pressed in presence of TM
  - Core: ZrB$_2$
  - Shell: (Zr,TM)B$_2$
  - Shell featured by precipitation of **nano-inclusions**

• **Nano-inclusions**
  - Nature depends on the **PCO/PO$_2$**
  - Shape depends on **interface properties**, wettability, ductility
  - Location: on **defects**
  - Amount depends on TM **solubility** within the shell

• **Strength >1 GPa @ 1800°C** and **>600 MPa @ 2100°C**:
  - Grain refinement by **dislocation intersection**
  - Local toughening by **ductile inclusions**

---

Material design through thermal treatment leads to **core/shell** structures with a **multi-scale nanostructured hierarchical** arrangement: is this the **X FACTOR** for **UHT** strength in boride-based ceramics?
Acknowledgements

EU-FP7
Super LIGHT-weight Thermal Protection System for space application (LIGHT TPS #607182)

NATO SPS
SUPER Strong ceramics for Protection in harsh ENvironments and defense (SUSPENCE #G5767)

US AFOSR
NAnocomposite Core-Rim structures for Enhanced toughness and Strength at extreme temperatures (NACREOUS #FA9550-21-1-0399)

US ARMY ACC-APC-RTP & ONR
Functionally graded fiber-Reinforced Ceramics for Extreme environments (FORCE #W911NF-19-2-0253)

Thank you!
laura.silvestroni@istec.cnr.it
Literature

1. Super-strong materials for temperatures exceeding 2000 °C
   Laura Silvestroni, Hans-Joachim Klebe, William G. Fahrenholtz & Jeremy Watts
   Ceramic-based composites for high-temperature applications have been developed to withstand temperatures above 2000 °C, a critical requirement for next-generation aerospace vehicles. These materials are designed to provide high-strength, high-temperature performance, enabling their use in advanced aerospace applications.

2. Design of ultra-high temperature ceramic nano-composites from multi-scale length microstructure approach
   Nicola Gilli, Jeremy Watts, William G. Fahrenholtz, Diletta Sciti, Laura Silvestroni
   This study focuses on the design of ceramic nano-composites for ultra-high temperature applications. The multi-scale length microstructure approach is used to develop materials with enhanced properties.

3. Method to improve the oxidation resistance of ZrB₂-based ceramics for reusable space systems
   Laura Silvestroni, Simone Failla, Irena Neshpor, Oleg Grigorev
   This research presents a method to improve the oxidation resistance of ZrB₂-based ceramics, crucial for the development of reusable space systems.

4. Microstructure evolution of a W-doped ZrB₂ ceramic upon high-temperature oxidation
   Laura Silvestroni, Diletta Sciti, Frédéric Monteverde, Kerstin Stricker, Hans-Joachim Klebe
   The microstructure evolution of a W-doped ZrB₂ ceramic upon high-temperature oxidation is investigated, providing insights into its thermal stability.

5. Critical oxidation behavior of Ta-containing ZrB₂ composites in the 1500–1650 °C temperature range
   Laura Silvestroni, Hans-Joachim Klebe
   This study examines the critical oxidation behavior of Ta-containing ZrB₂ composites in a wide temperature range, essential for understanding their applicability.

6. Understanding the oxidation behavior of a ZrB₂–MoS₂ composite at ultra-high temperatures
   Laura Silvestroni, Kerstin Stricker, Diletta Sciti, Hans-Joachim Klebe
   The oxidation behavior of a ZrB₂–MoS₂ composite at ultra-high temperatures is investigated, contributing to the development of advanced materials.

7. Effect of hypersonic flow chemical composition on the oxidation behavior of a super-strong UHTC
   Laura Silvestroni, Stefano Mangiagira, Diletta Sciti, Giuseppe D. Di Martino, Raffaele Savino
   This research explores how the chemical composition of hypersonic flows affects the oxidation behavior of super-strong UHTCs, important for aerospace applications.

8. Core-shell structure: An effective feature for strengthening ZrB₂ ceramics
   Laura Silvestroni, Simone Failla, Vladimir Vinokurov, Irena Neshpor, Oleg Grigorev
   The effective feature of core-shell structures for strengthening ZrB₂ ceramics is studied, offering insights into material design.

9. A simple route to fabricate strong boride hierarchical composites for use at ultra-high temperature
   Laura Silvestroni, Nicola Gilli, Andrea Migliori, Diletta Sciti, Jeremy Watts, Greg E. Blatchley, William G. Fahrenholtz
   A simple route to fabricate boride hierarchical composites for use at ultra-high temperatures is presented, advancing the field of high-temperature materials.
Literature

1. https://www.nature.com/articles/srep40730