Where we are with the understanding of metal/ceramic interactions: The case of transition metal borides

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Where are we with the understanding of metal/ceramic interactions, wetting & joining?

The case of transition metals diborides

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Ultra-High Temperature Ceramics
• Introduction- Wetting- Reactivity

• Models

• Wetting at lower temperatures

• Wetting at higher temperatures

• Phase diagrams

• Joining

• Conclusions
• **Introduction- Wetting- Reactivity**

• Models

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When designing new joining processes through brazing, it is fundamental to understand:

- how well the liquid wets the ceramic interface
- the interplay between liquid and solid chemistry
- the interfacial energetics
- how to control the interfacial reactions.

In this presentation, the behaviour of transition metal diborides (TiB$_2$, ZrB$_2$, HfB$_2$) in contact with molten metals will be reviewed with respect to their wettability, reactivity and joining through the experiments and thermodynamic calculations made in the last ≈15 years.
Experimental studies of the energetics of liquid metal/ceramic interfaces performed in the last 50 years highlighted major tendencies, classifying most of the ionic/covalent ceramic/pure metal couples as “non-wetting systems” (with a contact angle $\theta>90^\circ$). However, transition metal diborides have a metallic-like character, so that their wettability by liquid metals should be granted (i.e. $\theta<90^\circ$).

We must underline that wetting experiments with very refractory ceramics are performed using sintered polycrystalline specimens, so that impurities in these materials, their surface roughness, and frequently ill defined furnace atmospheres gave rise to a wide scatter in contact angles and consequently in the Work of Adhesion values (*)

$$W_{adh} = \sigma_{lv}(1+\cos\theta)$$

where $\sigma_{lv}$ is the liquid-vapour surface tension.

At the **solid/liquid-metal interface**, the following processes may happen:

- **dissolution** of the solid into the liquid,
- **penetration/diffusion** of the liquid components into the solid,
- **adsorption** of components of the liquid phase at the solid-liquid interface,
- **Reactions** and **formation of new phases**,
- dynamic **restructuring** of the solid surface.
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The adhesion between a liquid metal M1 and a ceramic material M2-X is mainly due to two kinds of chemical bonds:

- those of the M1-M2 type
- those of the M1-X type.

An efficient way to study these interactions and to quantify their effects in terms of adhesion energy is provided by modelling, through molecular dynamics approaches or by applying the Density Functional Theory (DFT).

As an example, a first-principles DFT study has been presented to investigate similar properties for the interfaces between ZrB$_2$ and the transition metals Ag and Au. The first value extracted from calculations is the Work of Separation, defined as:

$$W_{sep} = \left( E_{sl1} + E_{sl2} - E_{int} \right)/2A$$

where $E_{int}$ is the total energy of the supercell with the interface system, $E_{sl1}$ and $E_{sl2}$ are the total energies of the same supercell, when one of the slabs is kept and the other one is replaced by vacuum, and $A$ is the interface area within one supercell.
DFT on Au-ZrB$_2$ interface

\[ \text{Au-ZrB}_2 : \text{B terminated} \quad \text{Au-ZrB}_2 : \text{Zr terminated} \]

<table>
<thead>
<tr>
<th>Interface</th>
<th>Bulk mismatch (%)</th>
<th>$W_{sep}$ (J/m²)</th>
<th>$W_{ad}$ (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*Au/ZrB$_2$ - Zr</td>
<td>10.3</td>
<td>3.725</td>
<td>≈ 2100</td>
</tr>
</tbody>
</table>
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WETTING
at
900 °C < T < 1200 °C

Contact angles on TiB$_2$

Liquid metal - temp. °C

Contact angles on ZrB$_2$

Liquid metal - temp. °C

Contact angles on HfB$_2$

Liquid metal - temp. °C

\[ \theta = 90^\circ \]
These results mean that, when $\theta > 90^\circ$, the “diboride” surface should act as a iono-covalent body!

Thus, we must “destroy” this barrier.................
How to modify the metal-ceramic system wettability

Two principal methods are widely employed for (non-reactive) metal-ceramic systems:

• **modification of the ceramic surface (specific coatings) in order to let the liquid metals spread**

• **the addition of active elements to the metal to form intermediate products at the interface more readily wetted by the liquid alloy.**

E.g., the addition of Ti to Ag or Cu alloys involves the formation of Ti compounds (TiO, TiC or TiN on oxides, carbides and nitrides, respectively) at the metal-ceramic interface which, due to their more “metallic” character, are **wetted better** than the bulk ceramic.

**Active metals**, can also **adsorb** at the solid-liquid interface lowering the **interfacial energy** and consequently the **contact angle** (affecting also the spreading kinetics).
In particular, for our borides, we can get a better wetting by the following possible mechanisms: (remember: the experiments are performed under a very low oxygen partial pressure)

1) **Surface oxides reduction.**
The following reaction between B and the Trans. Metal oxide could occur:

$$1.5 \text{(TM)}O_{2}(s) + 2B(l) = B_{2}O_{3}(g) + 1.5 \text{(TM)}(l)$$

2) **B\textsubscript{2}O\textsubscript{3} removal**
B can react with \( B_{2}O_{3} \) at the surface, forming volatile \((BO)\text{\textsubscript{n}}\) boron oxides [c]:

$$2B + 2B_{2}O_{3} = 3(B_{2}O_{2})$$

The corresponding vapour pressure of the gaseous dimer \((BO)\textsubscript{2}\) [c] extrapolated to \( T=1500 \) °C , is \( P_{(BO)2} \approx 6 \times 10^{-3} \) atm.

3) **Boride stoichiometry variation**
Example: going from \( TiB_{1.95} \) to \( TiB_{1.9} \) the contact angles vary from 55° to 50° for Cu and from 15° to 10° for Au at 1150°C.

--

Wetting of $\text{ZrB}_2$ (+$\text{B}_4\text{C}$)

Kinetics of wetting of Ag, Au and Cu on $\text{ZrB}_2$ at $T=1.05\ T_m\ [K]$, Ar-5%H$_2$
Wetting of ZrB$_2$/SiC

Wetting by Cu, 1150°C; $\theta = 80^\circ$

Top view of the drop

No interlayers
Active metal additions

different Ag-X alloys on ZrB$_2$ - HIP

Active metal additions (ZrB$_2$/SiC)

Wetting by CuTi (Ti: 22 at.%, eutectic), $T = 950^\circ C$, $\theta = 19^\circ$

- **Bulk:**
  - $\text{Ti}_2\text{Cu}_3$
  - $\text{TiCu}_2$

- **Ti-rich interlayer:**
  - $\text{TiCu}$ (+Si)
  - $\text{Ti}_3\text{Cu}$ (+Si)

WETTING

at

$1300^\circ C < T < 1550^\circ C$
Main interest: high temperature applications, e.g. advanced brazing processes.

In recent years, wettability and/or reactivity data have been presented for: Fe, Cr, and Ni alloys.

**Fe - TiB\(_2\) at 1300 °C.** [a]

Pure Fe wets TiB\(_2\) at 1300°C (\(\theta = 38°\)) with strong substrate dissolution, but (Ti,B)-saturated Fe : \(\theta = 26°\) (and no dissolution).

**Cr - TiB\(_2\):** contact melting occurred at 1600°C, (Cr\(_{\text{m.p.}}\) =1857 °C). [b]

At 1600°C, \(\theta \approx 75°\) gradually decreases to \(\theta \approx 45°\) and eventually solidifies.

At 1950 °C, \(\theta \approx 15°\).

**Cr - ZrB\(_2\):** the liquid phase formed at higher temperatures.

Contact angles went from \(\theta \approx 90°\) at 1800 °C to \(\theta \approx 45°\) at 1950°C.

...and **Ni - (Ti,Zr,Hf)B\(_2\)**

Wetting and interfacial phenomena in NiB/HfB$_2$ system

Wetting of HfB$_2$ by Ni-B alloys

Different spreading kinetics in the three cases...
Ceramic: HfB$_2$

Metal: pure Ni

Temperature = 1520°C

Final contact angle = 18°

Fast initial spreading but...

...strong dissolution of the ceramic substrate!!!

However,....

... increasing the Boron content we arrive at suppressing the substrate dissolution.
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Wetting results are interpreted using **Multi-component phase diagrams** in order to:

- **predict the interfacial behavior of metal/ceramic systems** (dissolution, reactivity...)
- **assist the formulation of new alloy compositions**
- **interpret the liquid/solid phenomena**
- **interpret wetting and microstructural results.**
For **Ni-based alloys** in contact with **transition metals diborides**, no ternary diagrams were available in full details.

An **extensive study** has been done in the last three years to derive these diagrams by means of the **CALPHAD methods** with a view towards assessing optimized routes for joining (brazing) procedures.

These computations \([a,b]\) allow the resulting ternary isothermal sections at temperatures up to the melting point of the diborides to be drawn, with all the binary phases, the ternary liquid as well as the ternary \(X_2\text{Ni}_{21}B_6\) "tau" solid phase (X=Ti,Zr,Hf).

In addition, all necessary isopleths of the equilibrium transformations of the couples Ni-alloy/diborides are also made available, **making it possible to interpret the solidification structures**.

Calculated ternary phase diagrams, isothermal sections at $T=1500^\circ$C

With reference to the isothermal section at $T=1500^\circ$C, it is apparent that when molten Ni is brought into contact with $XB_2$ an equilibrium condition is established between the solid $XB_2$ and Ni-based phases which, when the temperature is high enough, are in the liquid state.
This shows how and why additions of boron to the Ni matrix can limit the dissolution of the substrate.*

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Singh and Asthana (a-d) carried out extensive research on the joining of ZrB$_2$-based UHTCs.

Systems: ZrB$_2$-SiC (“pure”, fibers, particles) to metallic systems by Ag-Cu based or Pd-based filler alloys

Results:
- Ag-Cu based alloys (with Ti additions from 1.7at% to 4.4at%) showed good joints with nearly no interactions at the interface
- Pd alloys with 40at%Ni or 35at%Co:
  - Well-bonded, crack-free joints have been obtained using the Pd-Co alloy, while with the Pd-Ni alloy adhesion problems exist due to the weakness produced by the presence of extensive reaction layers at the joint interface caused by the formation of brittle Ni borides and carbides.

Pure ZrB$_2$ and ZrB$_2$+SiC specimens have been joined using Ni as the filler metal (e). Good final strength of the joint was found, at around 60 MPa. In pure ZrB$_2$ specimens, dissolution of the ceramic phase in molten Ni was found, followed by boride recrystallization during cooling; while in the SiC containing specimens, interdiffusion of Ni and Si caused the formation of transition layers and homogenization of the joint area: both these effects contributed to good joint performance.


Very recently, a report on the wetting behavior of molten Ni-Nb alloys that will form during the TLP bonding using Ni/Nb/Ni interlayer on a HfB$_2$ +MoSi$_2$ addition has been presented (Noritaka Saito et al., HTC- March 2012- Eilat, Israel).

Good results have been obtained also by our Group (f) joining HfB$_2$ to HfB$_2$ by using Ni-B alloys as shown in the following slides.

Joining tests by capillary infiltration

HfB₂/NiB₅₀/HfB₂ joint

Ni₅₀B at% - HfB₂

T = 1300 °C

Hold. Time: 10’

Ar/H₂ 10⁻⁵ Pa

1 Ni₄₀ B₅₀ Si₁₀ at%
2 Ni₅₀ B₅₀


$\text{ZrB}_2 (+\text{Si}_3\text{N}_4)$

have been brazed to

$\text{Ti6Al4V}$

at around 1000°C

using $\text{Ag}$ and $\text{Cu}$ alloys with $\text{Ti}$ or $\text{Zr}$. 
Wetting of TiAlV

Wetting of Ti6Al4V by Cu, 950°C → contact melting

Ti2Cu (dark) + TiCu (bright)

TiAlV(Cu)

TiAlV
Wetting of Ti6Al4V by Cu, 1050°C, contact melting

Higher °T → more Ti$_2$Cu
**ZrB₂ / AgTi / TiAlV**

**Microhardness, HV 0.01/12**

Interlayer: 1687 ± 7; Ag-rich phase 141 ± 6

Ti-rich phase: 214 ± 11; TiAlV: 402 ± 5

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Shear test

\[ \sigma = 78.5 \text{ MPa} \]

Rupture in the ceramic part

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Very good wetting of both the metal and the ceramic substrates leading to the complete filling of the joint gap.

Joint region with bi-phasic columnar structure, where an Ag-Zr (Ag-Ti) phase is coupled with an Ag-Ti interdiffusion zone.
Joining ZrB$_2$ / Cu / TiAlV

Pure Cu, 40 μm, T = 1050°C

Microhardness, HV 0.01/12
Interlayer: 1495 ± 20
TiAlV + Cu: 576 ± 14

Shear test
Rupture occurs in the intermetallic interlayer
Both AgTi and pure Cu ensure good adhesion and are promising for joining ZrB$_2$/SiC with Ti6Al4V.

Pure Cu in contact with Ti alloy forms a liquid phase even at temperatures below the MP of Cu. The liquid phase can, in turn, evolve to Ti-Cu intermetallic compounds or to Cu dissolved in Ti as a consequence of diffusion phenomena.

This process can lead to an isothermal solidification, i.e. TLPB.
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• The study of the interfacial phenomena between liquid alloys and early-transition-metal diborides ($\text{TiB}_2$, $\text{ZrB}_2$, $\text{HfB}_2$) should be addressed from both the experimental and theoretical points of view.

• At high temperature the contact angle values and the formation of the interfacial dissolution regions (sigmoidal profiles) are the results of the competition between the strong dissolution of the ceramic in the liquid phase and the fast drop spreading along the substrate surface.

• The presence of surface oxides on the UHTC substrates is the main responsible of their bad wetting by liquid alloys: oxide elimination can be achieved by proper low oxygen partial pressure and through active-metals additions.
• Phase diagrams are essential to show how to suppress the substrate dissolution and how to interpret the evolution of the system as \( f(T, X_{n_i}) \).

• Sessile-drop experiments can be used to assess critical points of newly-calculated phase diagrams: e.g. the formation of compounds, isothermal transitions and so on.

• This kind of studies are essential for the design of joining processes, for creation of composite materials, etc. and are of a particular relevance when applied to UHTC materials.
Prof. Gabriele Cacciamani (DCCI-Univ. of Genoa)- Phase Diagrams

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Thank you for your attention!!!
Wetting tests by the **sessile drop technique**

**Experimental apparatus at CNR/IENI**

**Tubular furnace (alumina tube as reaction chamber) + optical line + SW ASTRAvie**

It can work under HV or controlled atmospheres; PO\textsubscript{2} is constantly monitored by oxygen gauges.