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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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- Introduction- Wetting- Reactivity
- Models
- Wetting at lower temperatures
- Wetting at higher temperatures
- Phase diagrams
- Joining
- Conclusions

- **Introduction- Wetting- Reactivity**

- Models
- Wetting at lower temperatures
- Wetting at higher temperatures
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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 [**iono-covalent ceramic/pure metal**] couples as "**non-wetting systems**" (with a contact angle **θ>90°**). However, **transition metal diborides** have a **metallic-like** character, so that their **wettability by liquid metals** should be granted (i.e. **θ<90°**)

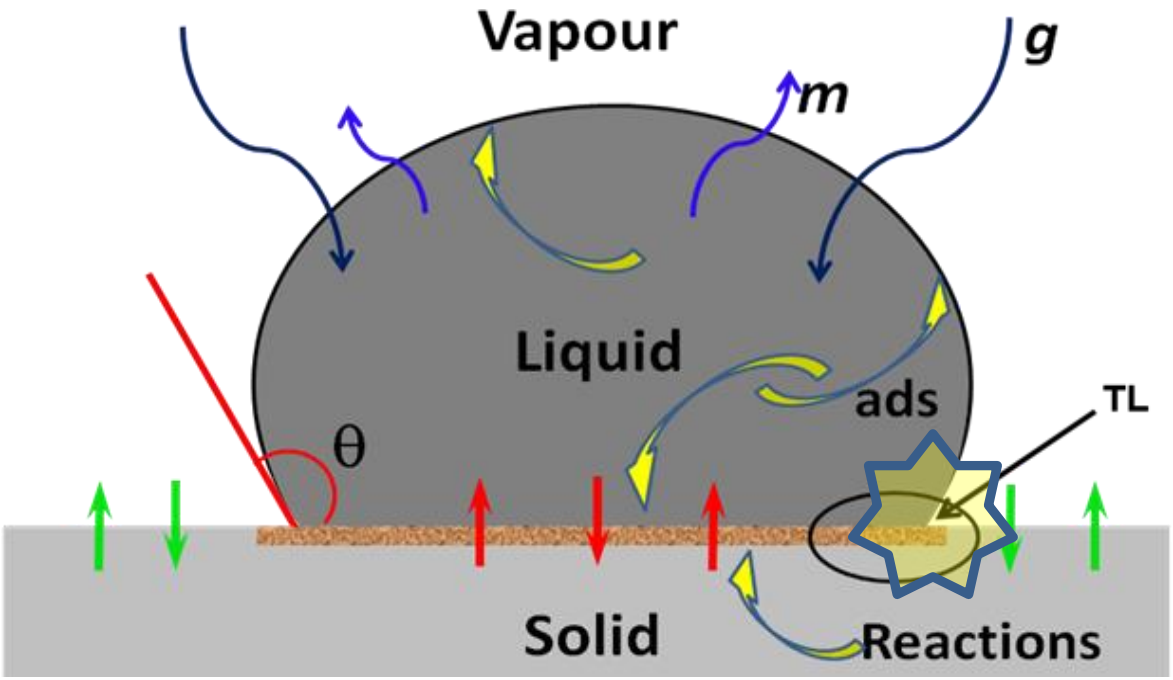
We must underline that wetting experiments with very refractory ceramics are performed using **sintered polycrystalline specimens**, so that **impurities** in these materials, their **surface roughness**, and frequently **ill defined** furnace atmospheres gave rise to a **wide scatter in contact angles**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

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

where σ_{lv} is the liquid-vapour surface tension.

* N. Eustathopoulos, N. Sobczak, A. Passerone and K. Nogi, *J. Mater. Sci*. 40, 2271-2280 (2005).

* N. Sobczak, M. Singh and R. Asthana, *Curr. Opin. Solid State Mater. Sci.* 9, 241 (2005).



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.

- Introduction- Wetting- Reactivity
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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.**

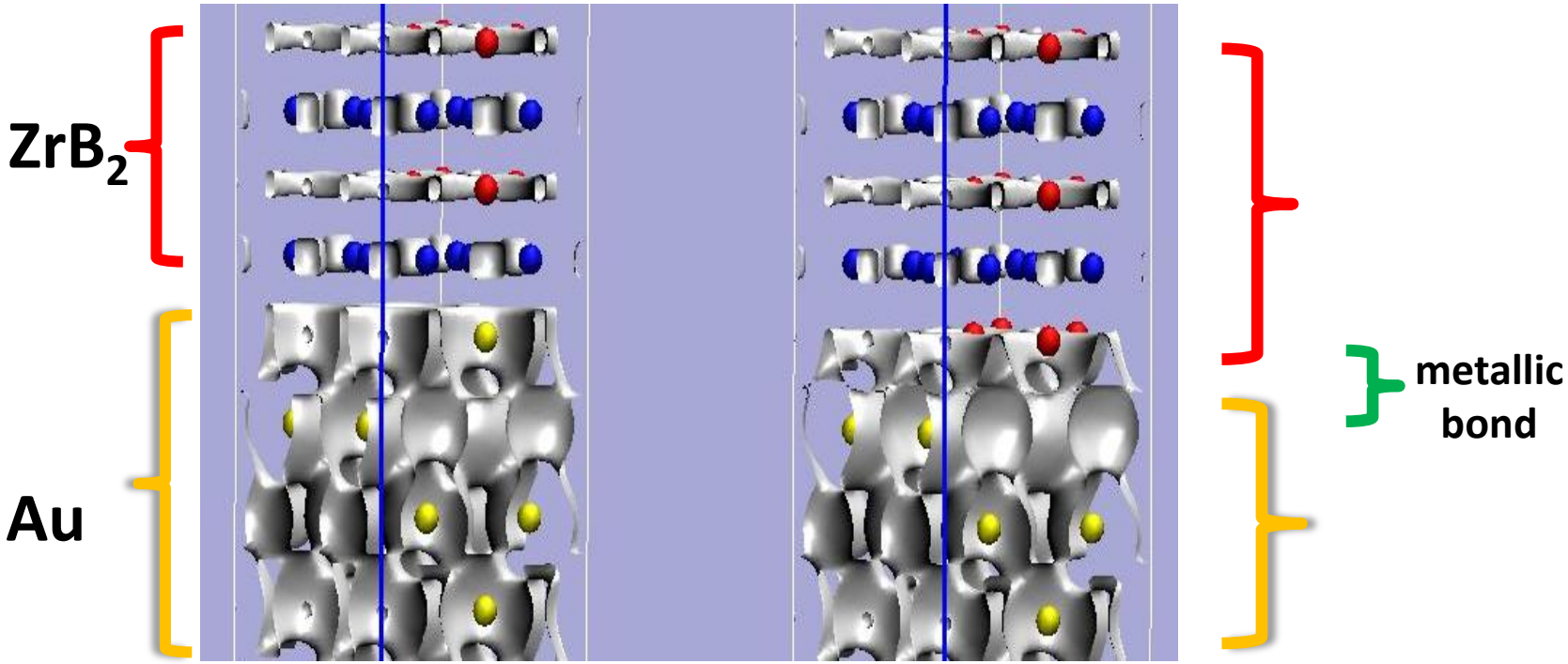
An efficient way to study these interactions and to quantify their effects in terms of adhesion energy is provided by modelling, through molecular dynamics approaches or by applying the Density Functional Theory (DFT).

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 :

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

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



Au-ZrB_2 : B terminated

Au-ZrB_2 :Zr terminated

Passerone A., Muolo M.L., Novakovic R., Passerone D. J. Eur. Ceram. Soc. (2007) 27: 3277

Interface	Bulk mismatch (%)	W_{sep} (J/m^2)	W_{ad} (J/m^2)
*Au/ZrB_2- Zr	10.3	3.725	≈ 2100

- Introduction- Wetting- Reactivity
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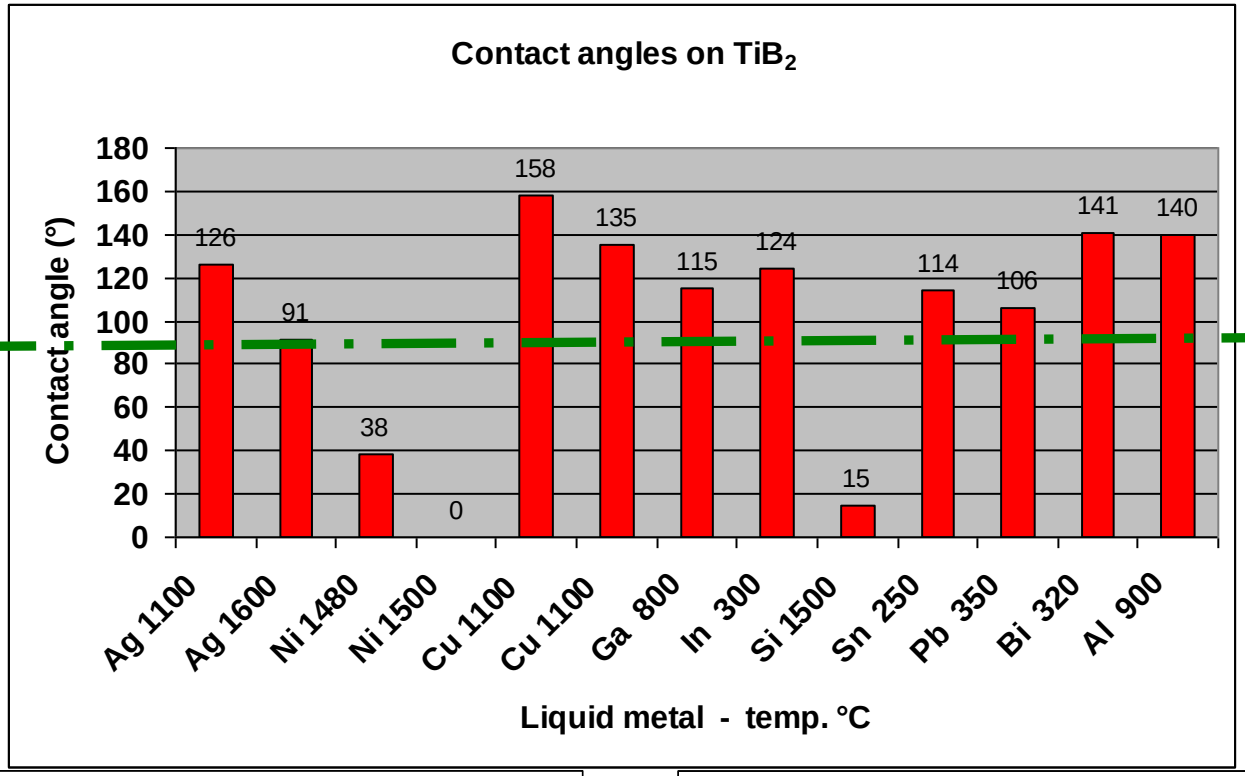
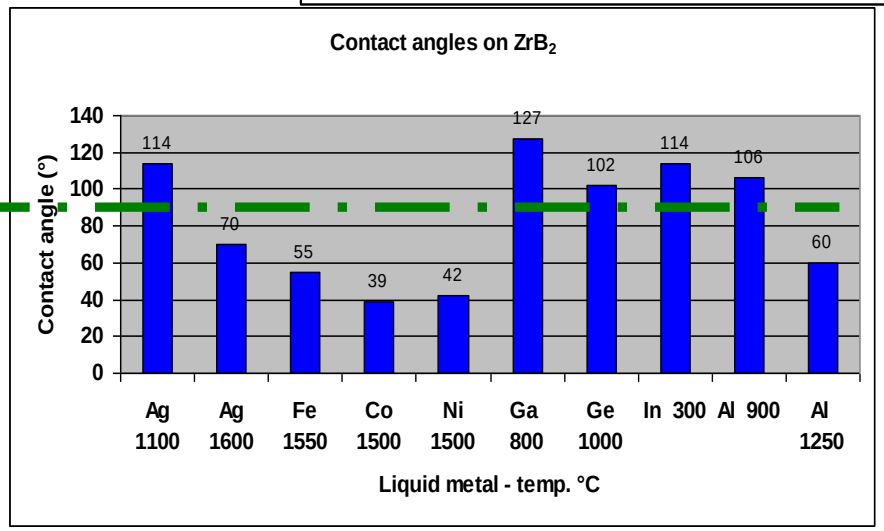
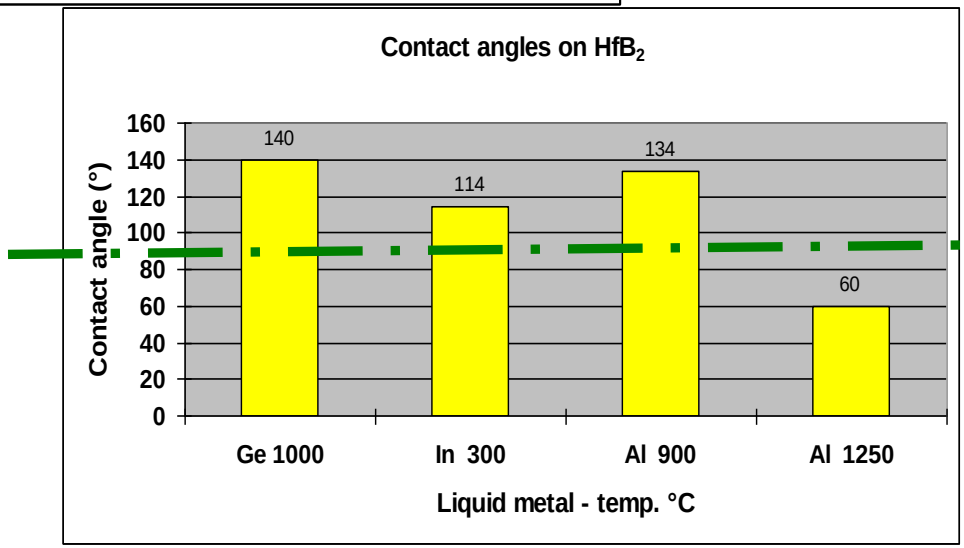
WETTING
at
900 °C < T < 1200 °C







Sansonov G.V., Panasyuk A.D. and Borovikova M.S., Poroshkovaya Metallurgiya 5 (1973) 61
Sansonov G.V., Panasyuk A.D. and Borovikova M.S., Poroshkovaya Metallurgiya 6 (1973) 51.
V. P. Ukov, O.A. Esin, N. A. Vatolin and E.L. Dubinin, in"Phys. Chem of Interf Phen. at High Temp." Naukova Dumka, Kiev, 1971, p.139

These results mean

that , when $\theta > 90°$,

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 **T**rans. **M**etal oxide could occur:

1.5 (TM)O_2(*s*) + 2B(*l*) = B_2O_3(*g*) + 1.5 (TM) (*l*)

2) B_2O_3 removal

B can react with B_2O_3 at the surface, forming volatile $(BO)_n$ boron oxides [**c**]:

$2B + 2B_2O_3 = 3(B_2O_2)$

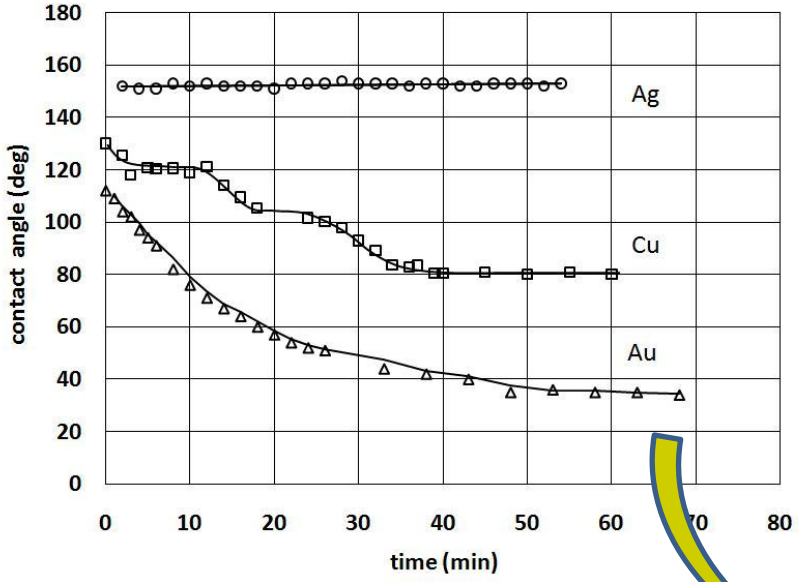
The corresponding vapour pressure of the gaseous dimer $(BO)_2$ [c] extrapolated to T= 1500 °C , is $P_{(BO)2} \approx 6\ 10^{-3}$ atm .

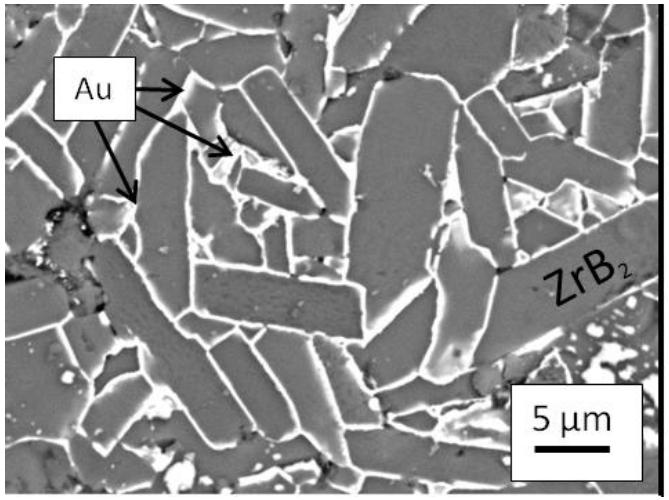
3) Boride stoichiometry variation

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.

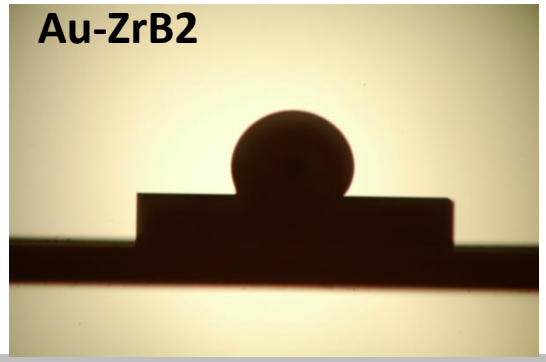
a) Aizenshtein M, Froumin N, Frage N (2012) J Mater Eng Perform 21:655-659
b) Kaufman L, Cacciamani G, Muolo ML, Valenza F, Passerone A (2010) CALPHAD 34:2-5
c) Scheer M (1958) J Phys Chem 62:490-493

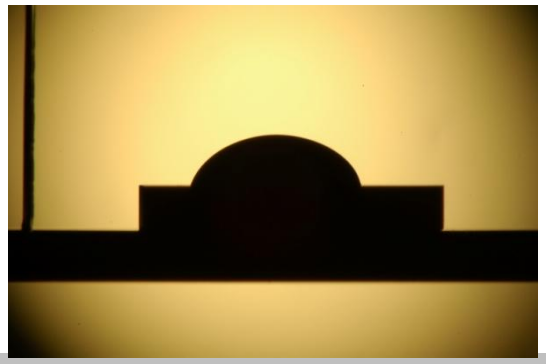
ZrB_2 (+B_4C)

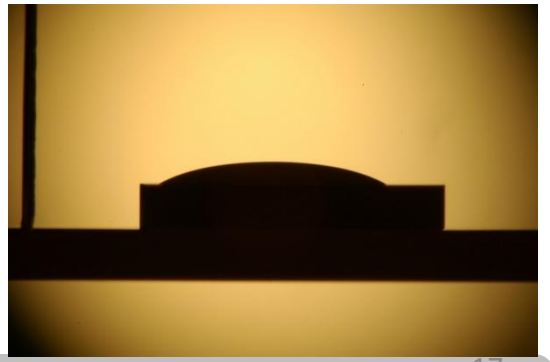




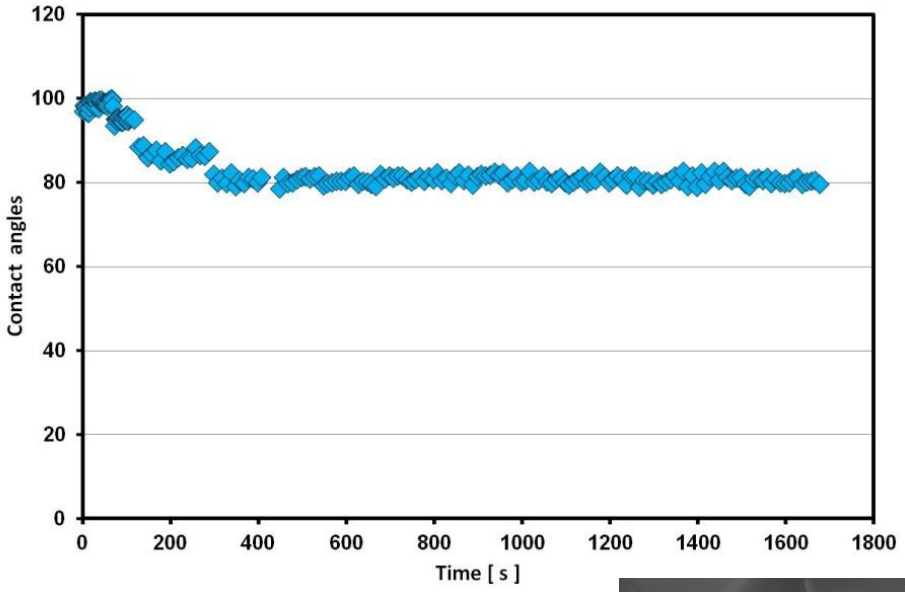
Kinetics of wetting of Ag, Au and Cu on ZrB_2 at T=1.05 T_m [K], Ar-5%H_2



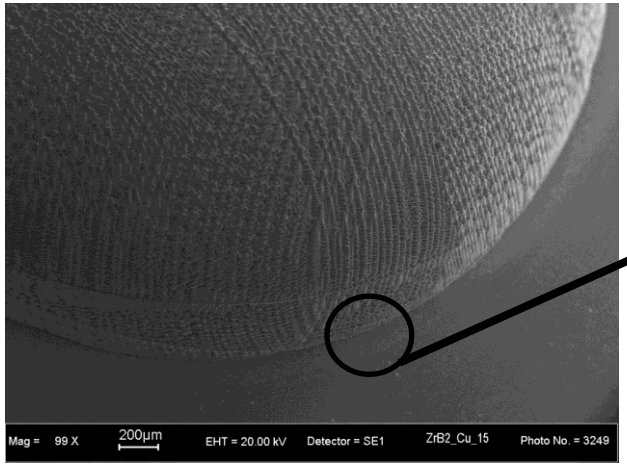




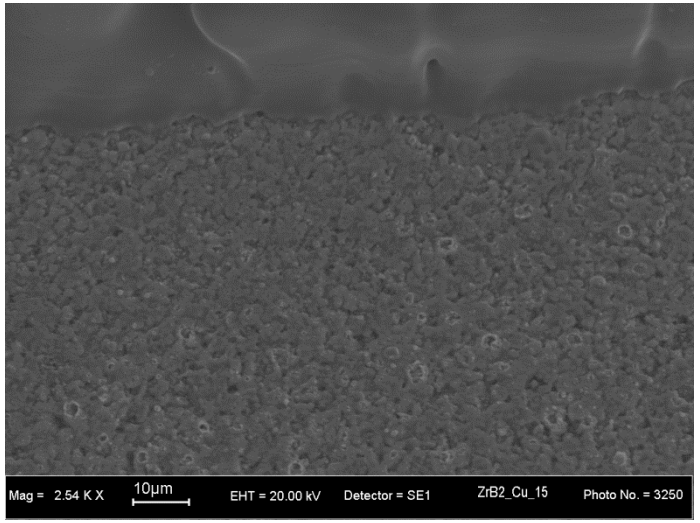
Wetting by Cu, 1150°C; **θ = 80°**

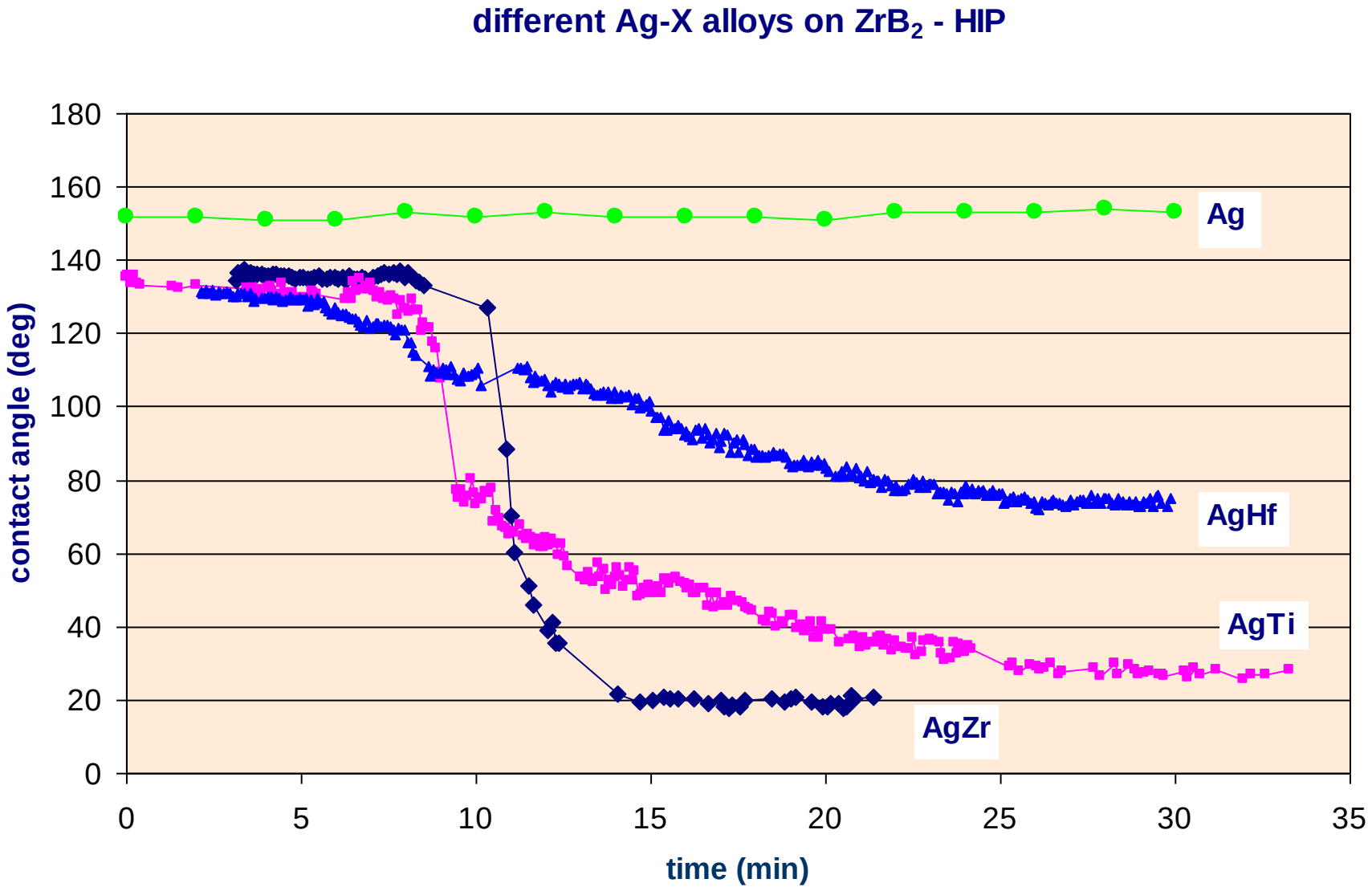


Top view of the drop



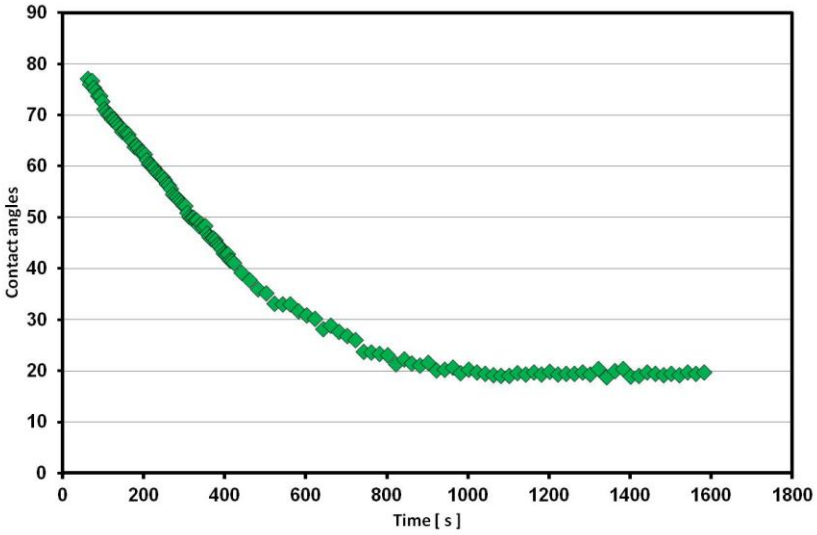
No interlayers

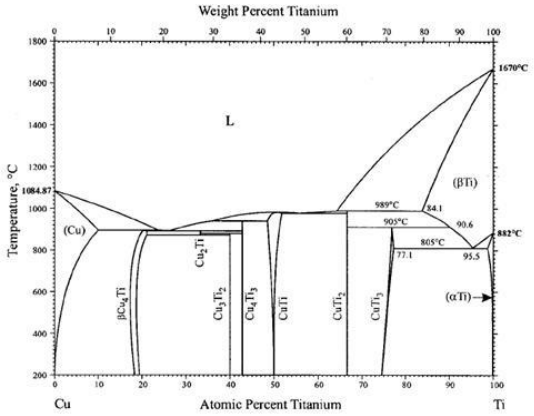



different Ag-X alloys on ZrB_2 - HIP
contact angle (deg)
time (min)
0
20
40
60
80
100
120
140
160
180
0
5
10
15
20
25
30
35
Ag
AgHf
AgTi
AgZr

Active metal additions (ZrB_2/SiC)

Wetting by CuTi (Ti: 22 at.%, eutectic), T = 950°C, **θ = 19°**



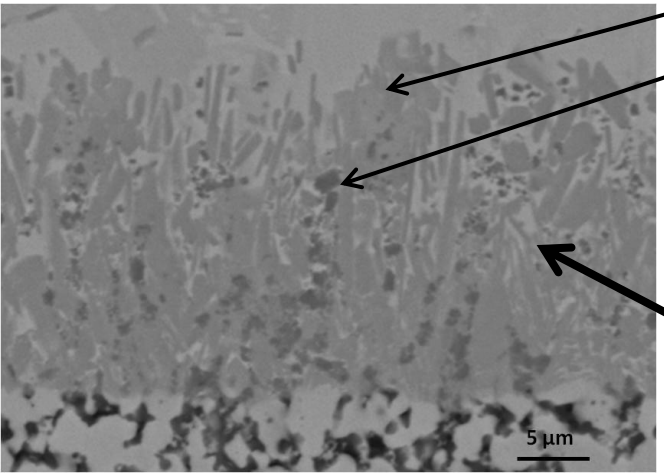


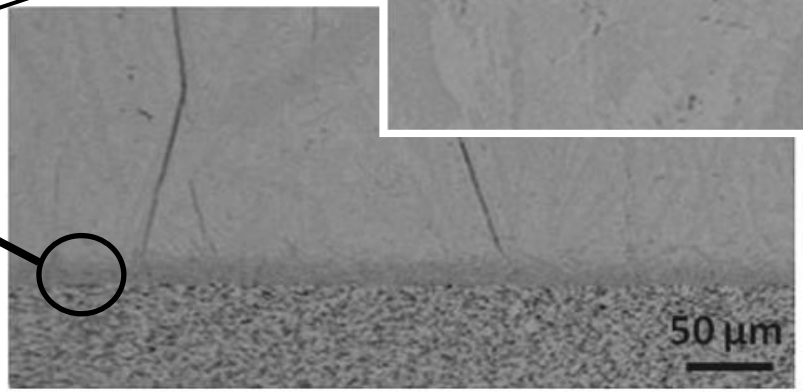
Ti-rich interlayer:

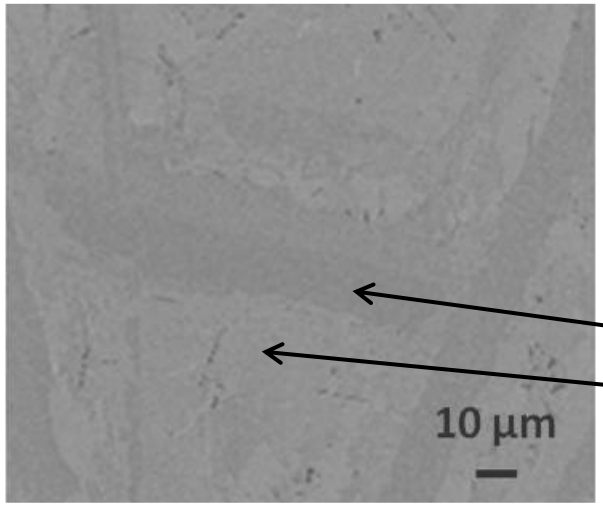
- TiCu (+Si)
- Ti_3Cu (+Si)

Bulk:

- Ti_2Cu_3
- $TiCu_2$







WETTING
at
1300°C < T < 1550 °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 (**θ= 38°)** with strong **substrate dissolution**, **but**
(Ti,B)-saturated Fe : θ= 26° (and no dissolution).

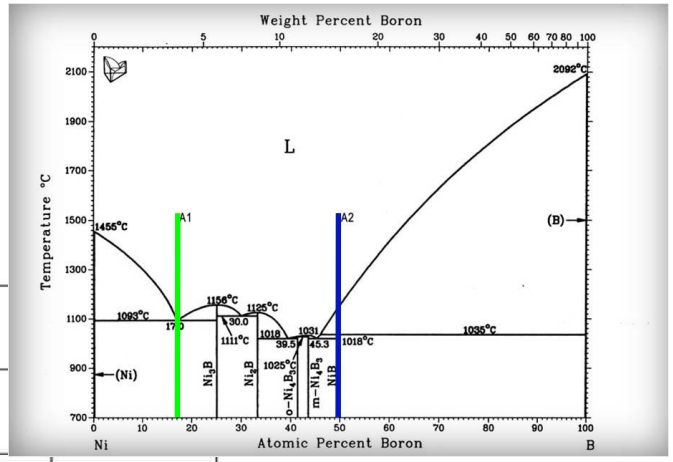
Cr -TiB_2: contact melting occurred at 1600°C, ($Cr_{m.p.}$=1857 °C). [b]
At **1600°C,** **θ≈75°** gradually decreases to **θ≈45°** and **eventually solidifies**.
At **1950 °C, θ≈15°.**

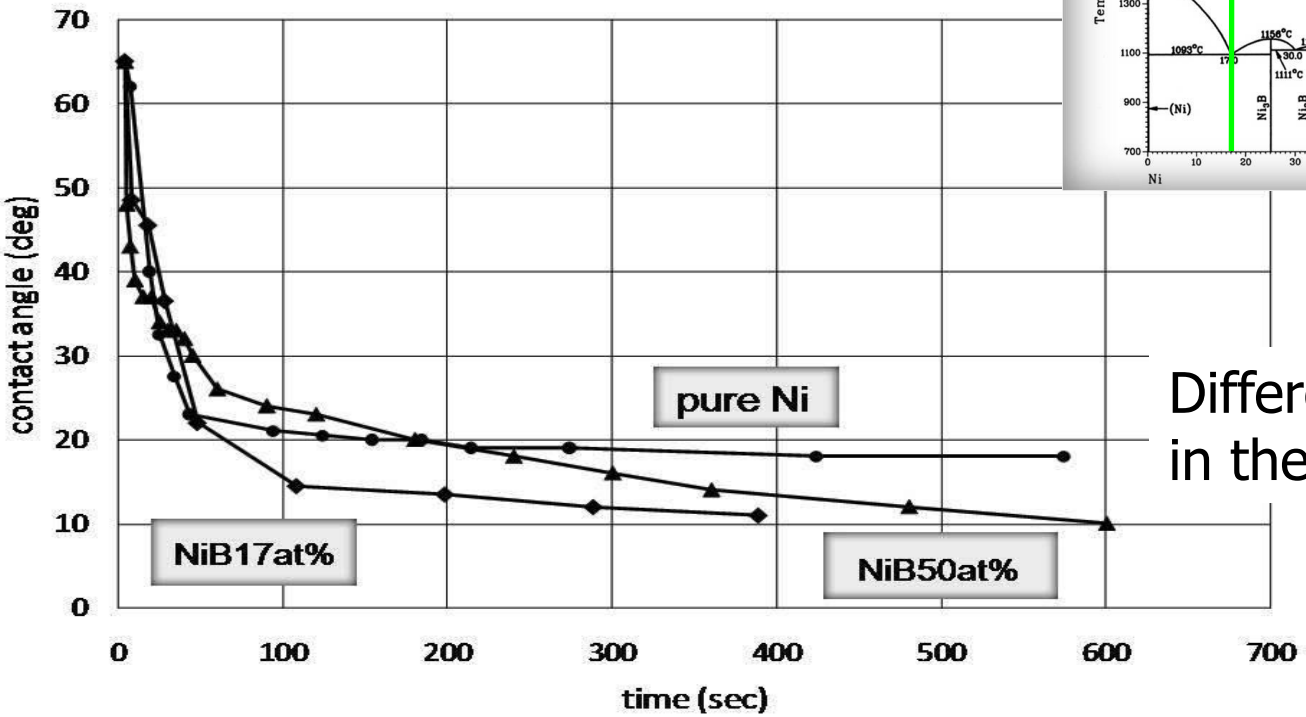
Cr - ZrB_2 : the liquid phase formed at higher temperatures.
Contact angles went from **θ≈90° at 1800 °C** to **θ≈45° at 1950°C**.

…and **Ni - $(Ti,Zr,Hf)B_2$**

[a] V. Ghetta, N. Gayraud and N. Eustathopoulos, *Solid State Phenomena* 25, 105-114 (1992).
[b] G.L. Zhunkovkii., T.M. Evtushok, O.N. Grigor'ev, V.A. Kotenko and P.V. Mazur, *Powder Metall. Metal Ceram.* 50, 212-216 (2011).

Wetting of HfB_2 by Ni-B alloys



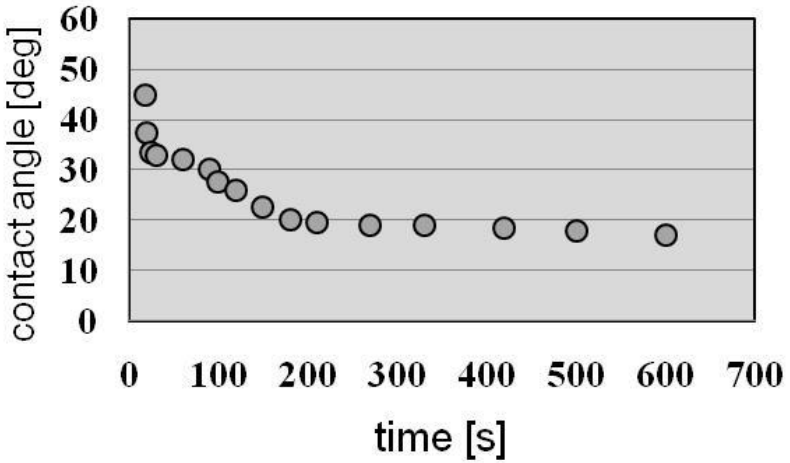


Different spreading kinetics in the three cases...

Ceramic: HfB_2

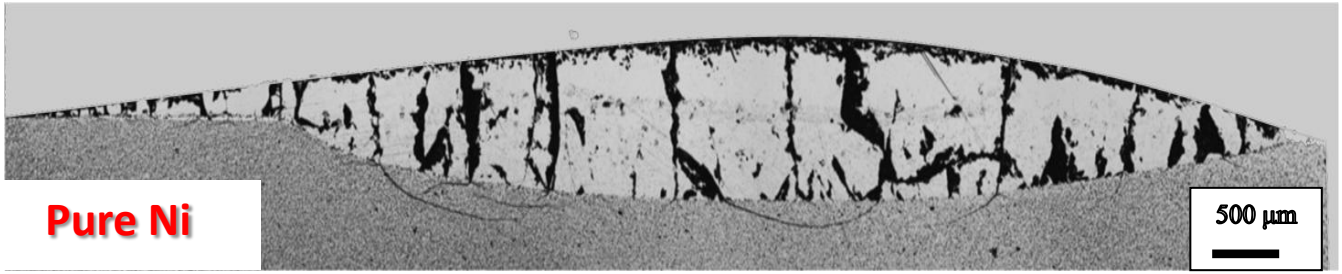
Metal: pure Ni

Temperature = 1520°C



Final contact angle = 18°

Fast initial spreading but…

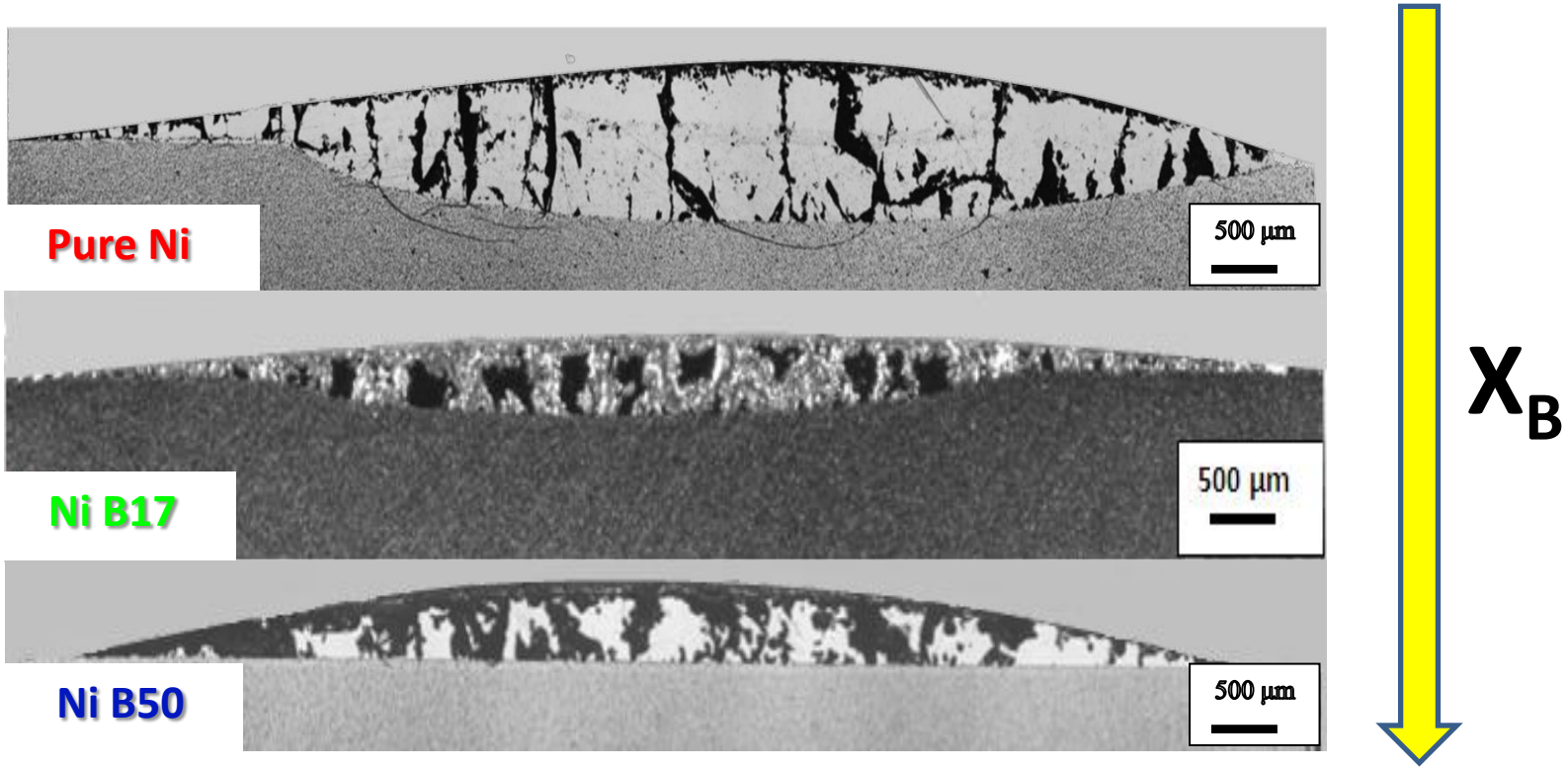


…strong dissolution of the ceramic substrate!!!

However,….

Passerone A, Muolo ML, Valenza F, Monteverde F, Sobczak N (2009) Acta Mater 57:356

… **increasing the Boron content** we arrive at suppressing the substrate dissolution



WHY?

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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.

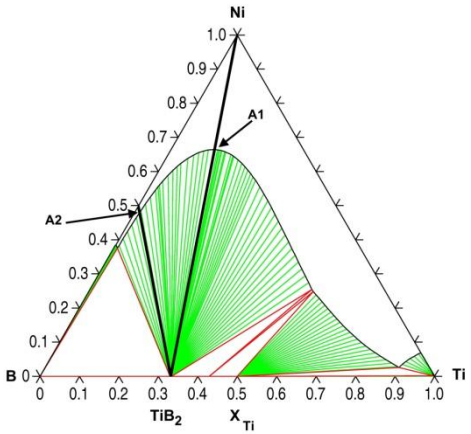
➢These computations [**a,b**] allow the resulting ternary isothermal sections at temperatures up to the melting point of the diborides to be drawn, with all the binary phases, the ternary liquid as well as the ternary $X_2Ni_{21}B_6$ ''tau'' solid phase (X=Ti,Zr,Hf).

➢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.**

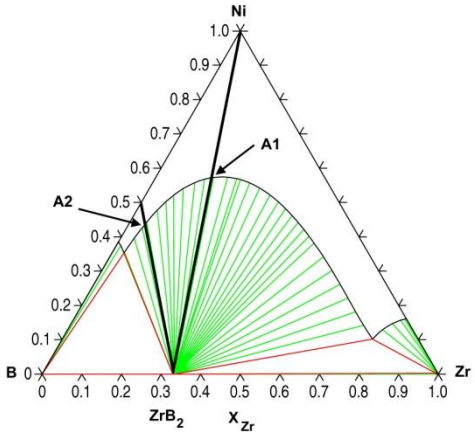
a) L. Kaufman, G. Cacciamani, M.L. Muolo, F. Valenza and A. Passerone, *CALPHAD* 34, 2-5 (2010).

b) G. Cacciamani, P. Riani and F. Valenza, *CALPHAD*, 35, 601-619 (2011).

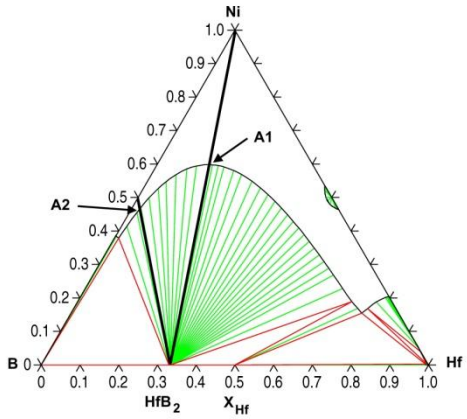
Calculated ternary phase diagrams, isothermal sections at T= 1500°C



Ti-Ni-B



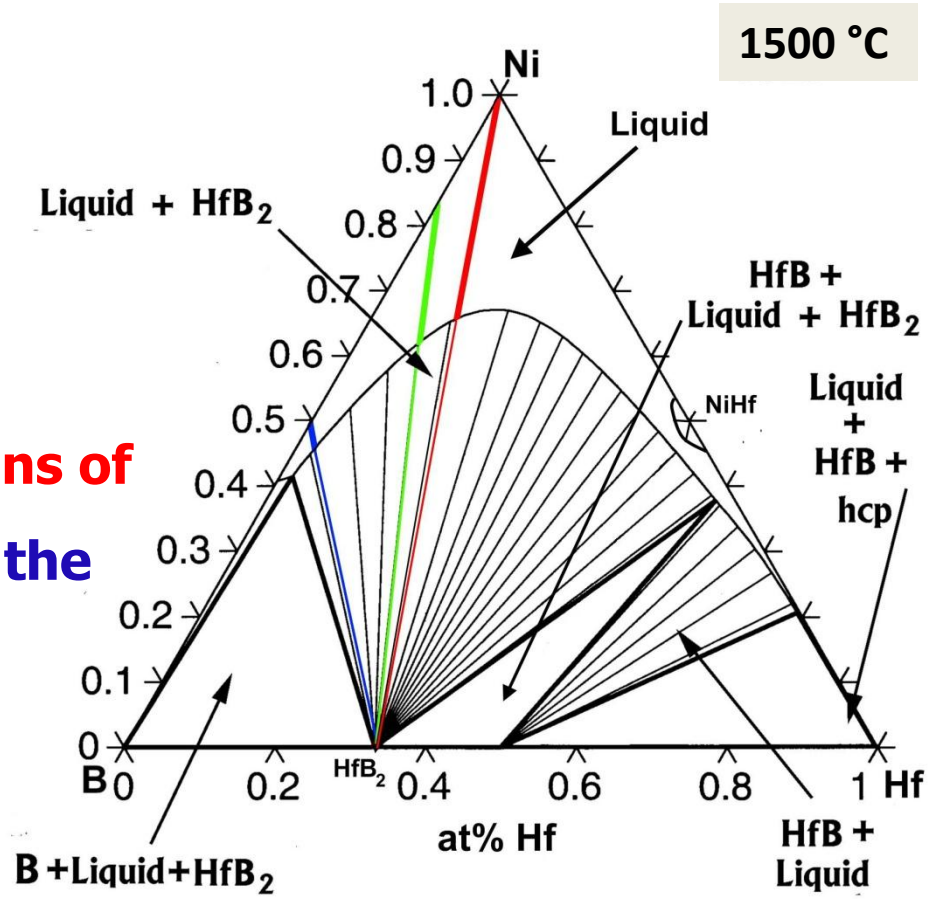
Zr-Ni-B



Hf-Ni-B

With reference to the isothermal section at T=1500°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*



*Passerone A, Muolo ML, Valenza F, Kaufmann L (2010) CALPHAD, 34:6
Kaufman L, Cacciamani G, Muolo ML, Valenza F, Passerone A (2010) CALPHAD, 34:2

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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.

a) Singh M, Asthana R (2007) Mater Sci Eng A 460-461:153-162
b) Singh M, Asthana R (2009) Int J Appl Ceram Technol 6:113-133
c) Asthana R, Singh M (2009) Scripta Mater 61:257-260
d) Singh M, Asthana R (2010) J Mater Sci 45:4308-4320

➢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**.

e) Yuan B, Zhang GJ (2011) Scripta Mater 64:17-20

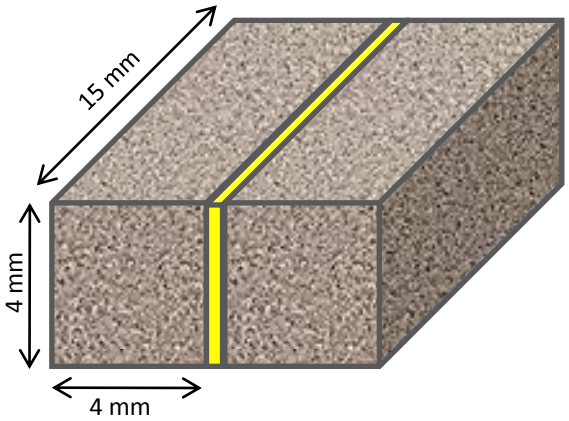
➢***Very recently***, a report on the wetting behavior of molten **Ni-Nb alloys** that will form during the TLP bonding using Ni/Nb/Ni interlayer on a **HfB_2 +$MoSi_2$** addition has been presented (Noritaka Saito et al.,HTC- March 2012- Eilat, Israel).

➢**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.

f) Muolo ML, Valenza F, Sobczak N, Passerone A (2010) Adv Sci Technol 6:98-107

Joining tests by capillary infiltration

HfB_2/NiB50/HfB_2 joint

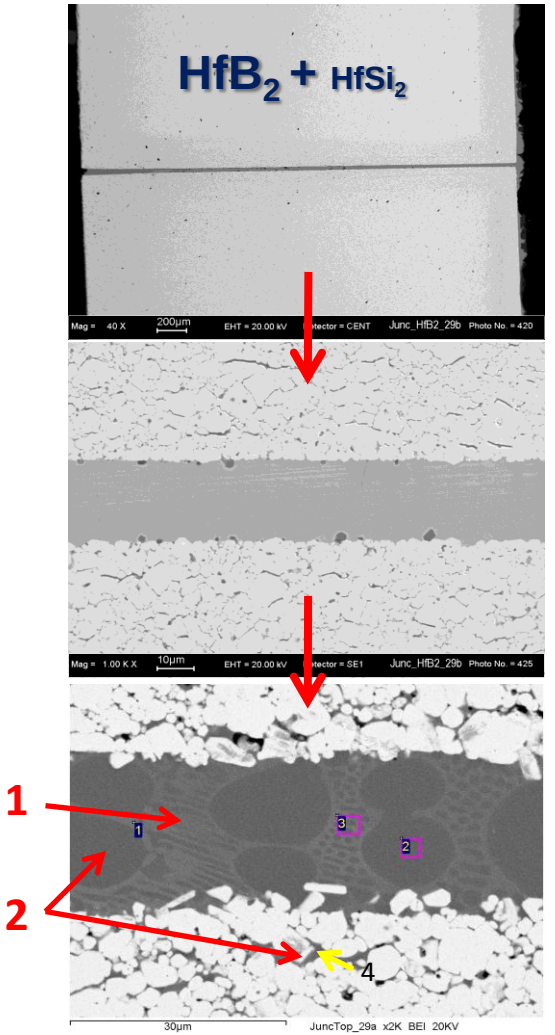


Ni50B at% - HfB_2

T= 1300 °C

Hold. Time: 10'

Ar/H_2 10^{+5} Pa



1 Ni40 B50 Si10 at%
2 Ni50 B50

Muolo M.L., Valenza F., Sobczak N., Passerone A., Advances in Science and Technology, Vol. 64 (2010) pp. 98-107

ZrB_2 ($+Si_3N_4$)

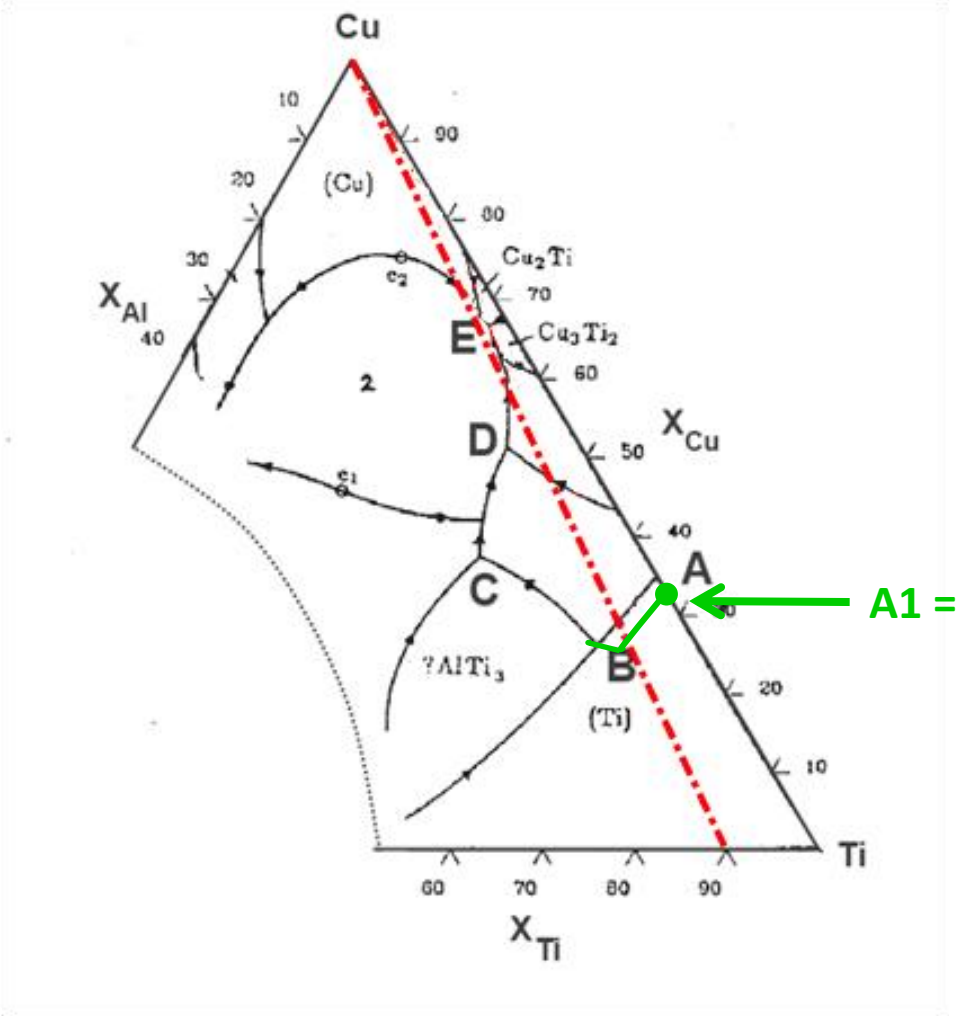
have been brazed to

Ti6Al4V

at around 1000°C

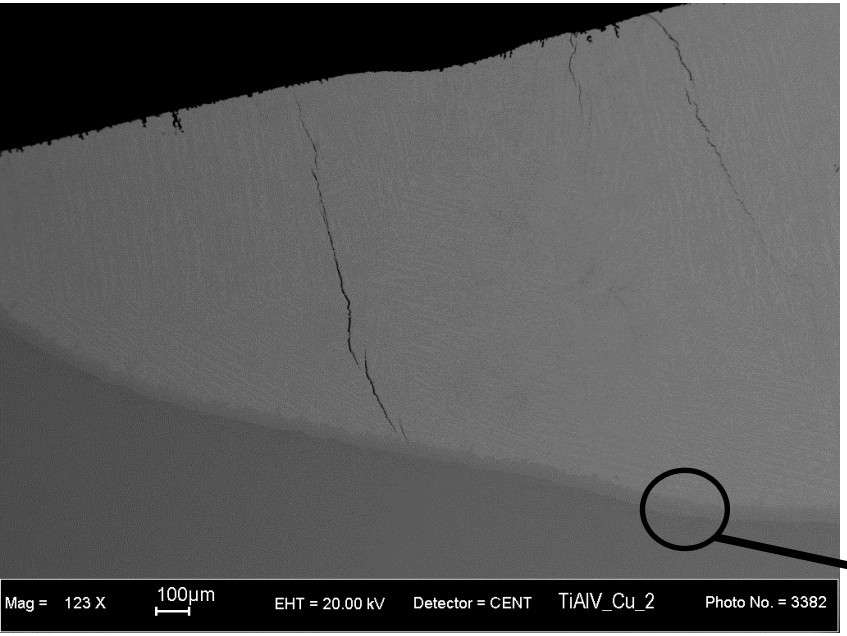
using Ag and Cu alloys with Ti or Zr.

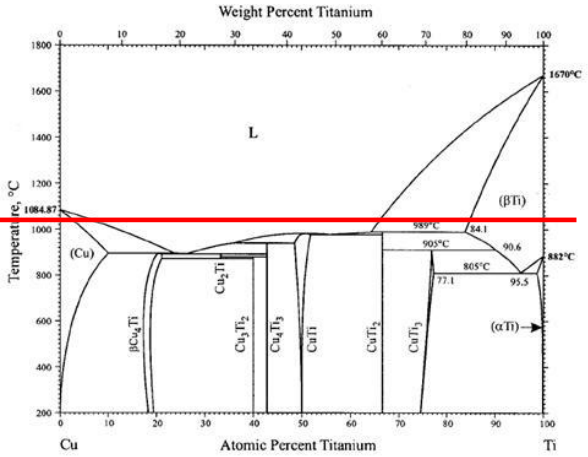
A T= 989 °C
B T= 980 °C
C T= 970 °C
D T= 940 °C
E T= 910 °C

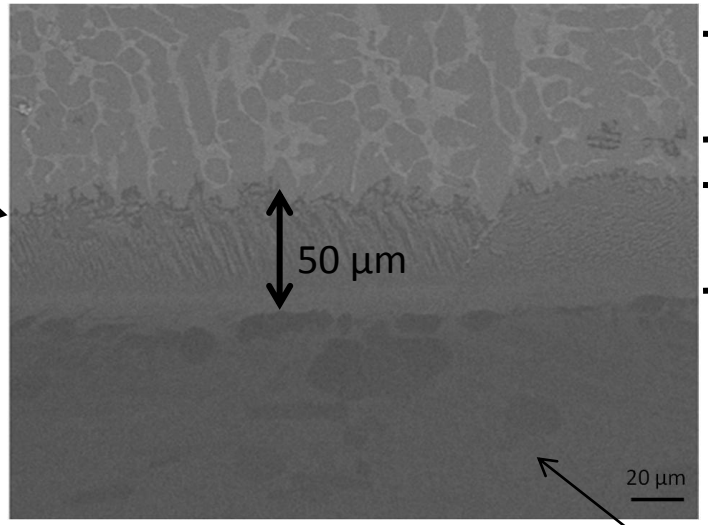


Adapted from: Shiue RK, Wu SK, Chen SY (2003) Acta Mater 51:1991-2004

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





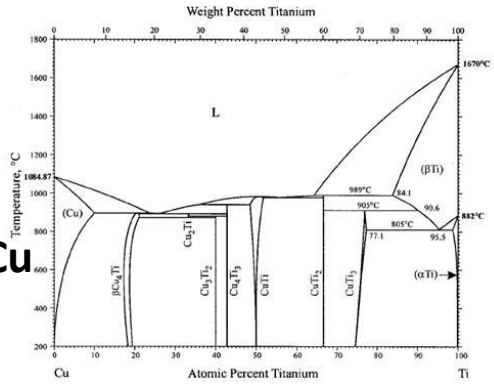


Ti_2Cu (dark) +
TiCu (bright)

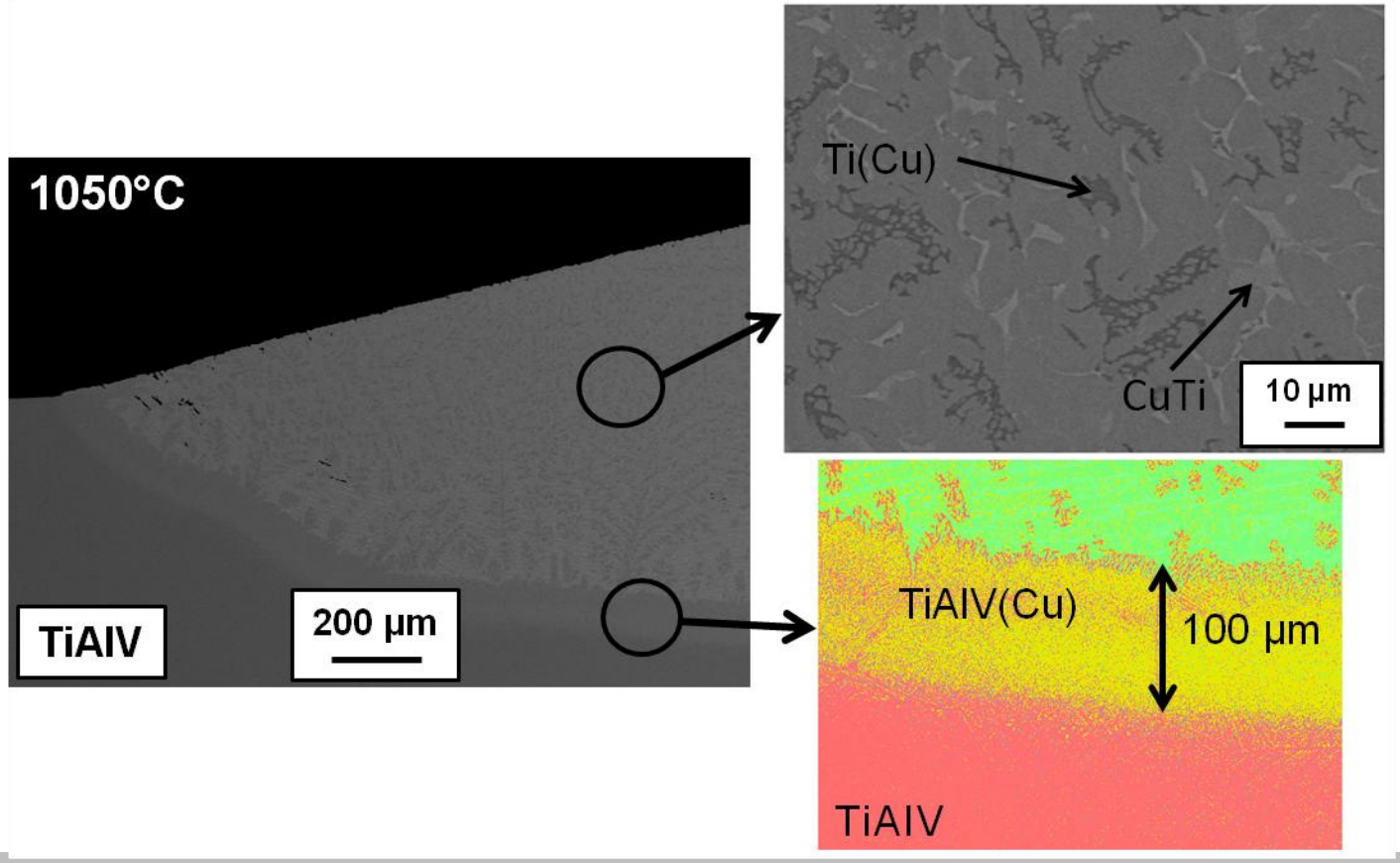
TiAlV(Cu)

TiAlV

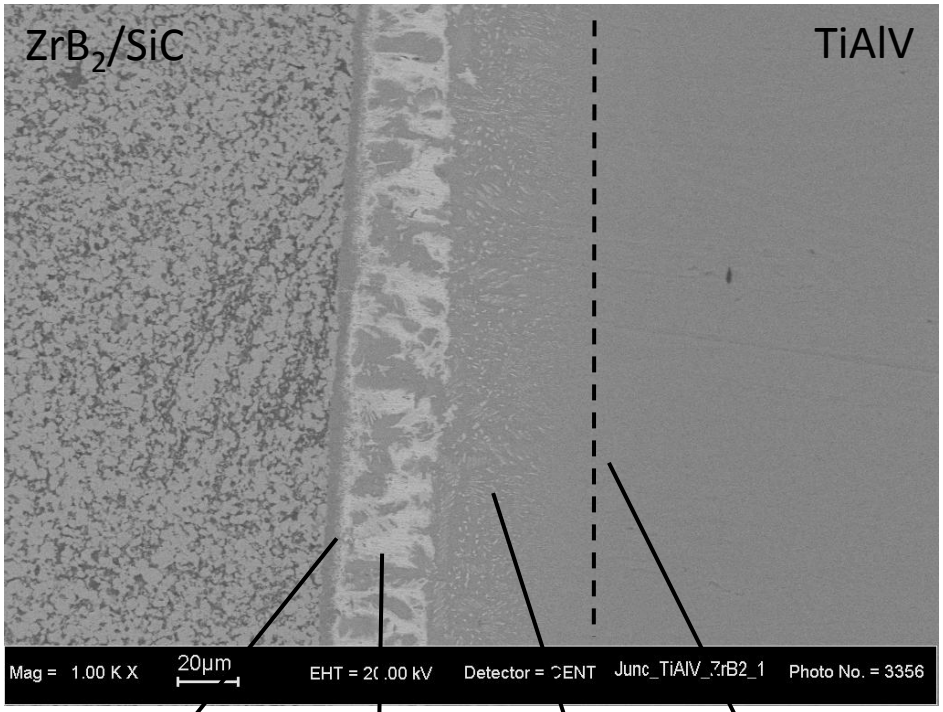
Wetting of **Ti6Al4V by Cu**, **1050°C**, contact melting



Higher °T → more Ti_2Cu



AgTi filler alloy, 60 µm, T = 1050°C



Ti (+Si) interlayer

Ag almost pure (bright)

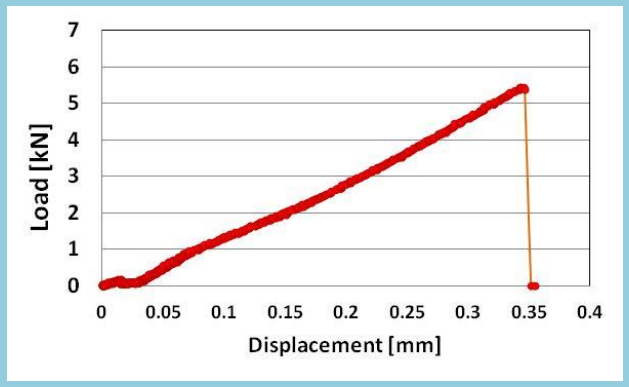
TiAlV + Ag

Ag limit

Microhardness, HV 0.01/12

Interlayer: 1687 ± 7; Ag-rich phase 141 ± 6
Ti –rich phase: 214 ± 11; TiAlV: 402 ± 5

Shear test



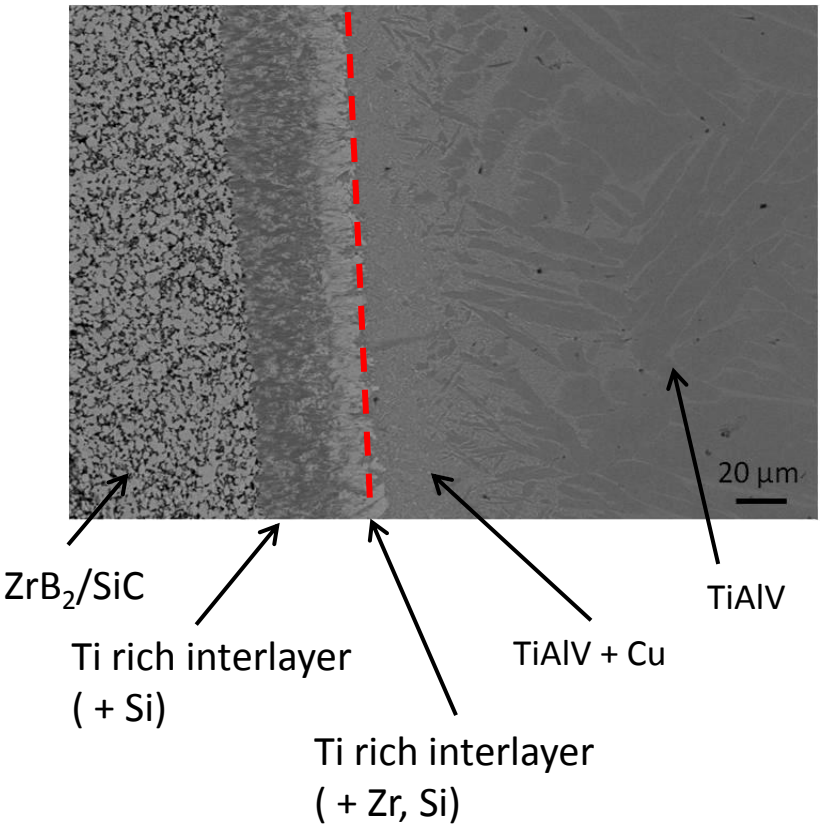
σ = 78.5 MPa

Rupture in the ceramic part

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.

Pure Cu, 40 µm, T = 1050°C

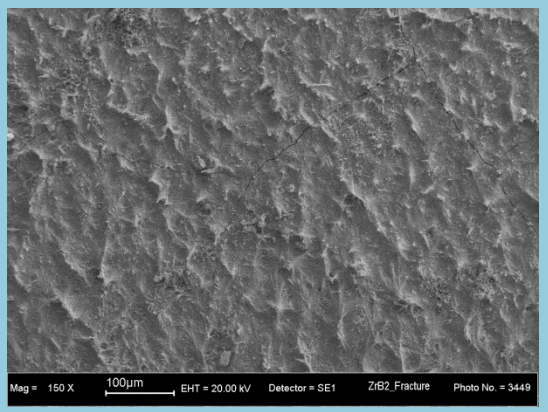


Microhardness, HV 0.01/12

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.

- Introduction- Wetting- Reactivity
- Models
- Wetting at lower temperatures
- Wetting at higher temperatures
- Phase diagrams
- Joining
- **Conclusions**

- The study of the interfacial phenomena between liquid alloys and early-transition-metal diborides (TiB_2, ZrB_2, 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, Xn_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

ISTEC-CNR (Faenza-I) for supplying part of the ceramic materials

Dr. G. Battilana for assistance in SEM/EDS analysis

Mr. F. Mocellin for technical support

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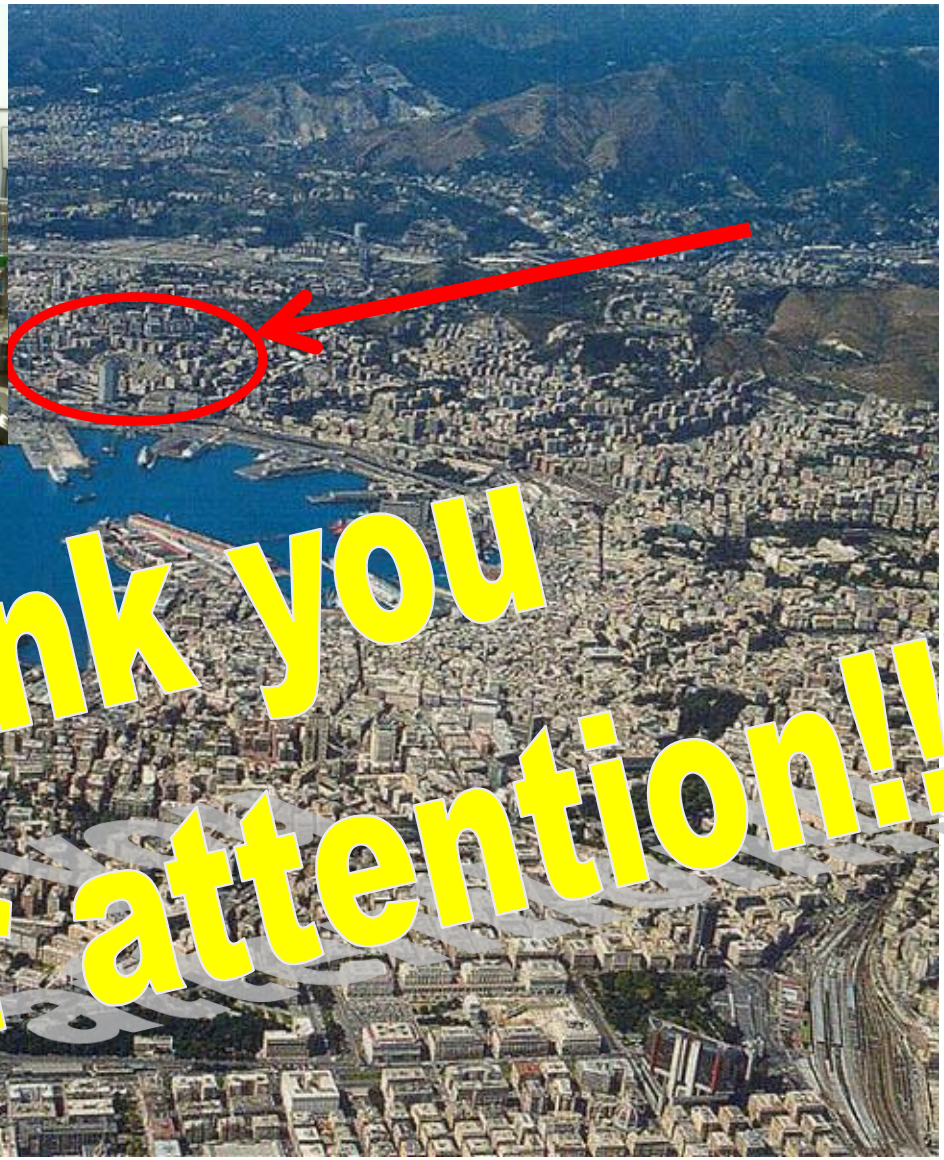
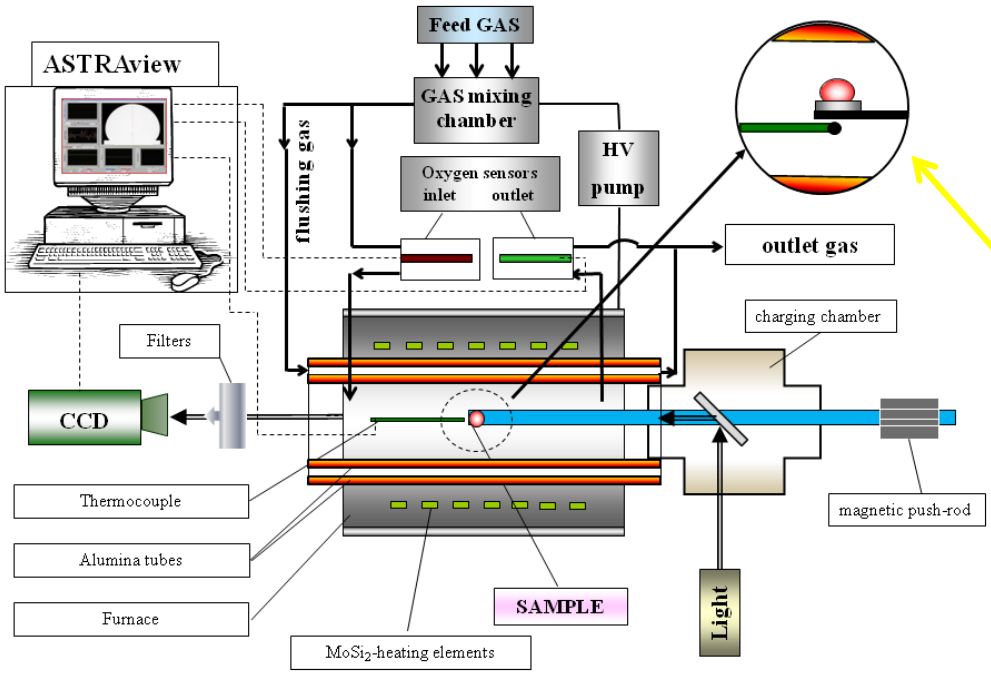
"**Innovative metal-ceramic joints for high and ultra-high temperature applications**".

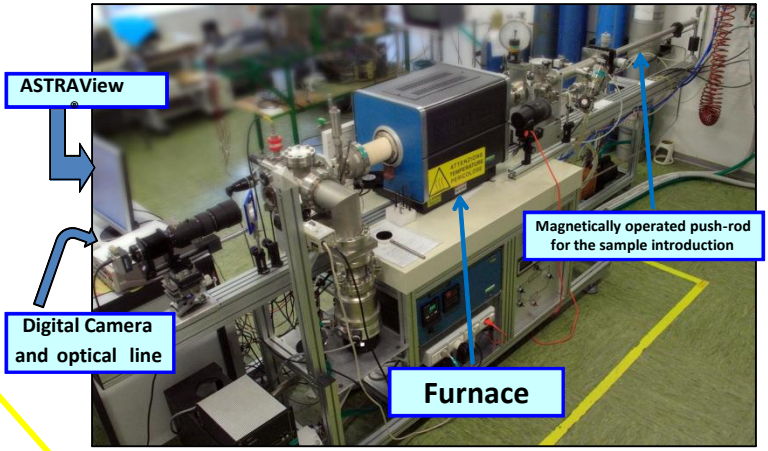


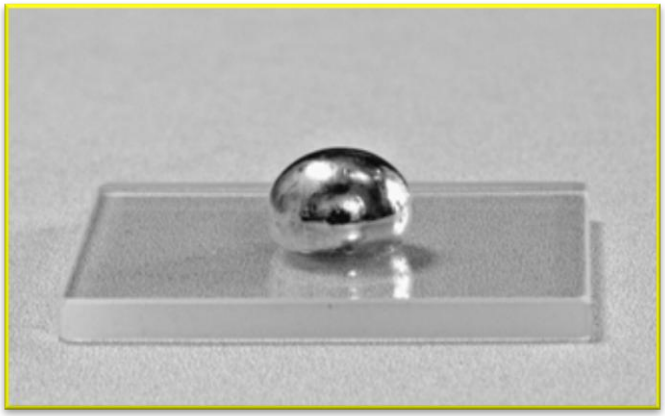
Thank you for your attention!!!

Wetting tests by the **sessile drop technique**

Experimental apparatus at CNR/IENI







Tubular furnace (alumina tube as reaction chamber) + optical line + SW ASTRAview®

It can work under HV or controlled atmospheres; PO_2 is constantly monitored by oxygen gauges.