TA-NI- AND TI-AL-BRAZE-ALLOYS FOR HIGH TEMPERATURE STABLE CERAMIC – CERAMIC JUNCTIONS

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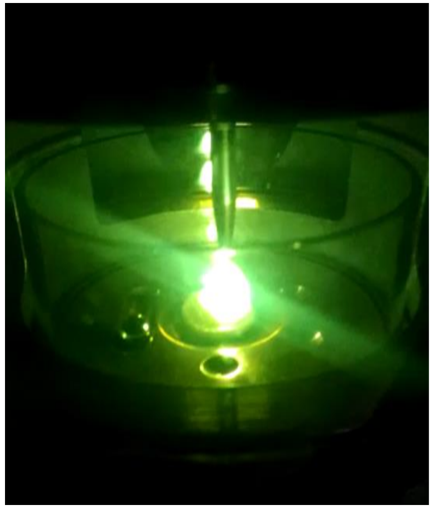

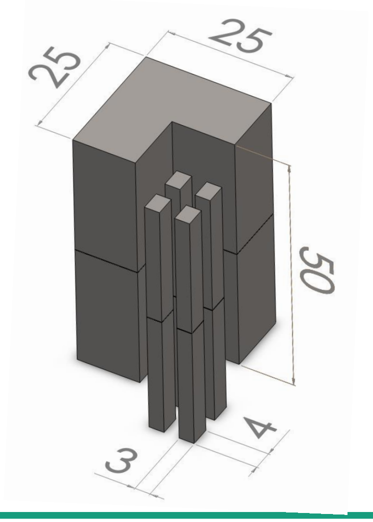

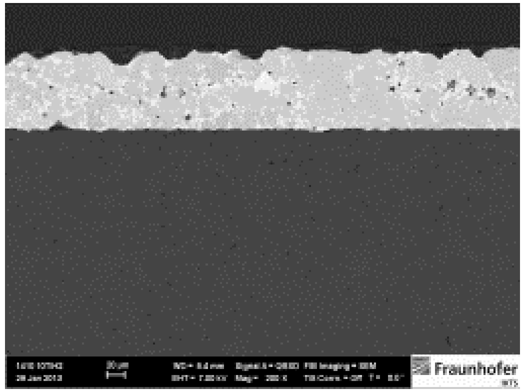

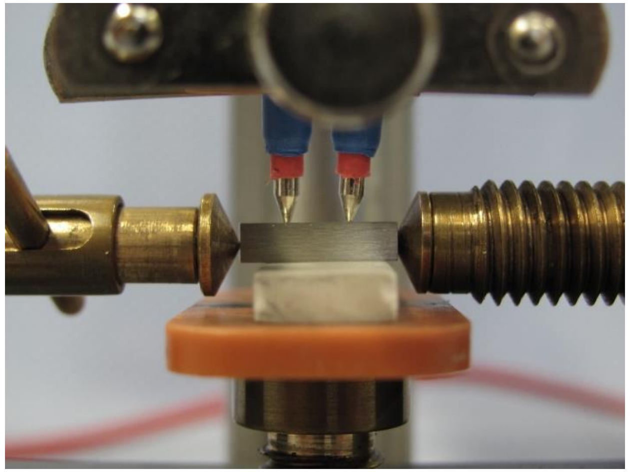

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- Tai-Al-braze-alloys
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  - Brazing Al_2O_3, SiC, Si_3N_4, ZrO_2
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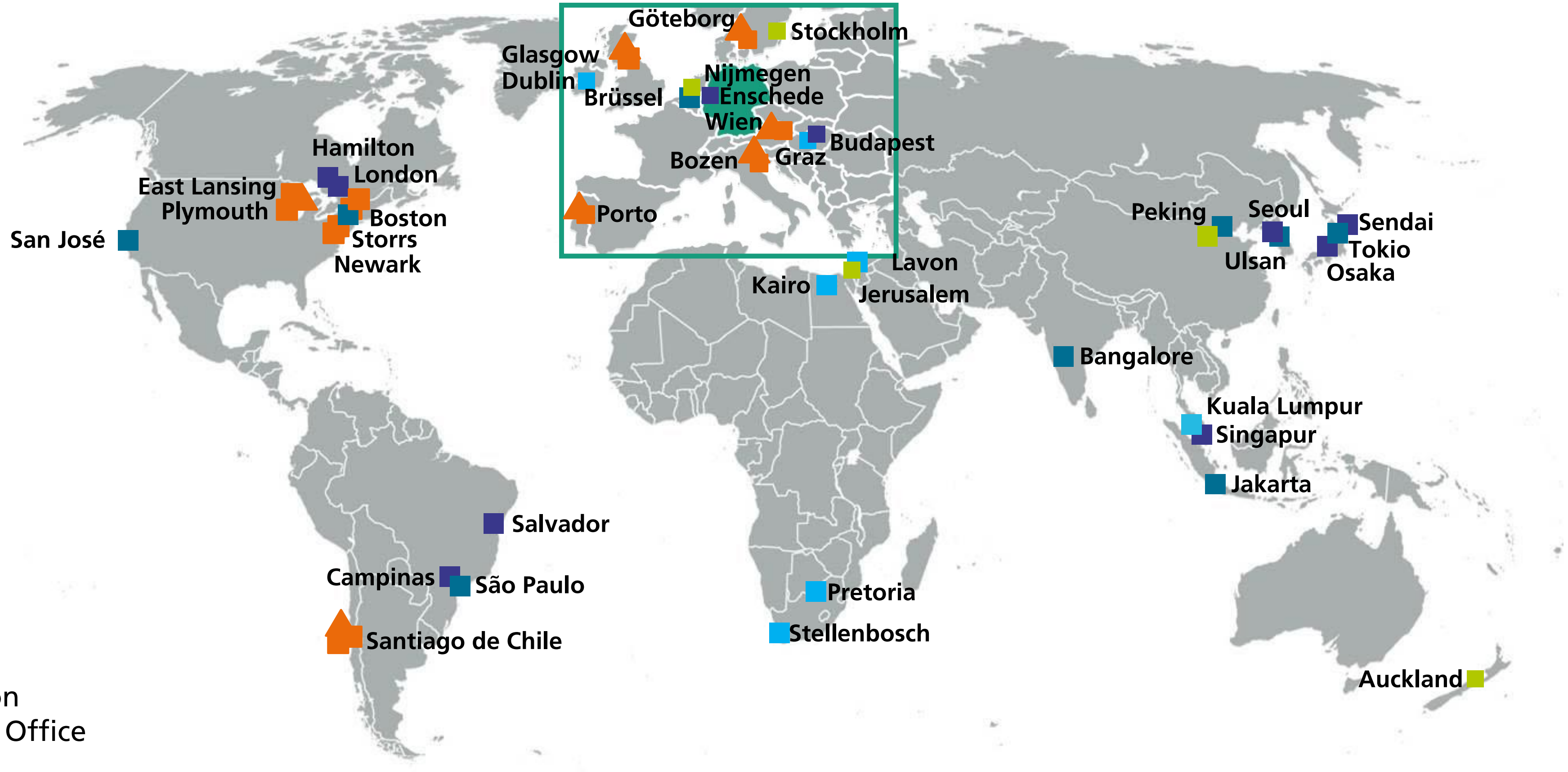
Fraunhofer worldwide



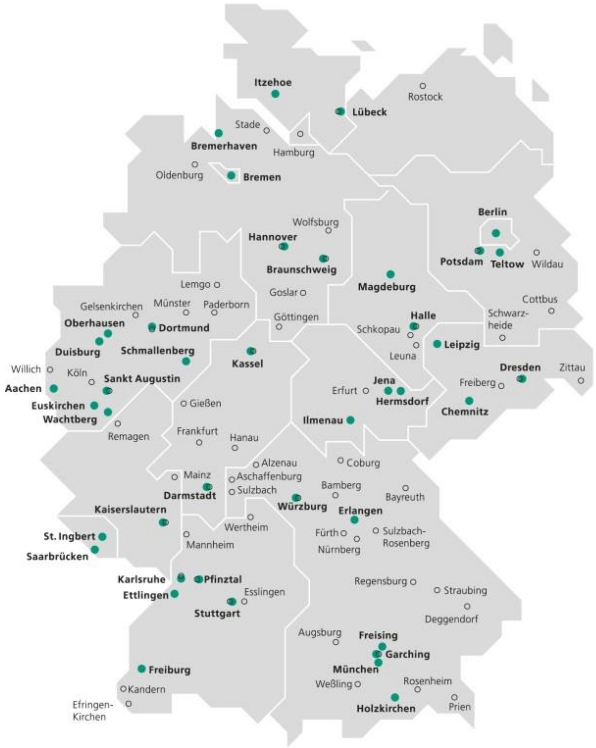
- ▲ Subsidiary
- ■ Center
- ■ Project Center
- ■ ICON / Strategic Cooperation
- ■ Representative / Marketing Office
- ■ Senior Advisor

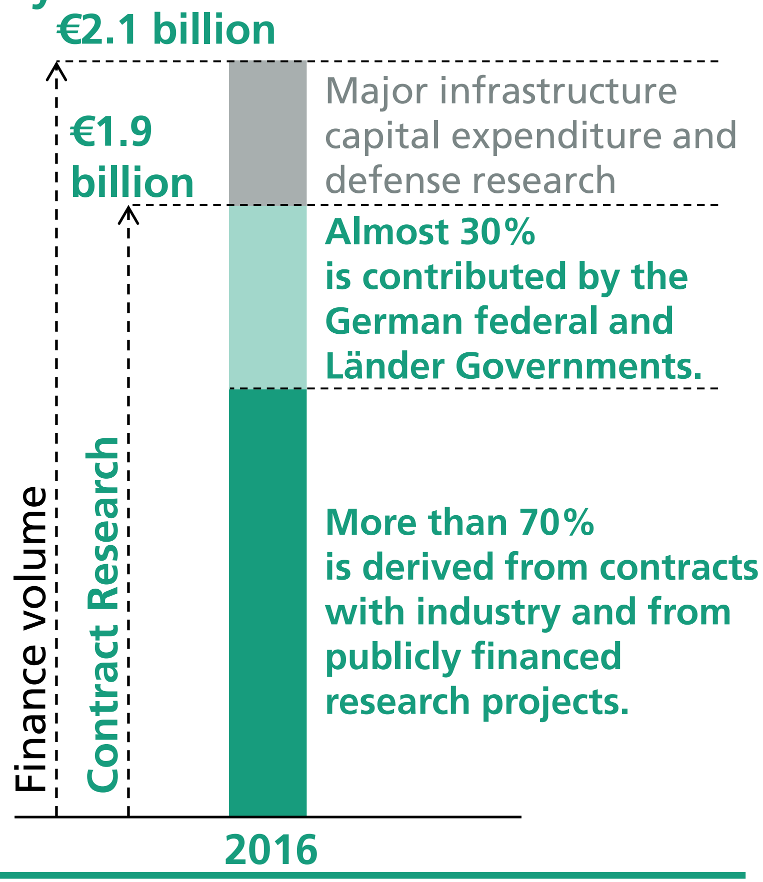
The Fraunhofer-Gesellschaft at a glance

Applied research for the immediate benefit of the economy and society

Nearly **24,500** employees

69 institutes and research units





Fraunhofer IKTS in figures










Sites	Head-quarters	Hermsdorf site	Dresden-Klotzsche site	Total
Personnel (heads)	**374**	**150**	**151**	**675**
- Scientists, technicians, admin. personnel	308	117	141	566
- PhD candidates, students, trainees	66	34	9	109
Overall budget in million €	**28.7**	**13.6**	**11.3**	**53.6**
Industrial revenues in million €	**10.1**	**5.4**	**4.1**	**19.6**

Latest update: December 31, 2016

Institute Director:
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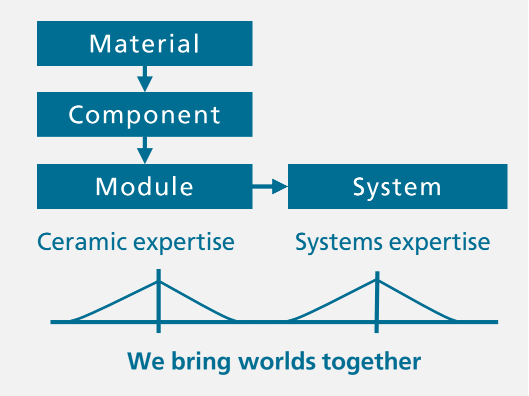
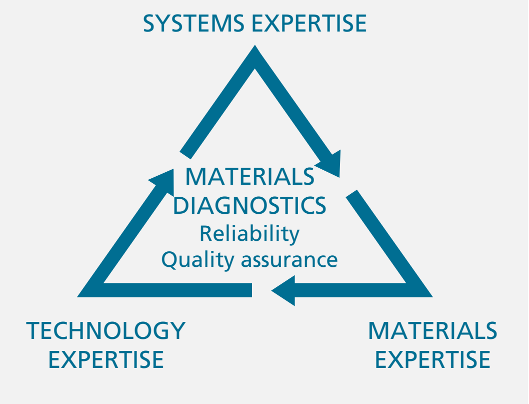
Unique capabilities of Fraunhofer IKTS

- **Complete production line**
  From material to system
- **Multiscale development**
  From laboratory to pilot scale
- **Structural and functional ceramics**
  Combination of different technology platforms
- **Material, component and process analysis**
  Throughout the entire product life cycle
- **Network creator**
  More than 500 national and international partners





FRAUNHOFER IKTS IN PROFILE
CURRENT RESEARCH PROJECTS

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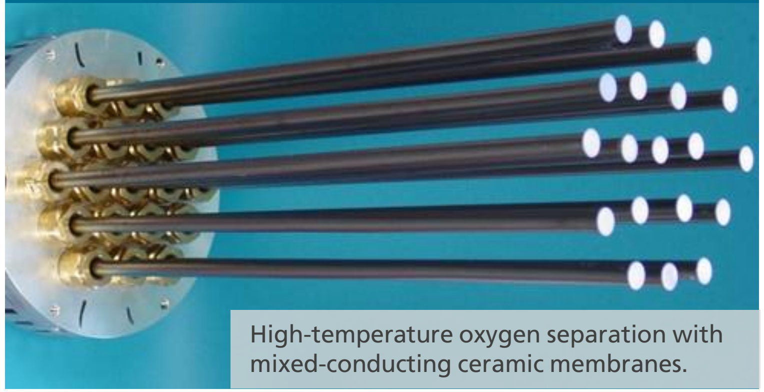
Current research projects

Air separation O_2 generator



High-temperature oxygen separation with mixed-conducting ceramic membranes.

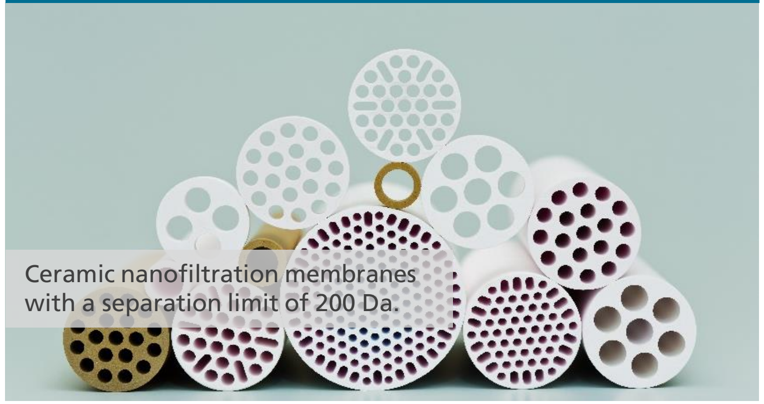
Recycling of valuables from waste water

Process chain to recycle water, energy, and fertilizer from food industry residues.

Material solutions for Li-ion batteries

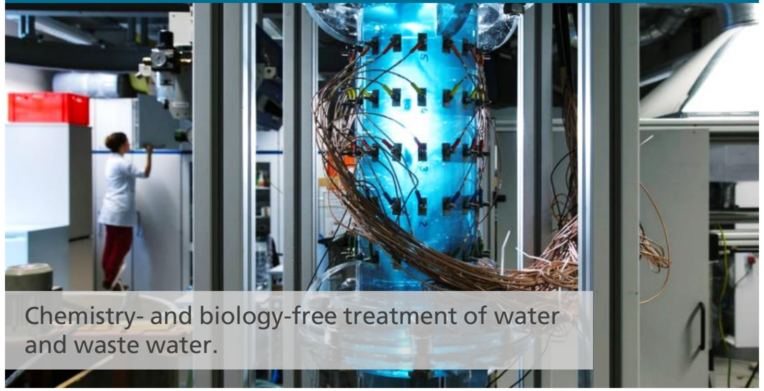
Top-down and bottom-up development of new active materials.

Nanofiltration



Ceramic nanofiltration membranes with a separation limit of 200 Da.

Photocatalytic water treatment



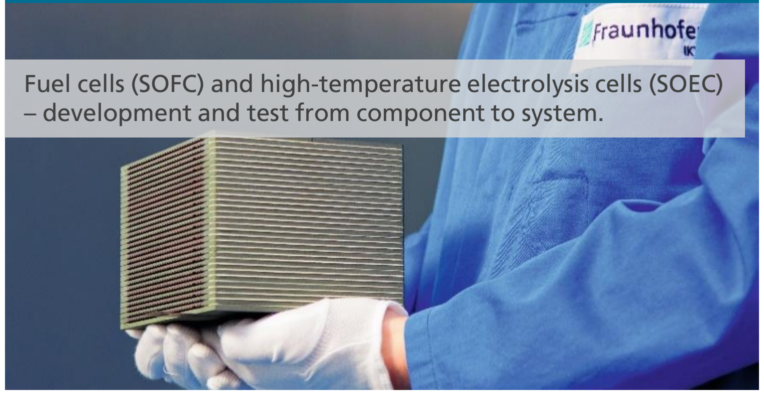
Chemistry- and biology-free treatment of water and waste water.

Power and heat from biogas

Pilot plant at the sewage disposal facility Dresden-Kaditz.

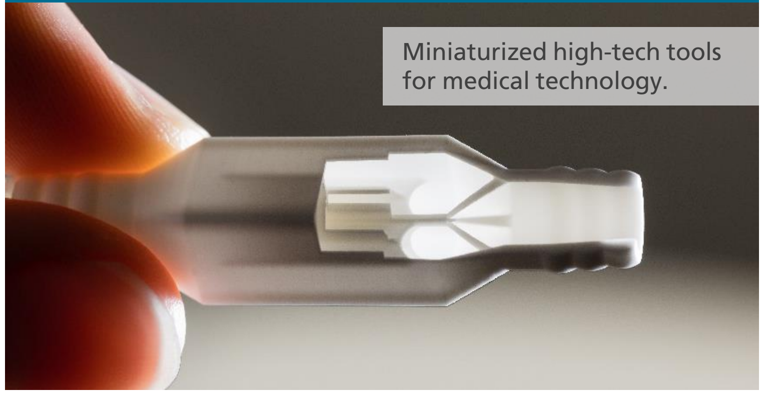
Current research projects

Fuel cell technologies



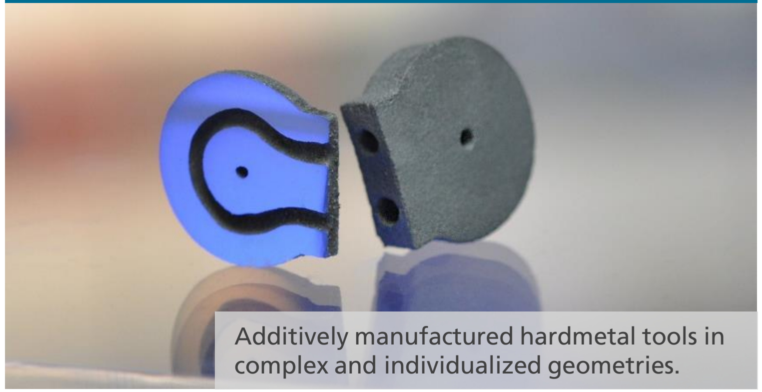
Fuel cells (SOFC) and high-temperature electrolysis cells (SOEC) – development and test from component to system.

Additive manufacturing



Miniaturized high-tech tools for medical technology.

Complex hardmetal tools

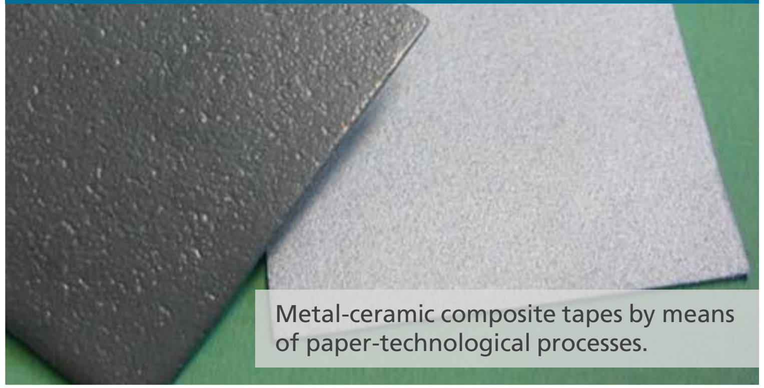


Additively manufactured hardmetal tools in complex and individualized geometries.

High-temperature energy storage

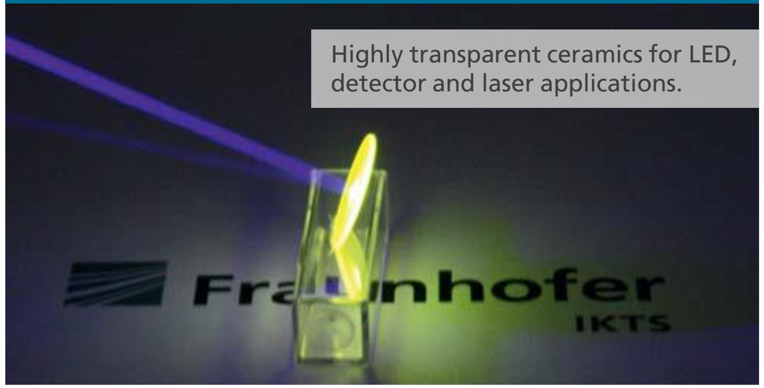
cerenergy® – Na/$NiCl_2$ battery system for stationary storage.

Composites



Metal-ceramic composite tapes by means of paper-technological processes.

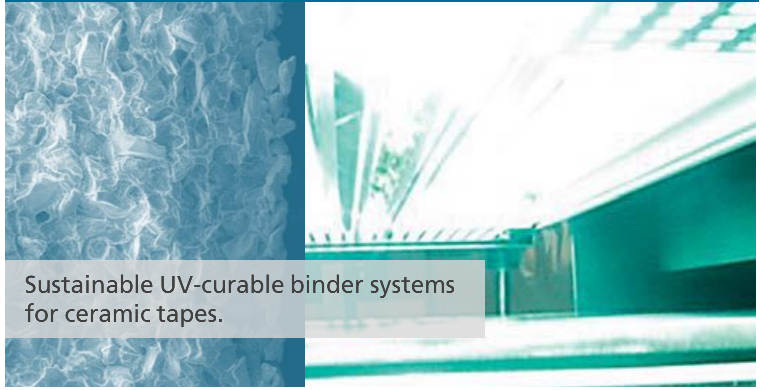
Active optoceramics



Highly transparent ceramics for LED, detector and laser applications.

Current research projects

Ceramic tapes (specifically UV-curable)

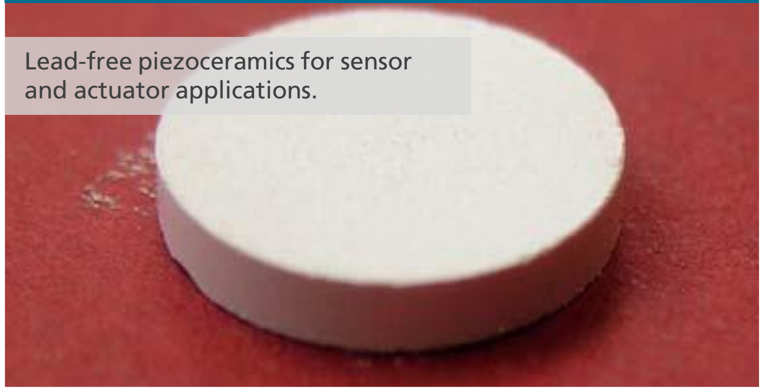


Sustainable UV-curable binder systems for ceramic tapes.

Personalized ceramic implants

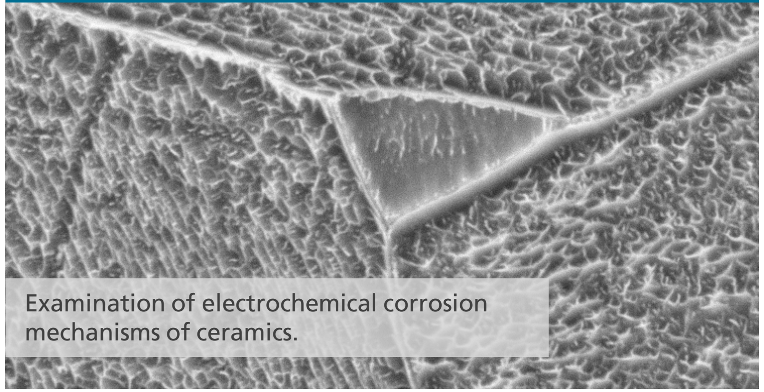
Biocompatible ceramic bone replica with additively manufactured coating and freeze-foamed filling.

Smart materials



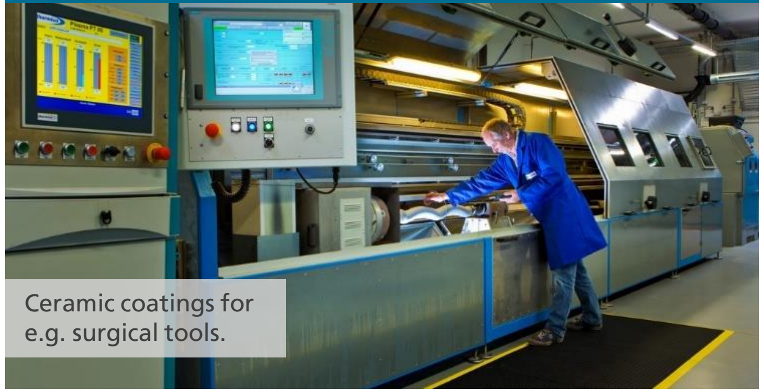
Lead-free piezoceramics for sensor and actuator applications.

Corrosion of ceramic materials



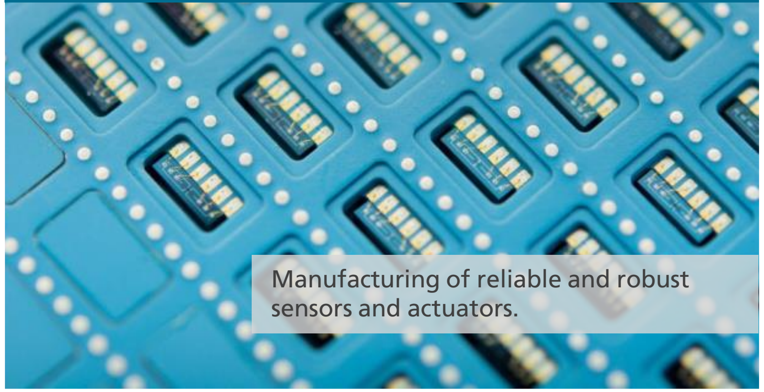
Examination of electrochemical corrosion mechanisms of ceramics.

Plasmagel coatings



Ceramic coatings for e.g. surgical tools.

LTCC-MEMS packaging



Manufacturing of reliable and robust sensors and actuators.

Ta-Ni-braze-alloys for high temperature stable ceramic – ceramic junctions

Brazing Experiments

- Brazing regime and atmosphere

CALPHAD calculations

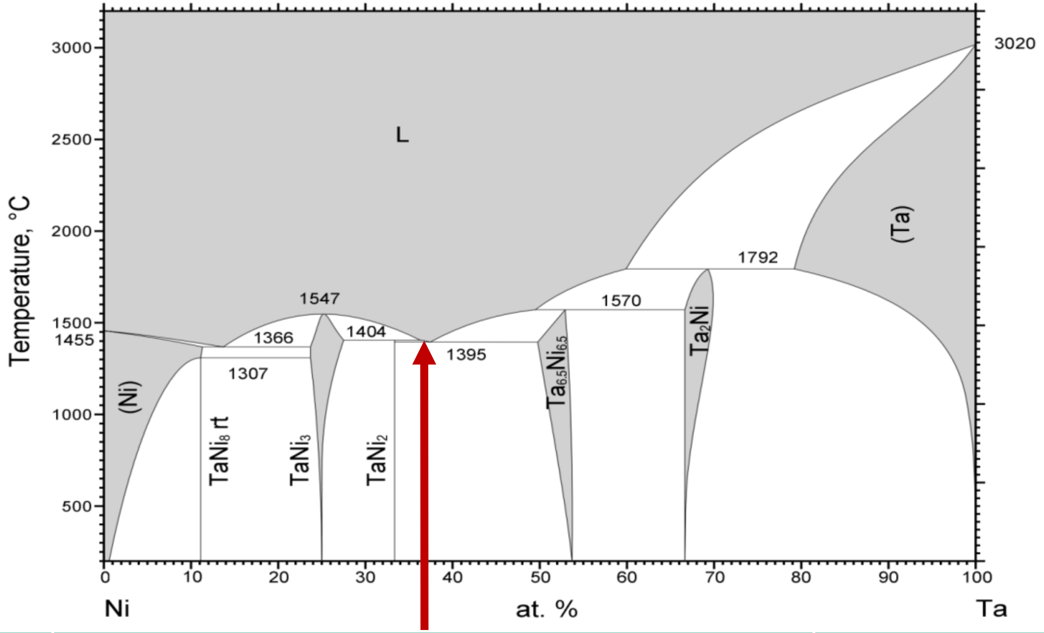
- Braze + ceramics → reaction products and their melting points (aim > 1300 °C)
- Partial pressure of gas phases

Data-Matrix

- Thermoanalysis → c_p, ΔH, T (reactions, phase transition, solidus, liquidus)
- SEM, EDX, XRD → phase composition, microstructure
- Thermal and electrical conductivity
- Hardness
- CTE

[1] Triebert A, Matthey B, Martin H-P. Untersuchungen zu Ta–Ni-Legierungen als Hochtemperaturlot für SiC–SiC Verbunde. Keram. Z. 2011;63(5):322–328.
[2] Martin H.-P., Triebert A. Keramikverbunde mit Ta-Ni-Loten für Hochtemperaturanwendungen: Kapitel 3.9.2.3. In: Kriegesmann Jochen, ed. Technische Keramische Werkstoffe (DKG). Ellerau: HvB-Verlag 2014:1–28.
[3] Valenza F, Gambaro S, Muolo ML, et al. Wetting and interfacial phenomena of Ni-Ta alloys on CVD-SiC. Int. J. Appl. Ceram. Technol. 2016;2015:551.

Joining SiC-NiTa-SiC

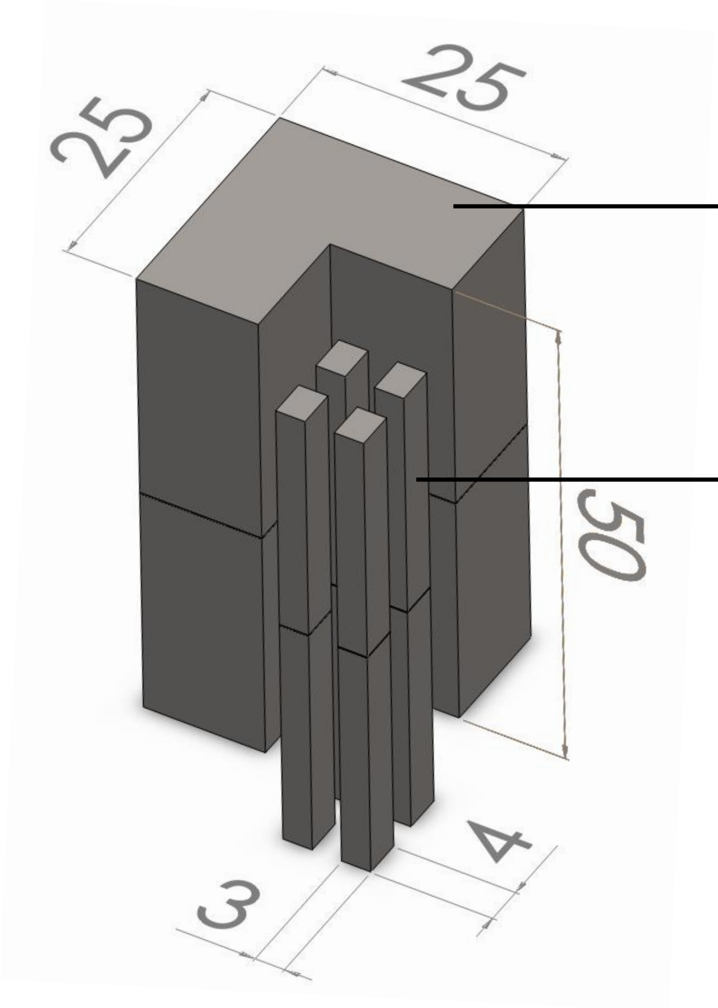


Ta-Foil, Ni-Paste

Vakuum pressure < 10^{-5} Pa

ceramic (HC Starck)	Braze composition Ta/Ni at. %	Brazing temperature °C
S-SiC	38/62	1700
S-SiC	38/62	1600
S-SiC	38/62	1500
S-SiC	38/62	1410

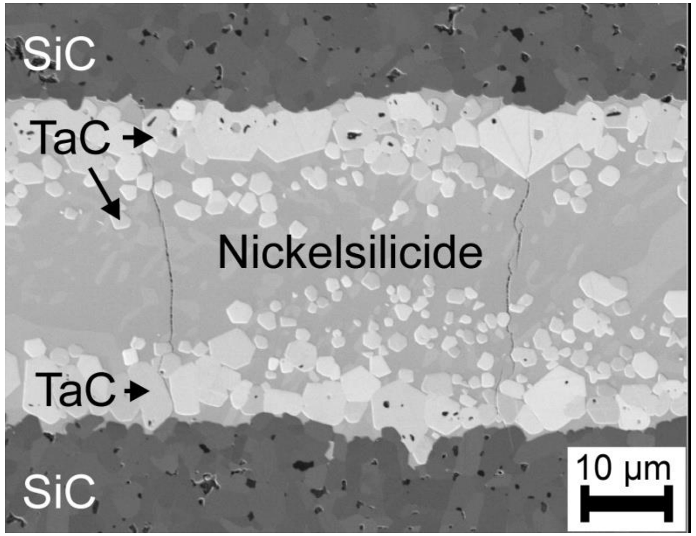
Geometry of samples for joining experiments and bending test



samples for joining experiments

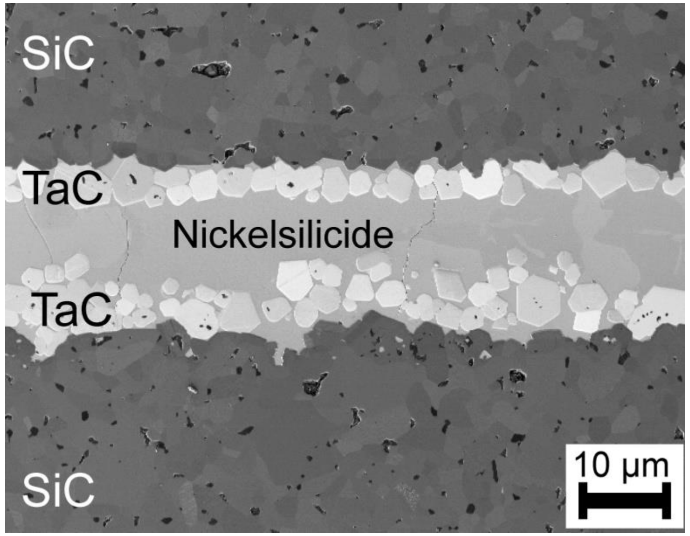
bars for bending test
according to DIN-EN- 843-1

Cross section structure of joining zone



1410 °C

some perpendicular cracks

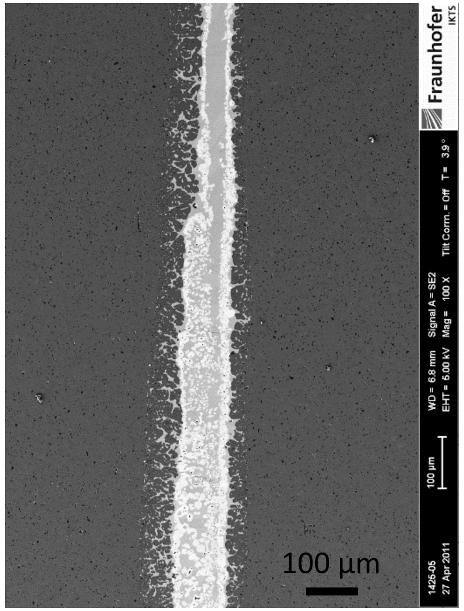


1500 °C

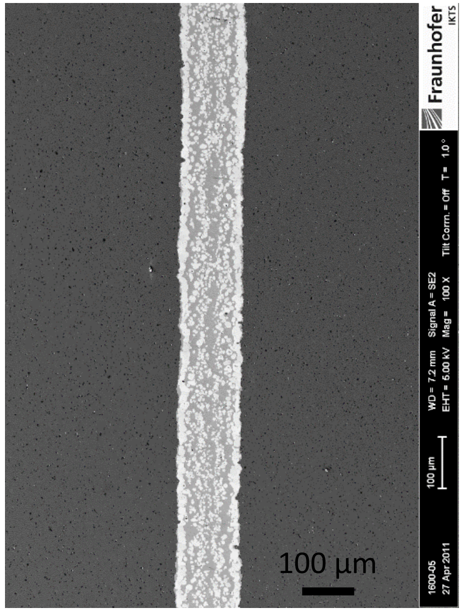
Some perpendicular cracks

- Nickel silicide located in the center
- TaC concentrated on the interface

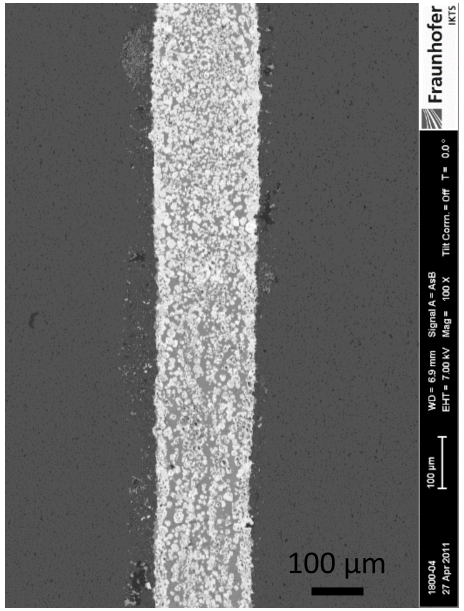
Cross section structure images depending on temperature



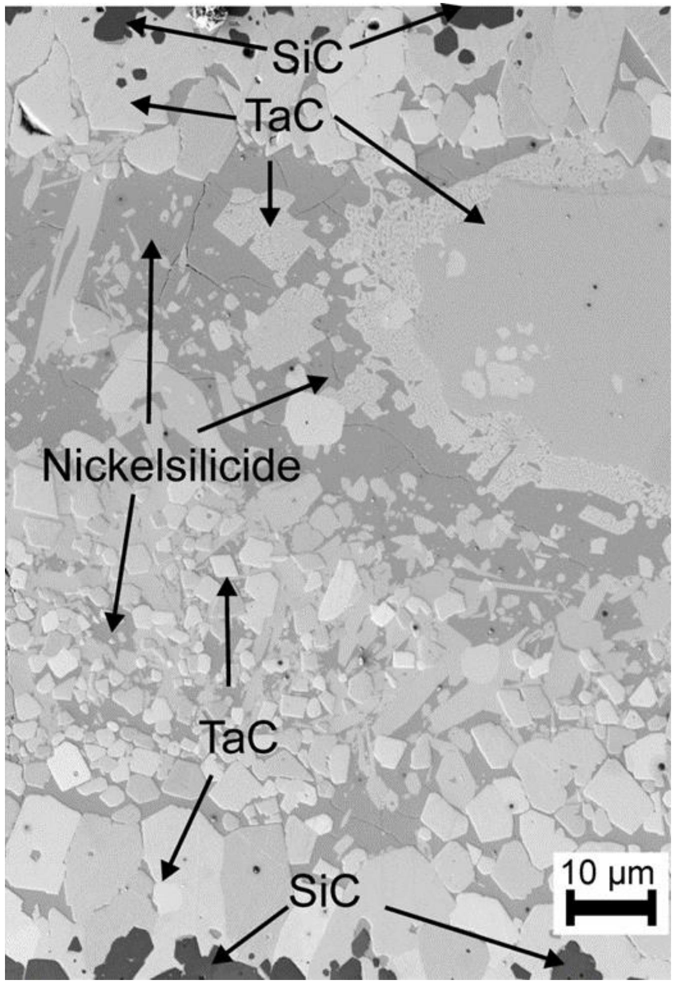
1410 °C



1600 °C

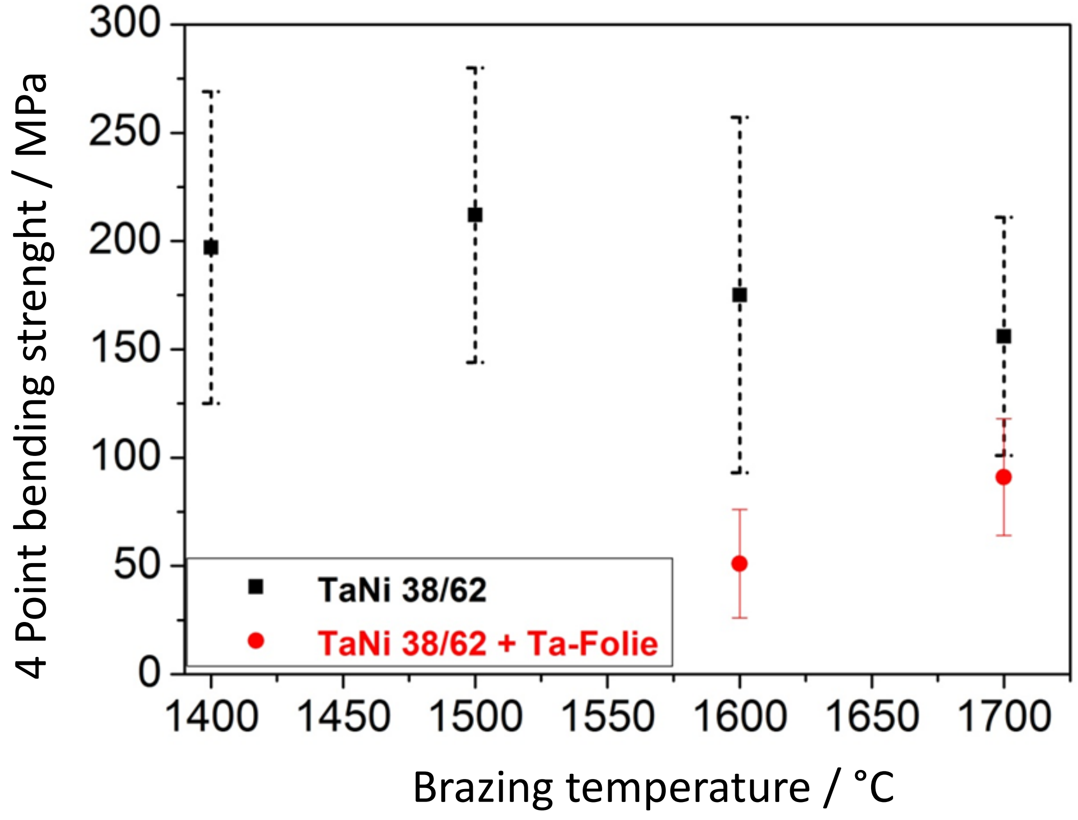


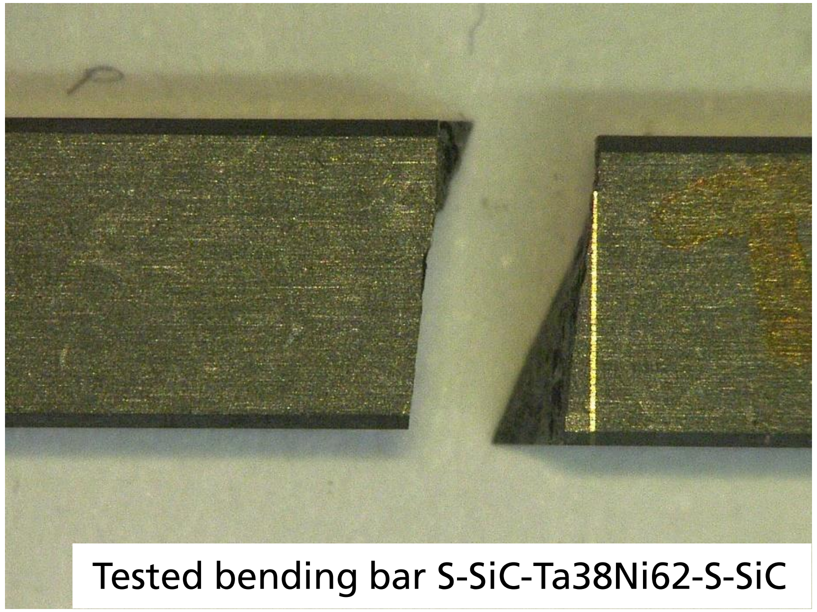
1700 °C



1600 °C

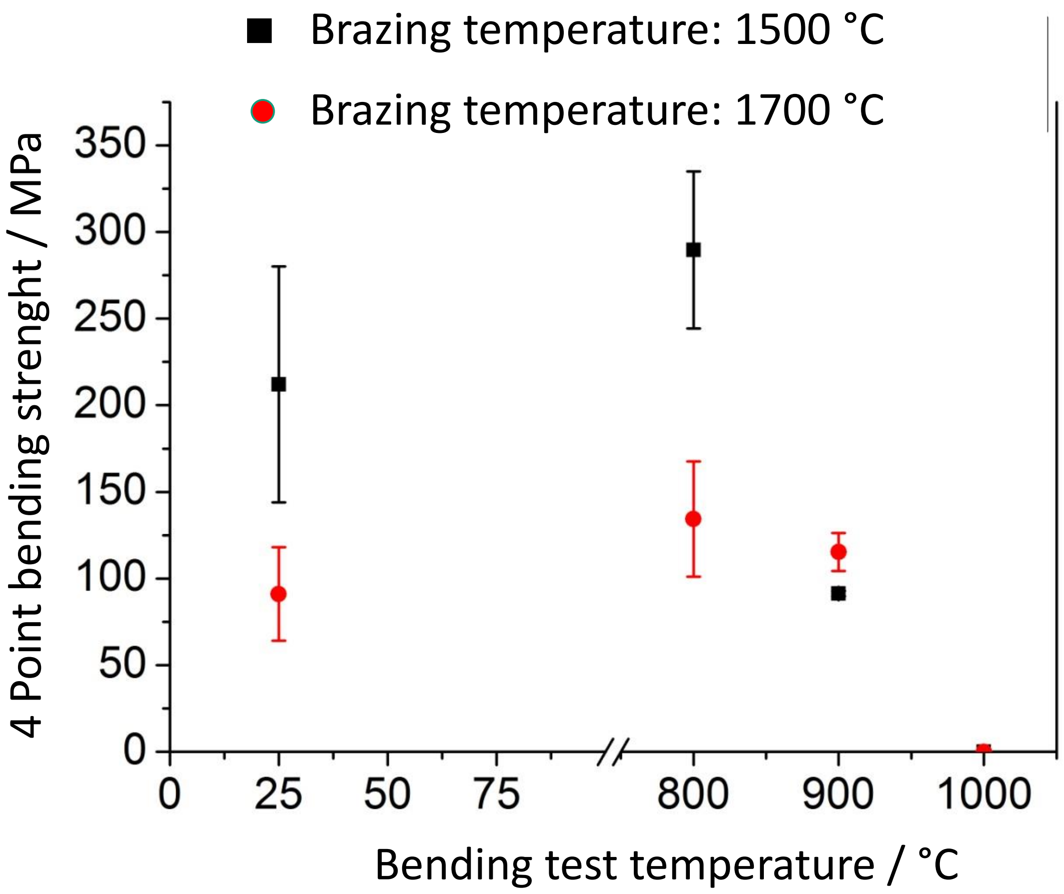
Bending strength at ambient temperature





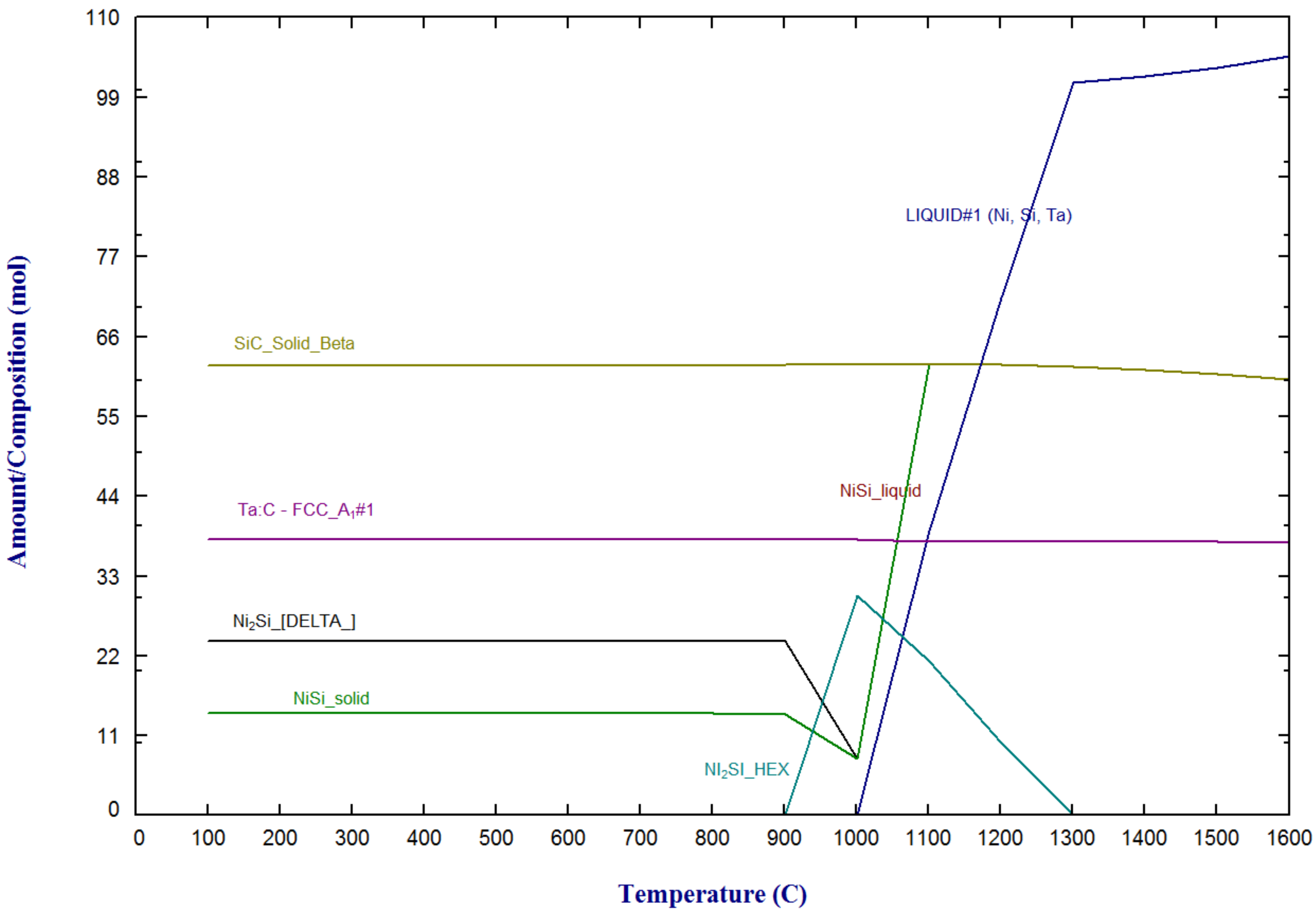
Tested bending bar S-SiC-Ta38Ni62-S-SiC

Bending strength at high temperature

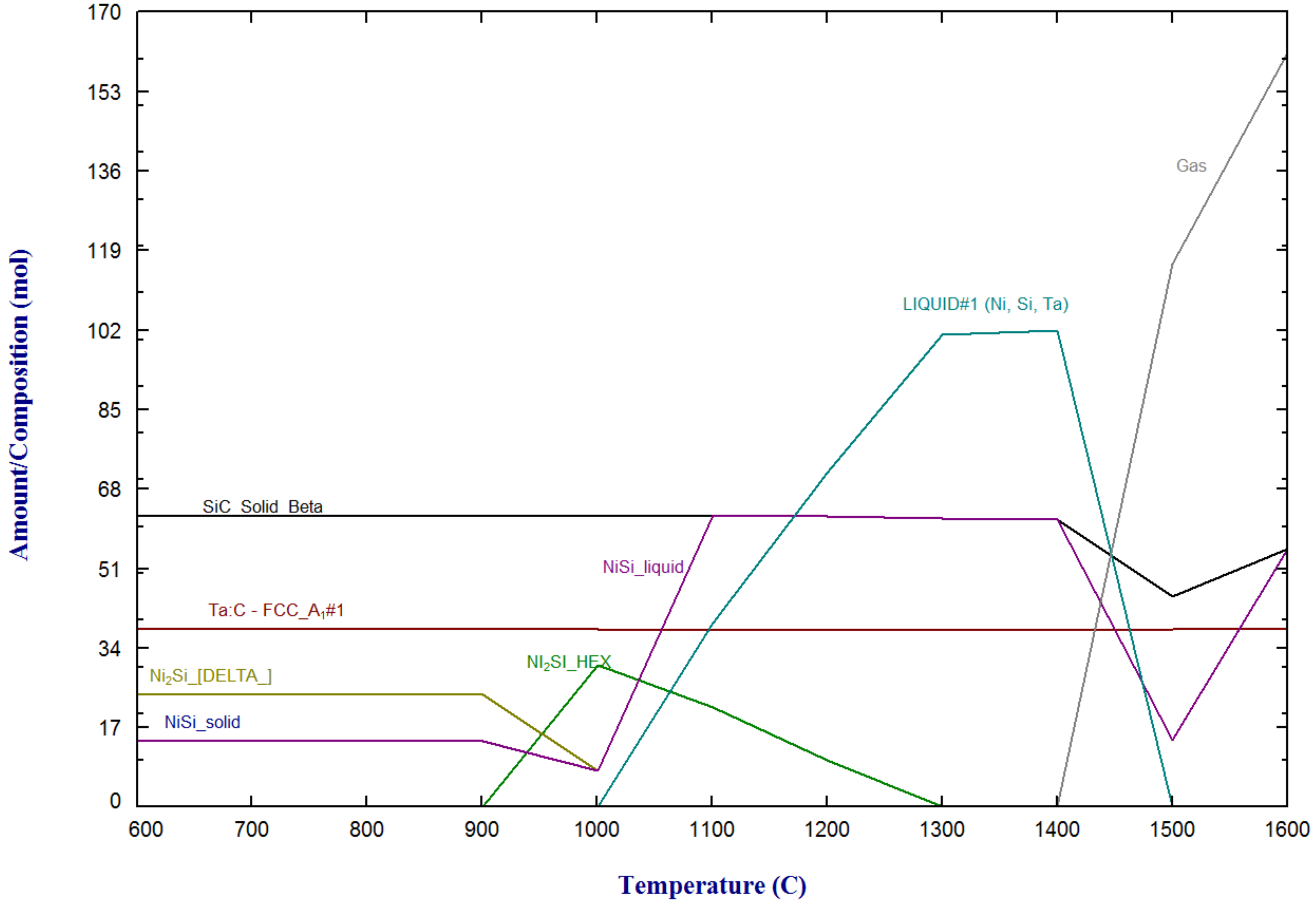


- Increase of bending strength at high temperatures up to 800 °C
- Considerabel strength level of over 200 MPa
- Strong decrease in strength at 900 °C

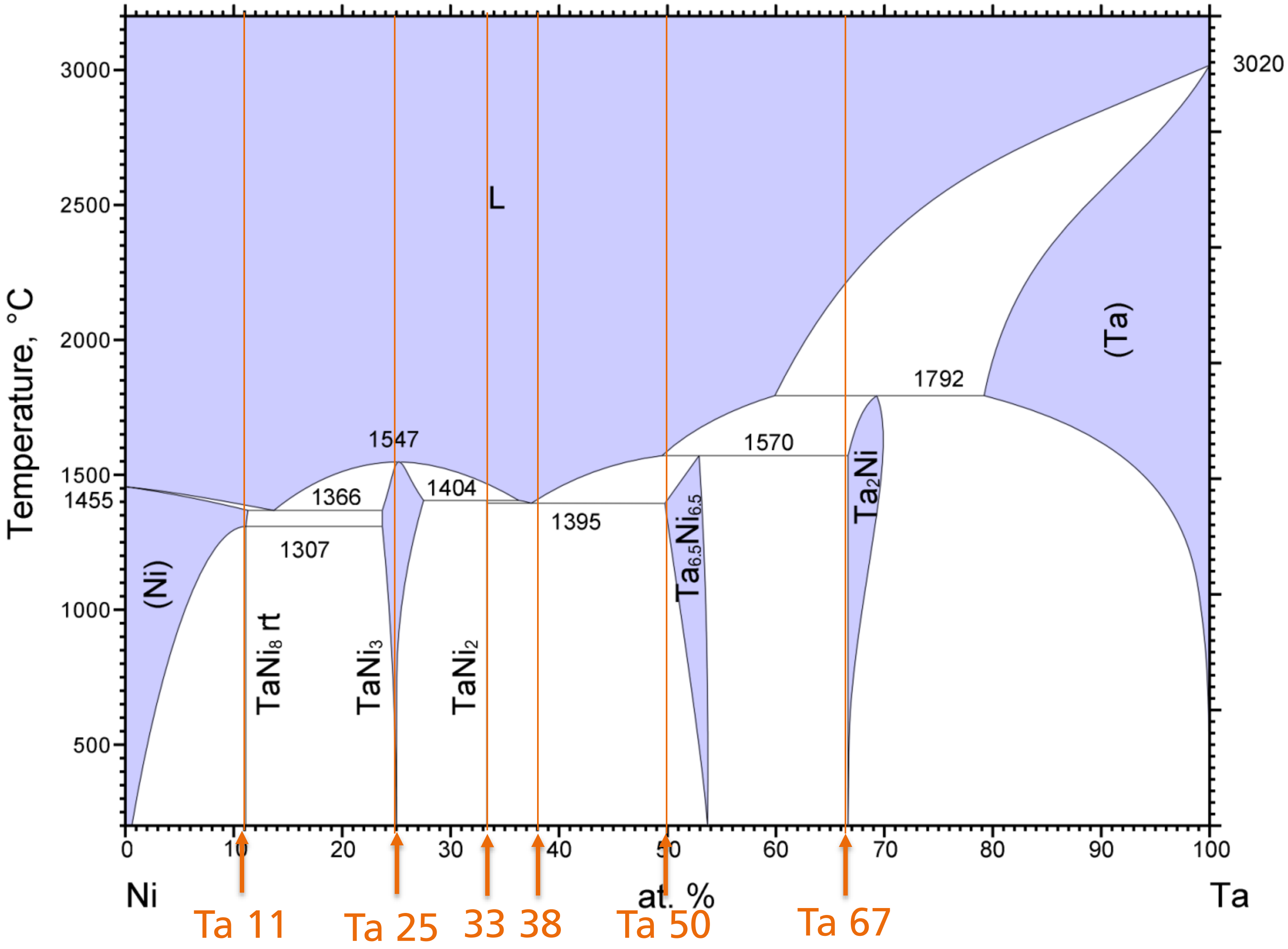
CALPHAD calculations (Factsage), 100 SiC + 38 Ta + 62 Ni, 100 mbar



CALPHAD calculations (Factsage), 100 SiC + 38 Ta + 62 Ni, 10^{-4} mbar



6 Samples 11 to 67 at% Tantalum, Ni-Ta phase diagram



Eutectics:

- 1366 °C / 13 at% Ta
- 1395 °C / 38 at% Ta

Dystecticum:

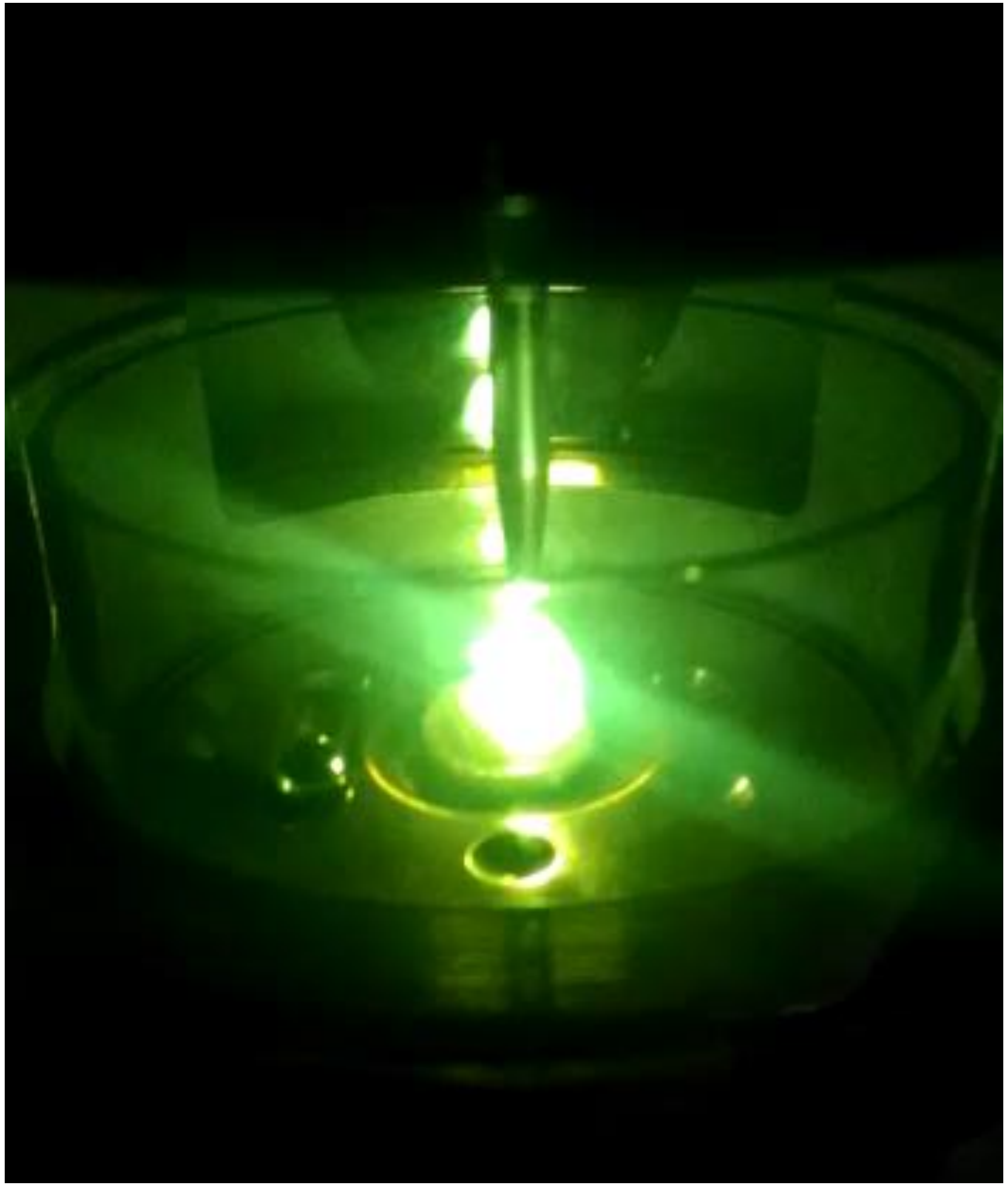
- 1547 °C / 25 at% Ta

Peritectics:

- 1570°C / 50 at% Ta
- 1792°C / 60 at% Ta

Arc-Melting, sample preparation

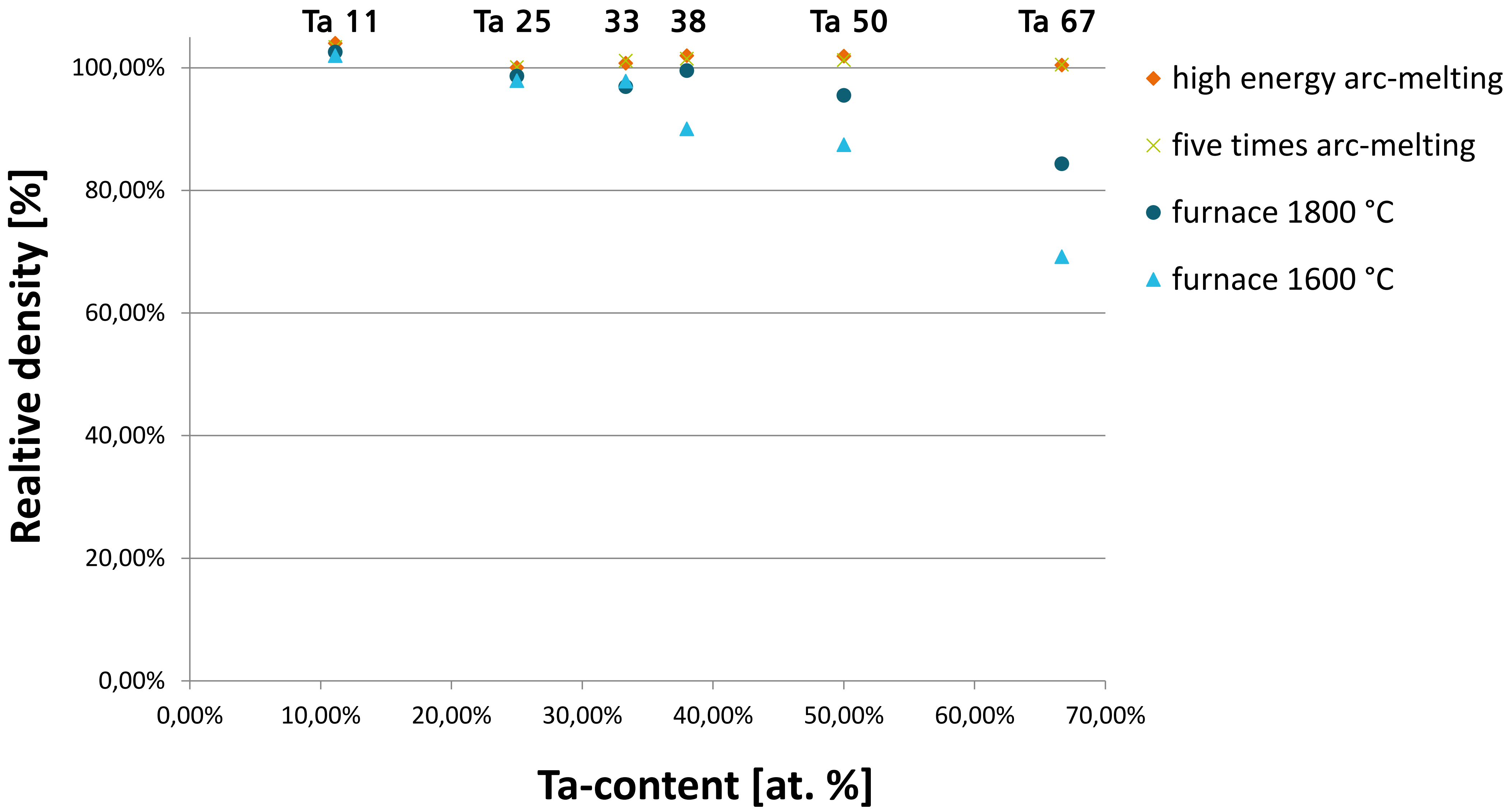
- Stable 64 foils of pure Ni and Ta
- Five turns arc-melting at ICMATE (Genova)
- One turn with higher arc energy at MPI CPfS (Dresden)



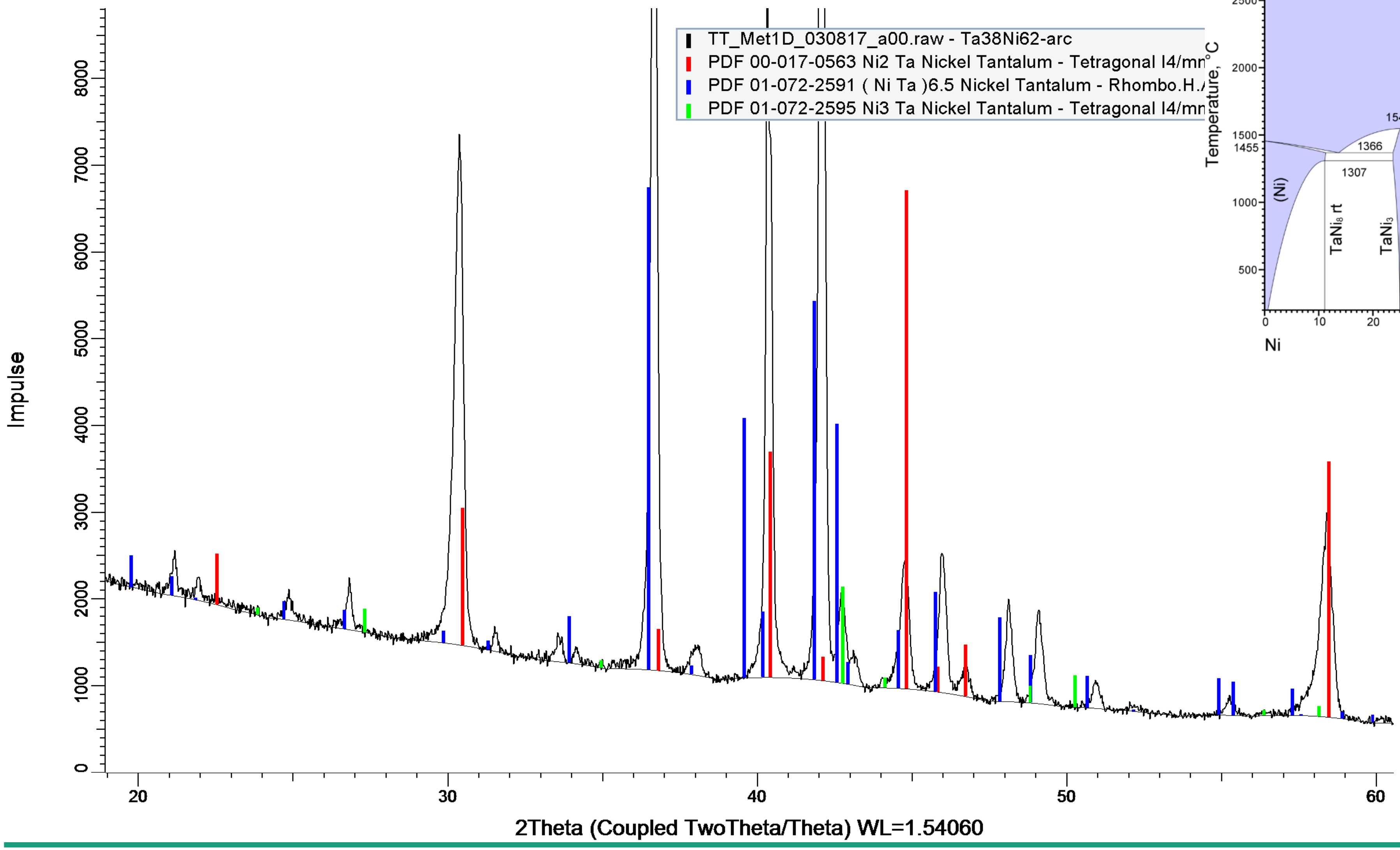
Arc-Melting, samples after five turnes

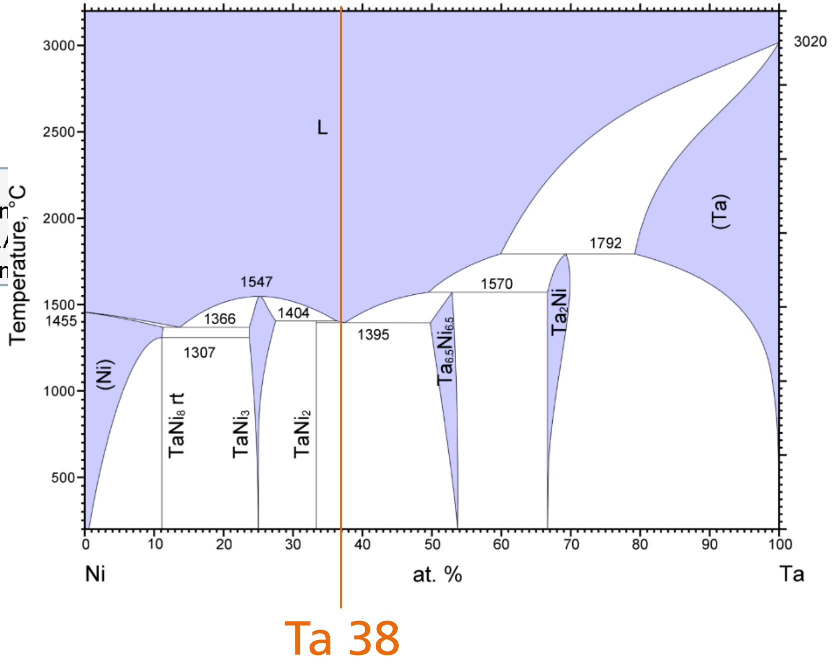
Arc-Melting, samples after additional high energy turn

Density

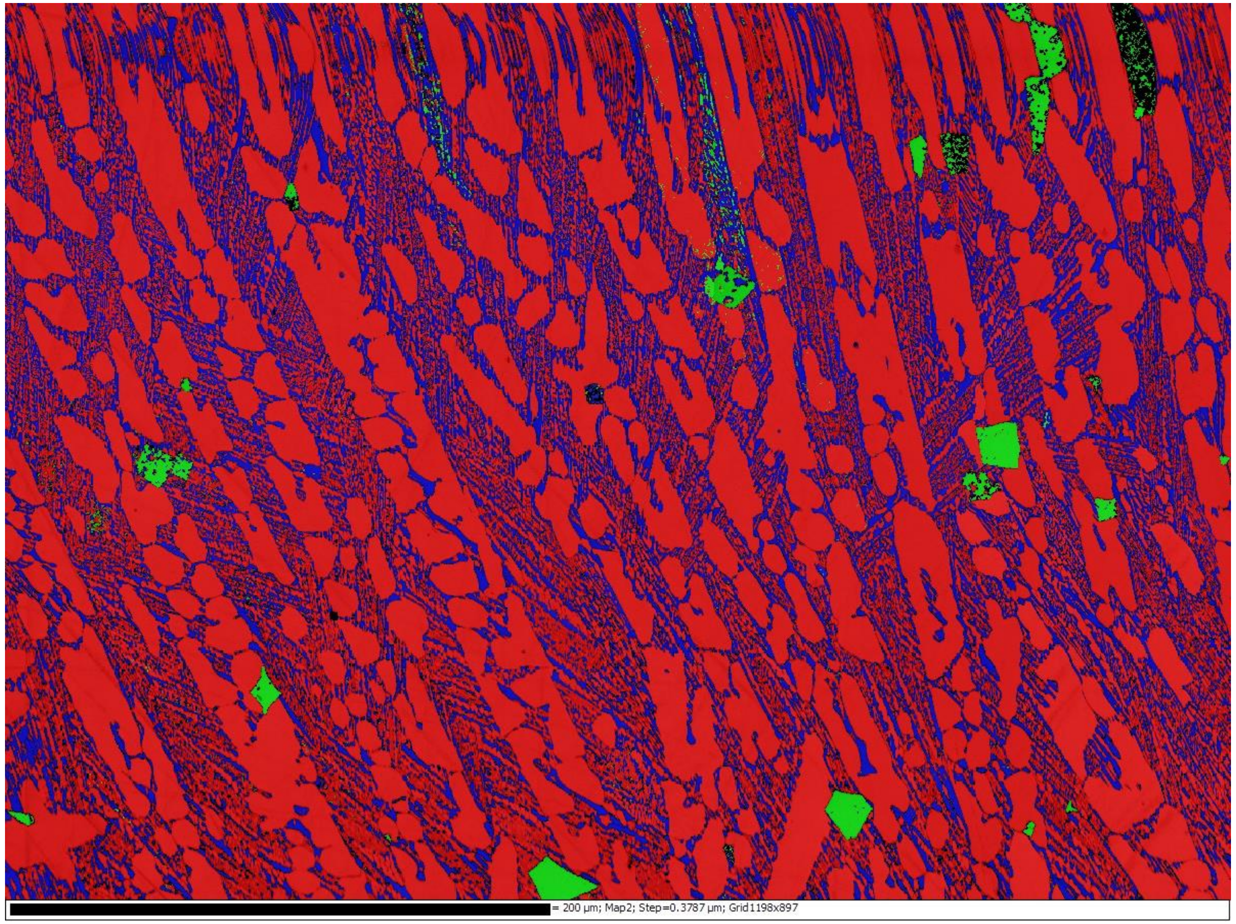

Ta 11
Ta 25
33
38
Ta 50
Ta 67
100,00%
80,00%
60,00%
40,00%
20,00%
0,00%
Realtive density [%]
0,00%
10,00%
20,00%
30,00%
40,00%
50,00%
60,00%
70,00%
Ta-content [at. %]
high energy arc-melting
five times arc-melting
furnace 1800 °C
furnace 1600 °C

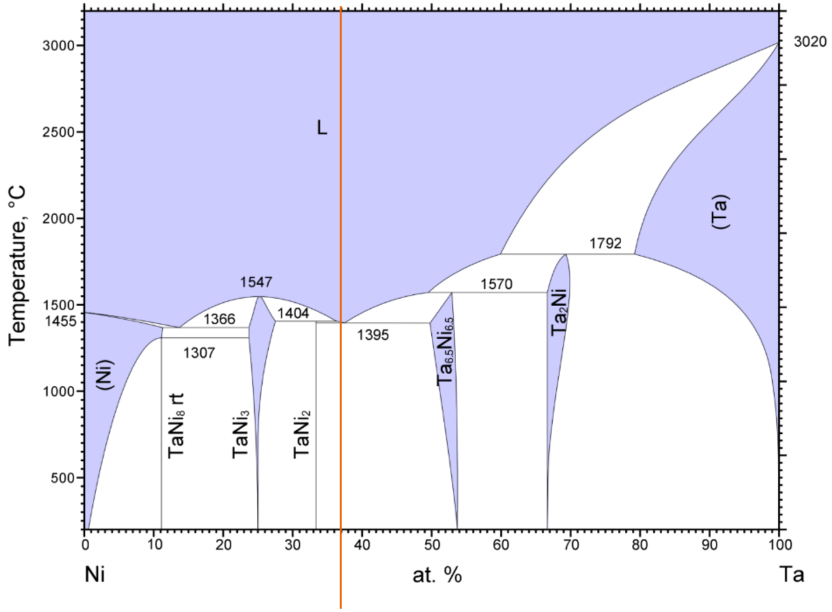
XRD, sample 38 at. % Ta





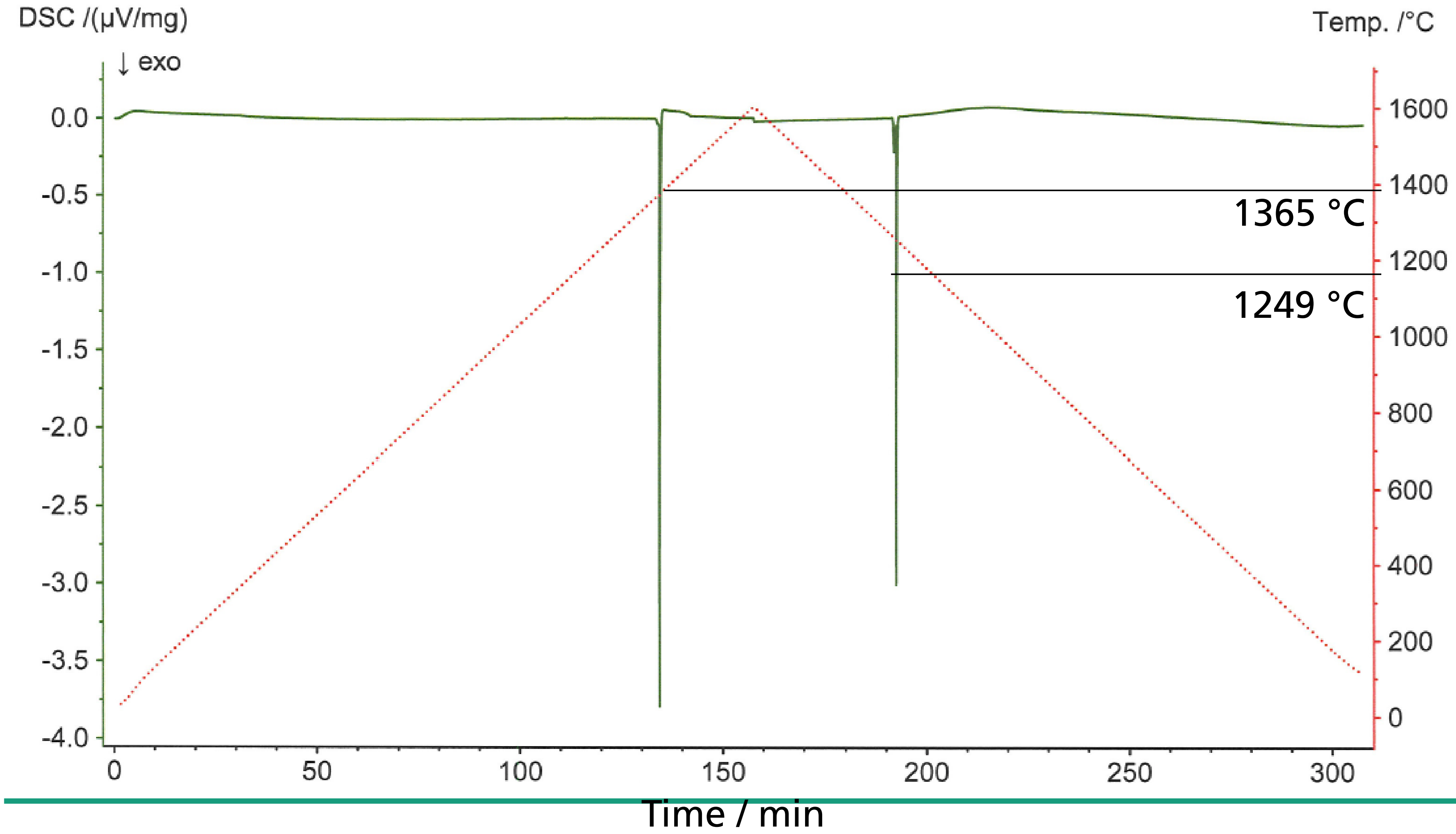
EBSD – band contrast and phase analysis, sample 38 at. % Ta

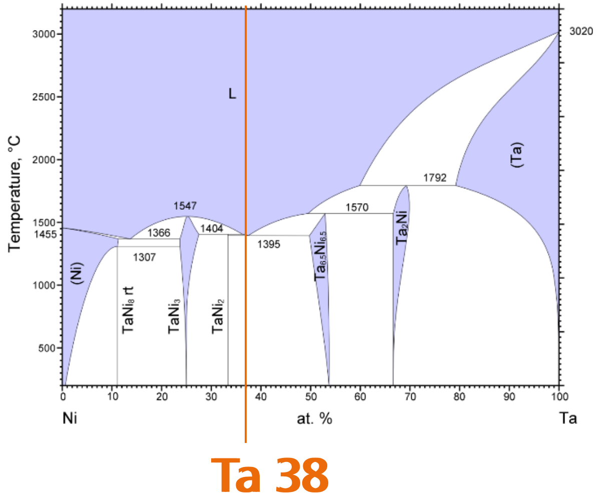




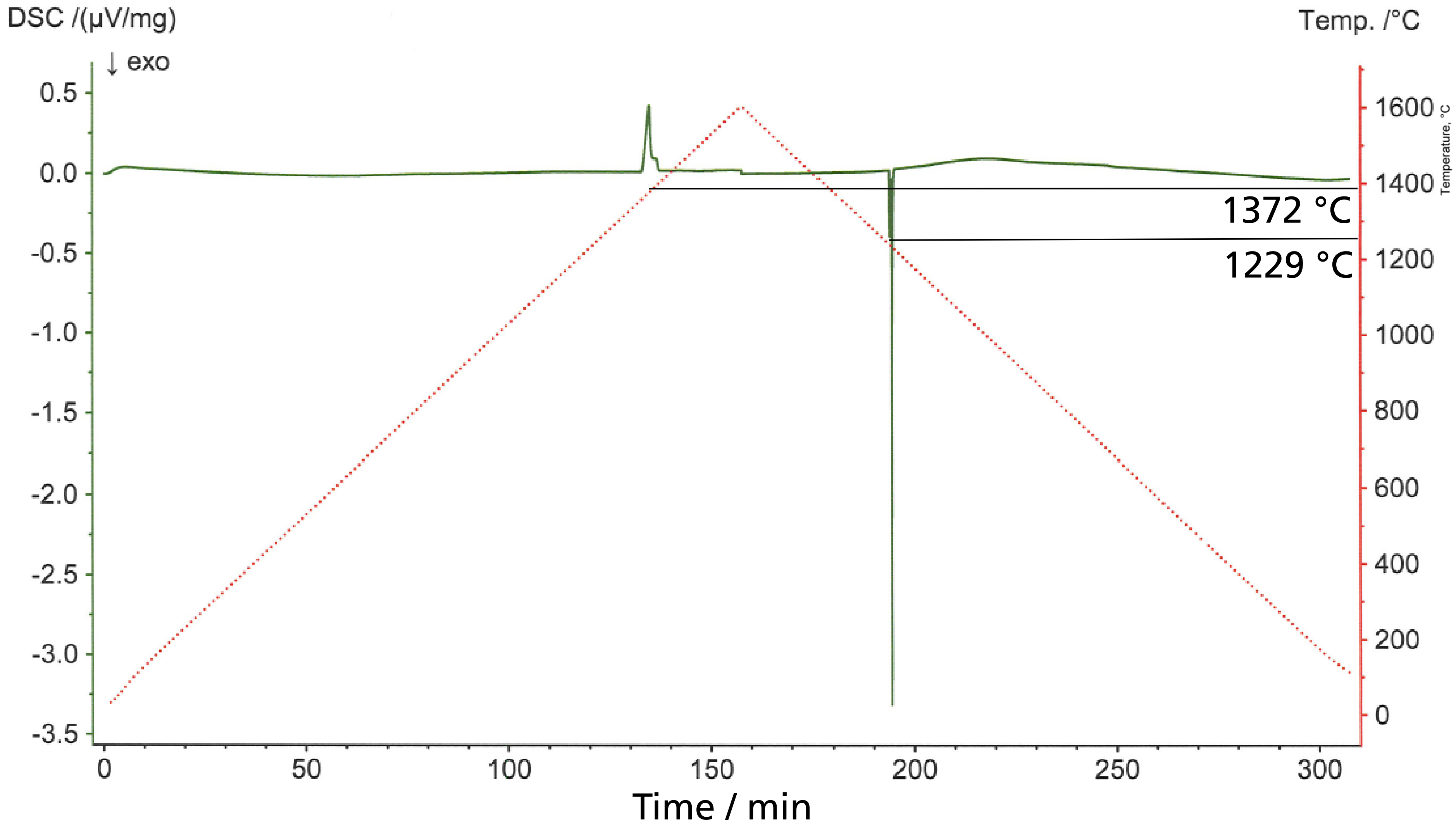
Phase	Gehalt (Vol.%)
TaNi_R-3m_646850	25.8
TaNi2_I4mmm_105388	71.7
$Ta(Ni)_x$???	2.5

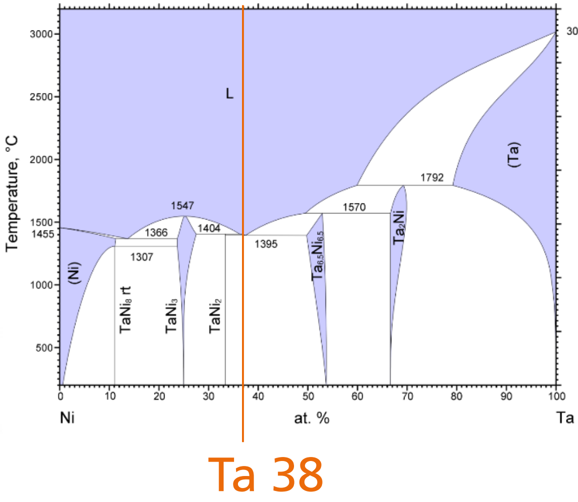
Thermoanlaysis, pure Ni (68 at. %) and Ta (38 at. %) foils, strong exothermic reaction



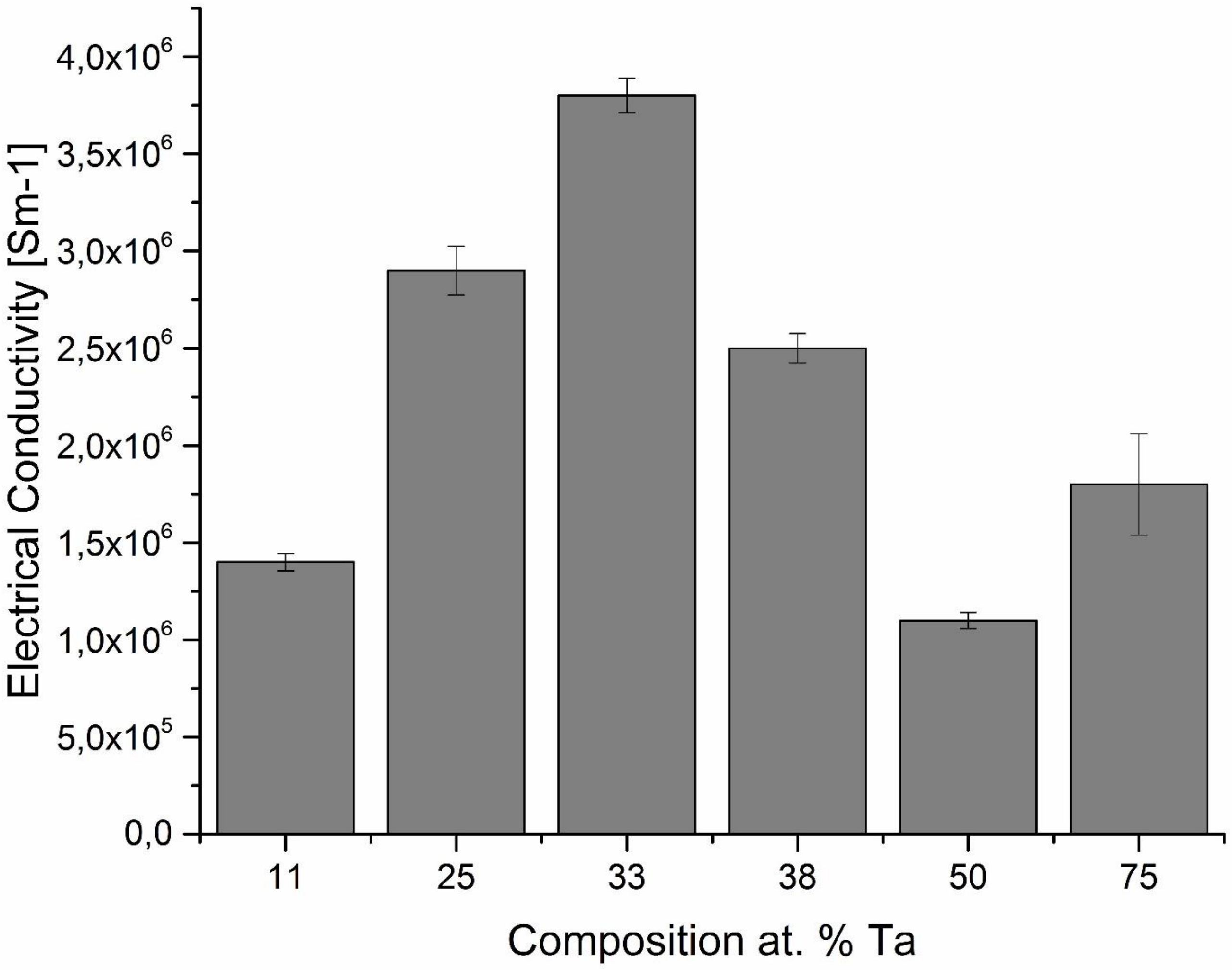


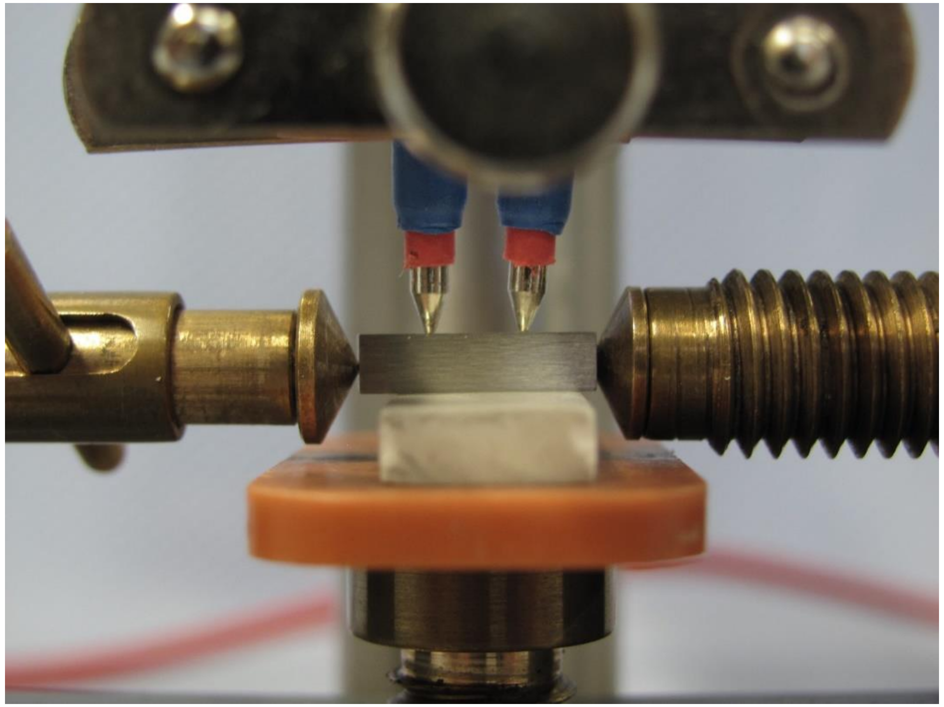
Thermoanlaysis, bulk alloy Ta 38



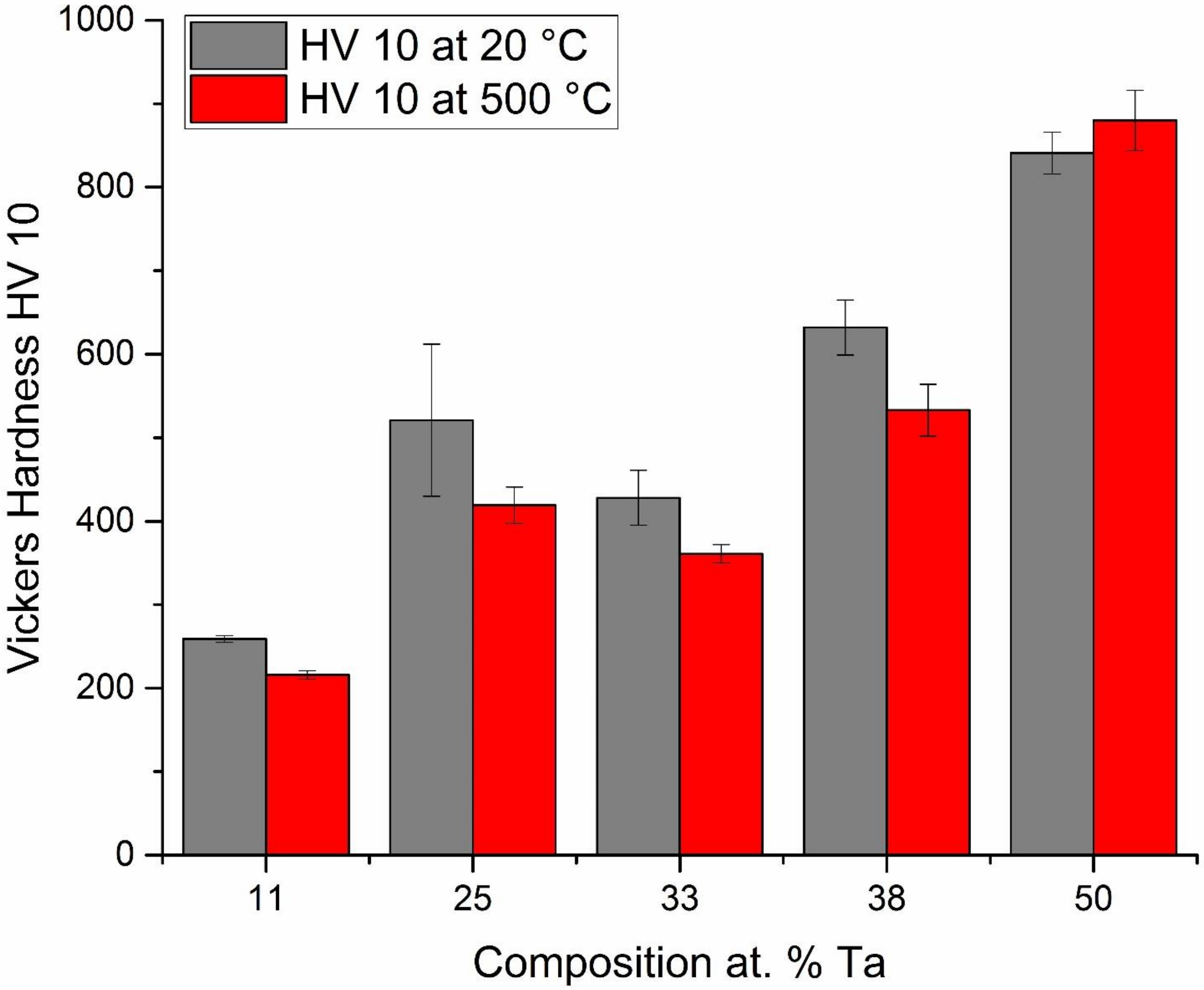


Electrical Conductivity at room temperture

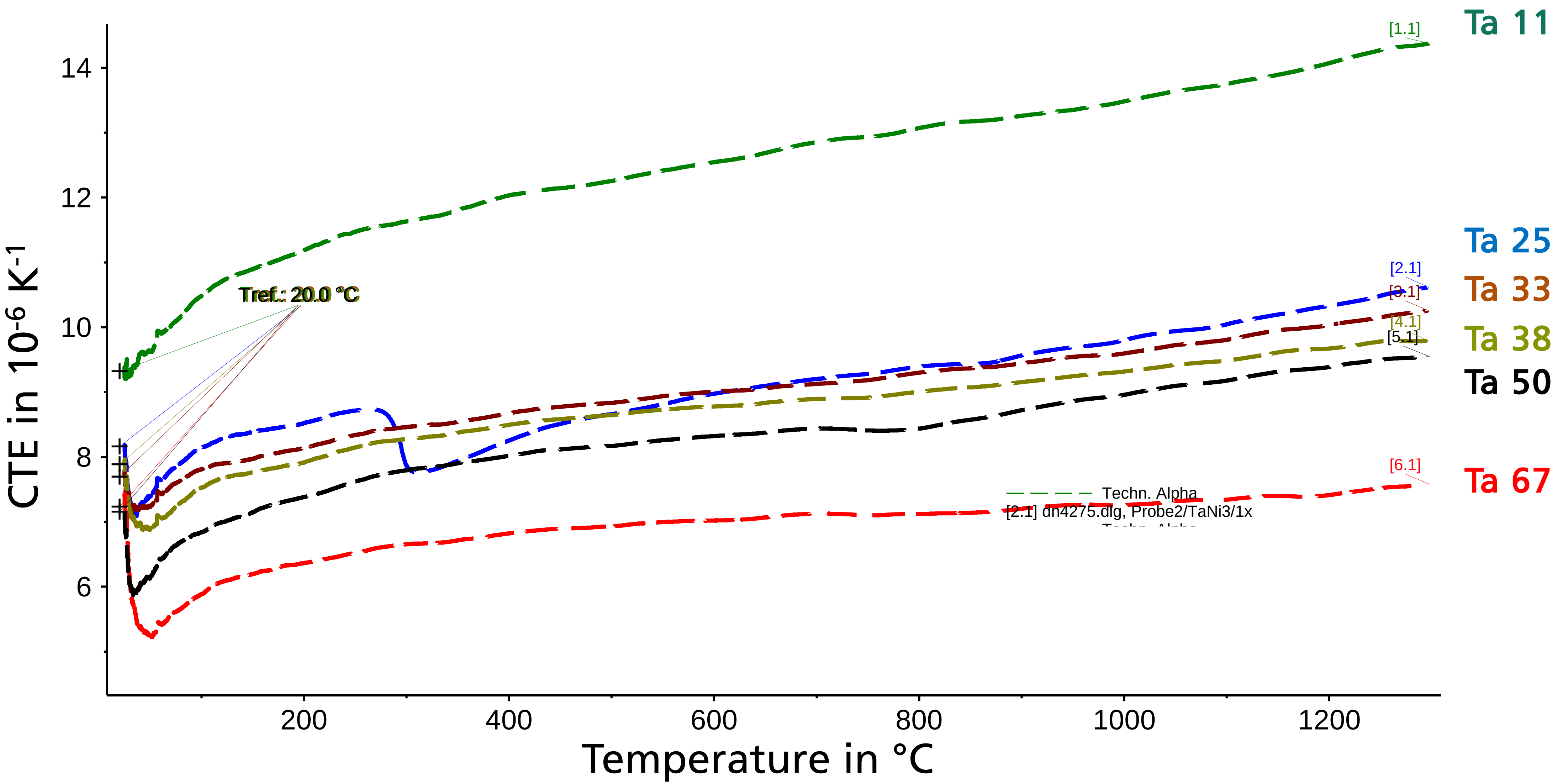




Vickers Hardness



Coefficient of thermal expansion (CTE)

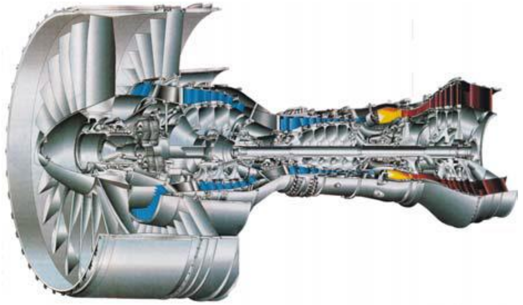


Summary and outlook NiTa braze alloys

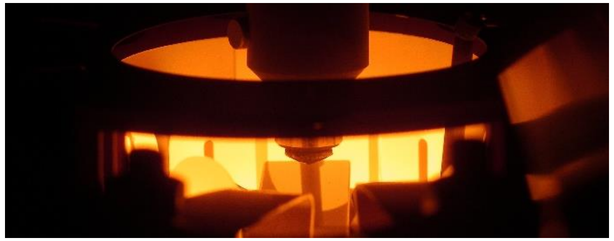
- Bending strength of S-SiC-TaNi joints up to 275 MPa at 800 °C
- Thermoanalysis shows strong exothermic reaction (Ta 38), which is supporting the alloying prozess
- Increase of hardness with increasing Ta content
- CTE decreases with increasing Ta content from 12 $\cdot 10^{-6}$ K^{-1} (Ta 11) to 6 $\cdot 10^{-6}$ K^{-1} (Ta 67)
  - → individual alignment of the brazes CTE to the ceramics CTE possible
- The generated Data-Matrix is viable tool to design further ceramic – ceramic junctions
- Ta-Ni brazes are promising brazes for high temperatures
- Outlook:
  - Use of barrier coatings at SiC surface to avoid low melting point nickel silizide formation
  - Show that aligned CTE reduces stress in braze joint and increases mechanical strength level

Manufacture of joined ceramics by use of high temperature stable titanium aluminides

- Ti-Al development
  - 1990-2005 Ti-Al material development for use as high temperature alloys
  - γ-TiAl performs as a high temperature stable alloy with moderate toughness
  - economic manufacture routes for TiAl alloys get established after 2000

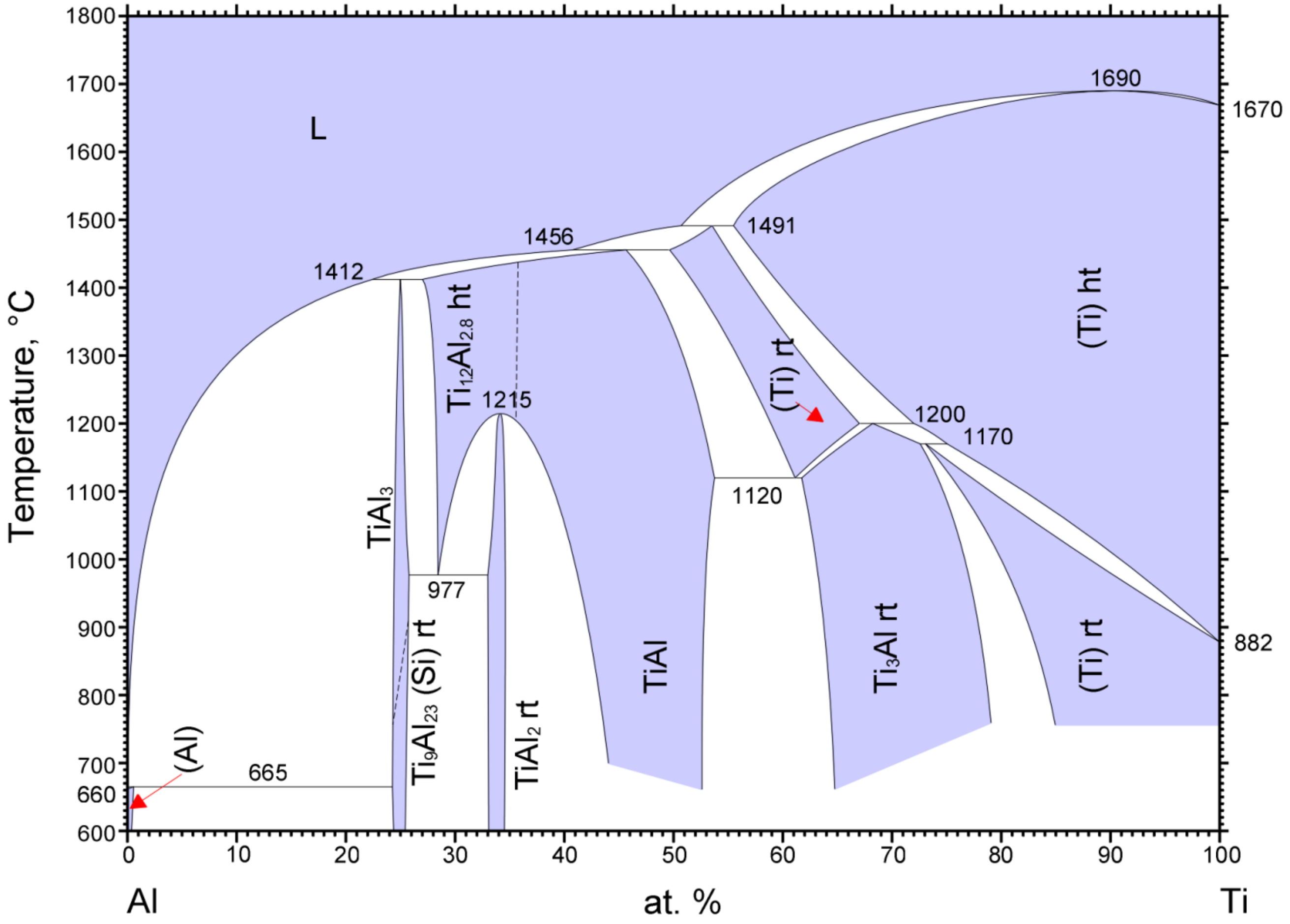


- Ceramic joining
  - Ceramics are favoured materials for high temperature applications
  - active filler brazing based on Ag/Cu/Ti established
  - inferior performance of Ag/Cu/Ti brazed ceramics > 500 °C
  - little economic braze alternatives available



Ti-Al system

phase diagram

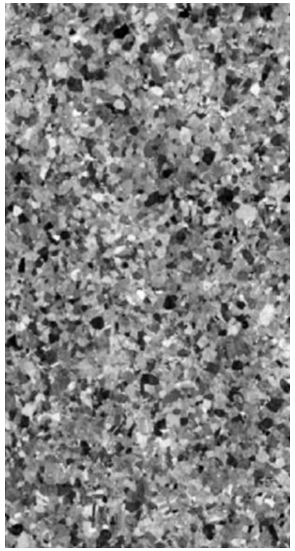


ASM International 2009 Diagram No 100048

- γ-TiAl 45-55 at% Ti
- melting range 1450…1490 °C
- phases next to TiAl are:
  - $TiAl_2$
  - Ti_3Al

Ti-Al system
properties of Ti-Al intermetallics

			Ref.	20 °C	600 °C
thermal conductivity	W/mK	Ti-47Al-4(Nb,W,B)	[1]	15	21
CTE	10^{-6} K^{-1}	Ti-47Al-4(Nb,W,B)	[1]	8.5	11.5
Young modulus	GPa	Ti-47Al-4(Nb,W,B)	[1]	165	150
specific heat	J/gK	Ti-47Al-4(Nb,W,B)	[1]	0.6	0.7
yield strength	MPa	Ti-46.5Al-4(Cr,Nb,Ta,B)	[2]	810	800
electrical resistivity	10^{-6} Ωcm	Ti-47Al-4(Nb,W,B)	[1]	75	110

[1] W.J. Zhang et al. Physical properties of TiAl-base alloys, Scripta Materialia 45 (2001), 645-651

[2] H. Kestler et al. Strangpressverfahren zur Herstellung von TiAl-Ventilen, in: Titan-Aluminid-Legierungen… IBSN 3-89336-318-1

Ceramic materials used in this work

			bending strength MPa	CTE $10^{-6}\ K^{-1}$	Young modulus GPa
Alumina	Al_2O_3	Frialit 99.7	350	8.2	380
Silicon carbide	S-SiC	IKTS	400	4.4	420
Silicon nitride	Si_3N_4	IKTS	910	3.2	320

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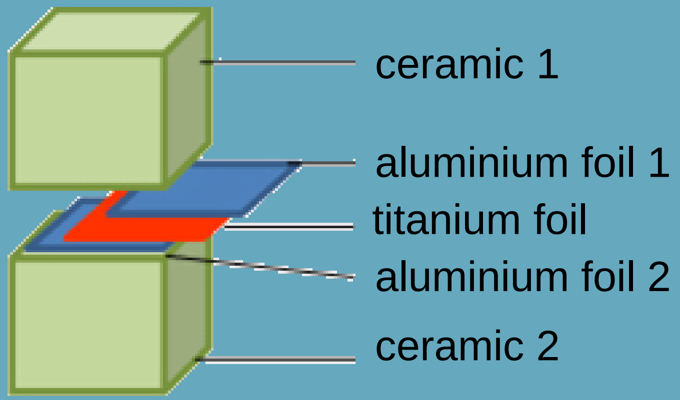
Experiments

- Basic investigations
  - DTA experiments
    - Ti- 40 Al (Ti + Al powder mix) + 50 wt%
      - Al_2O_3
      - SiC
      - Si_3N_4
  - Phase analysis of DTA samples by XRD

- Joining experiments

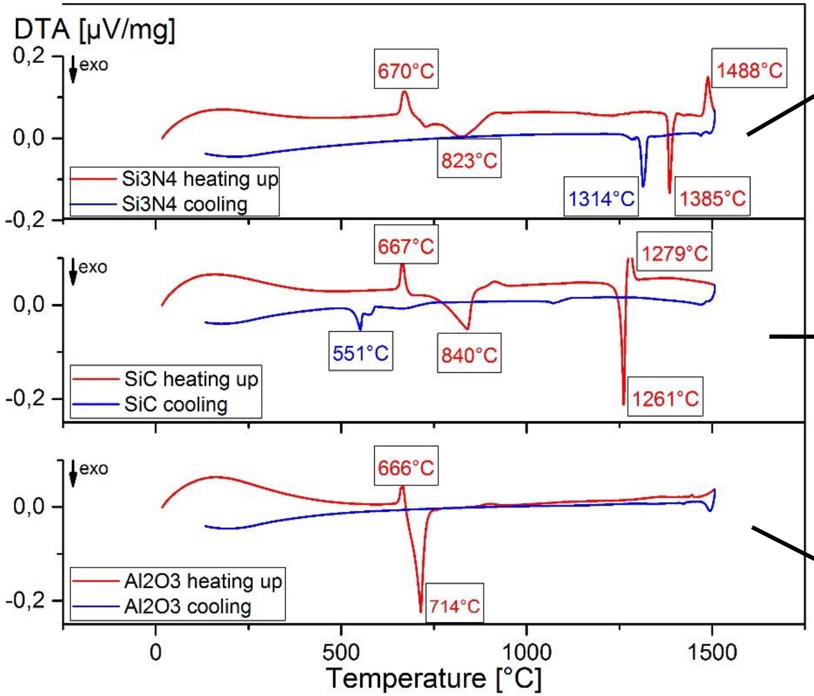


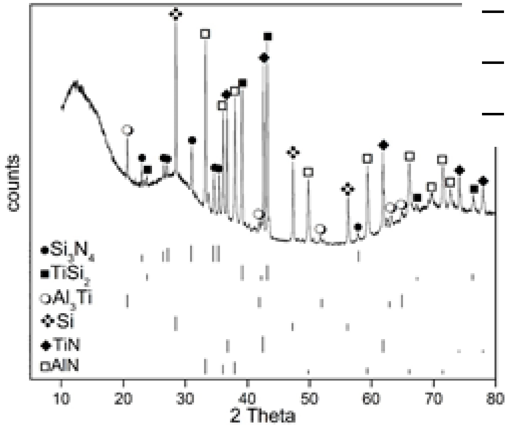
Brazing temperatures tested:

1200 °C
1300 °C
1400 °C
1450 °C
1500 °C

Basic investigations
DTA and XRD analysis

Ti + Al + Si_3N_4

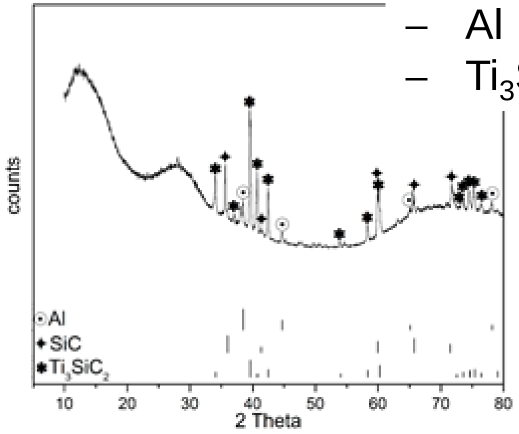




Formation of:

- Al_3Ti
- $TiSi_2$
- TiN
- AlN

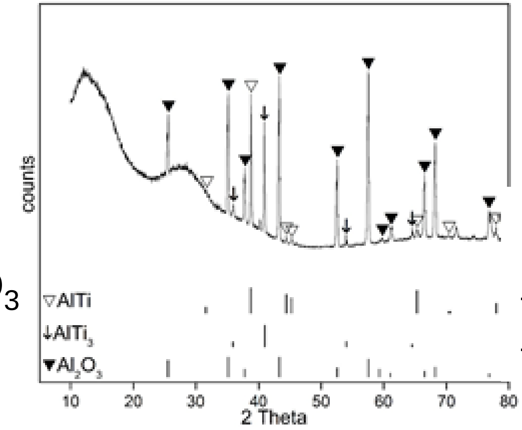
Ti + Al + SiC



Formation of:

- Al
- Ti_3SiC_2

Ti + Al + Al_2O_3

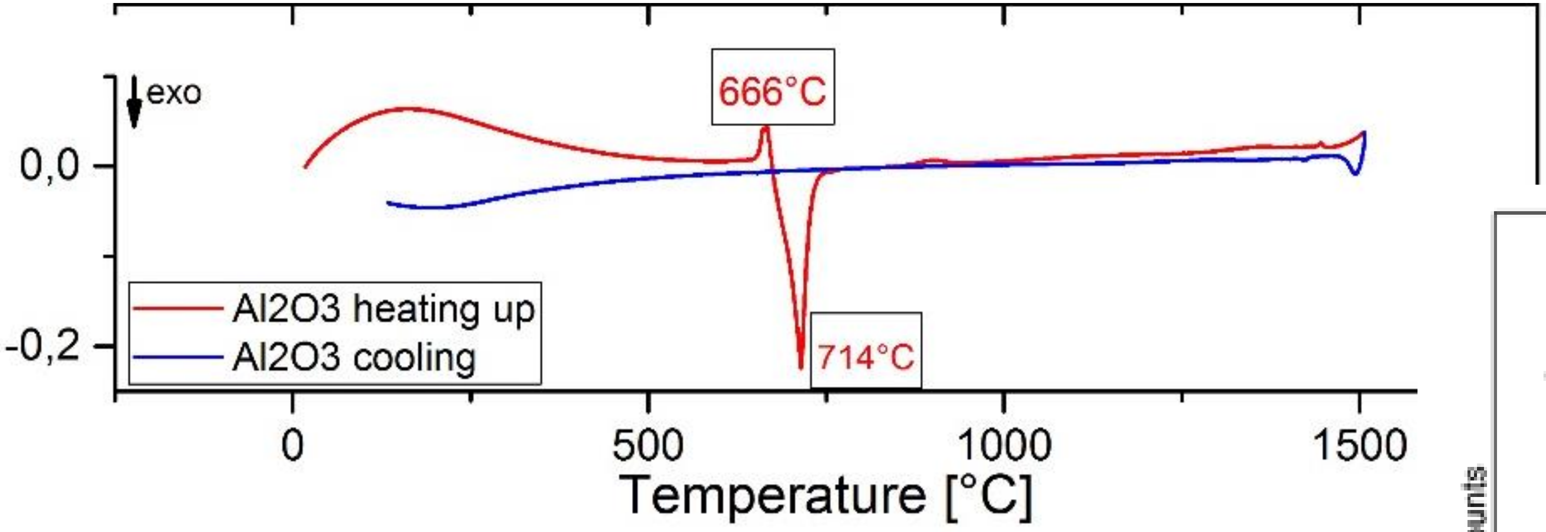


Formation of:

- AlTi
- $AlTi_3$

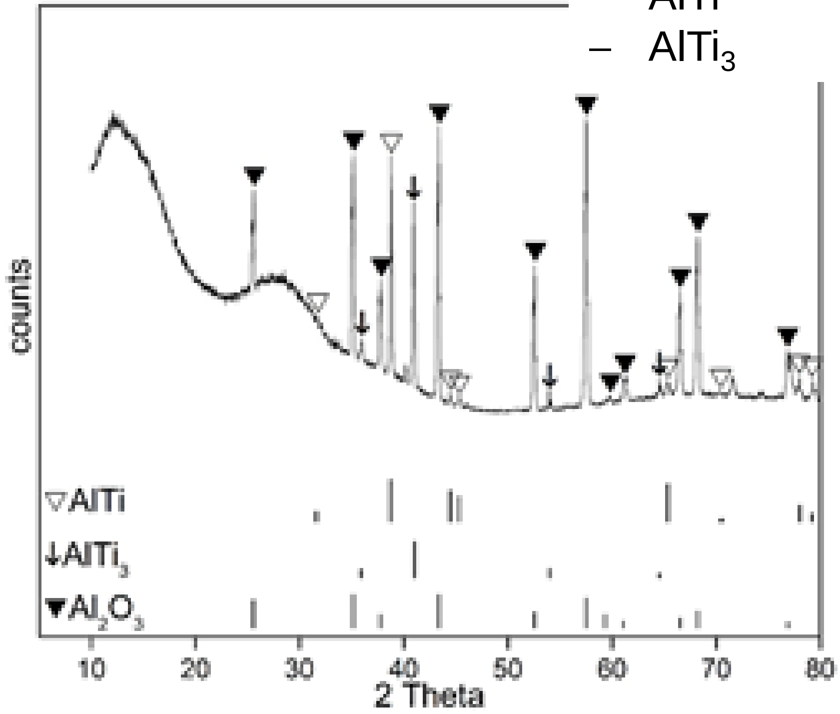
Basic investigations

DTA and XRD analysis



Formation of:

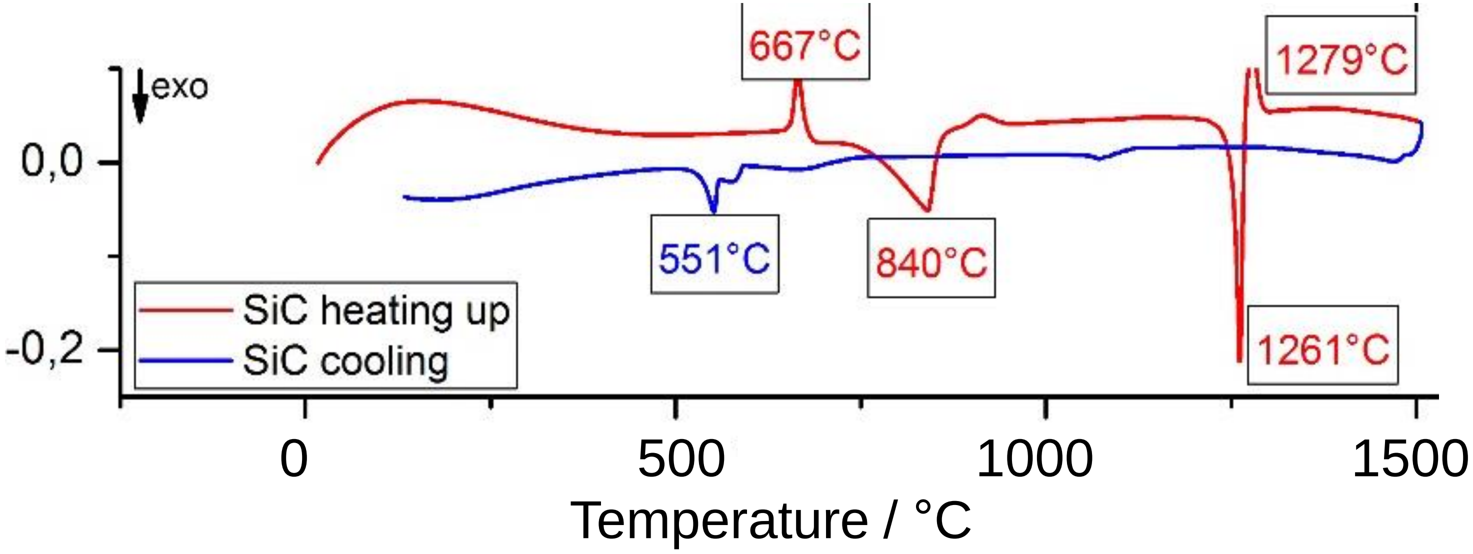
- AlTi
- $AlTi_3$



$$Ti + Al + Al_2O_3$$

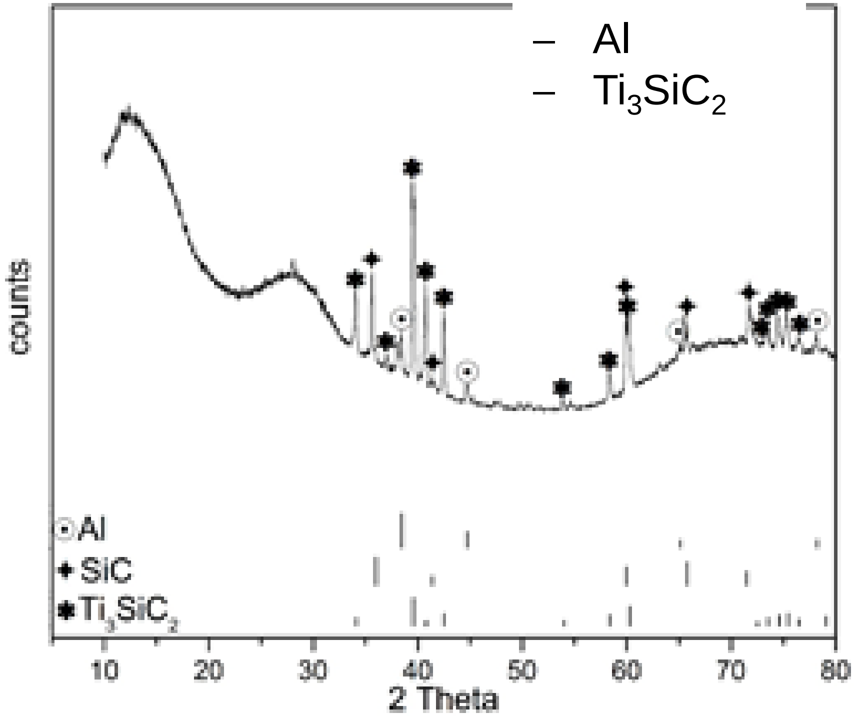
Basic investigations

DTA and XRD analysis



Formation of:

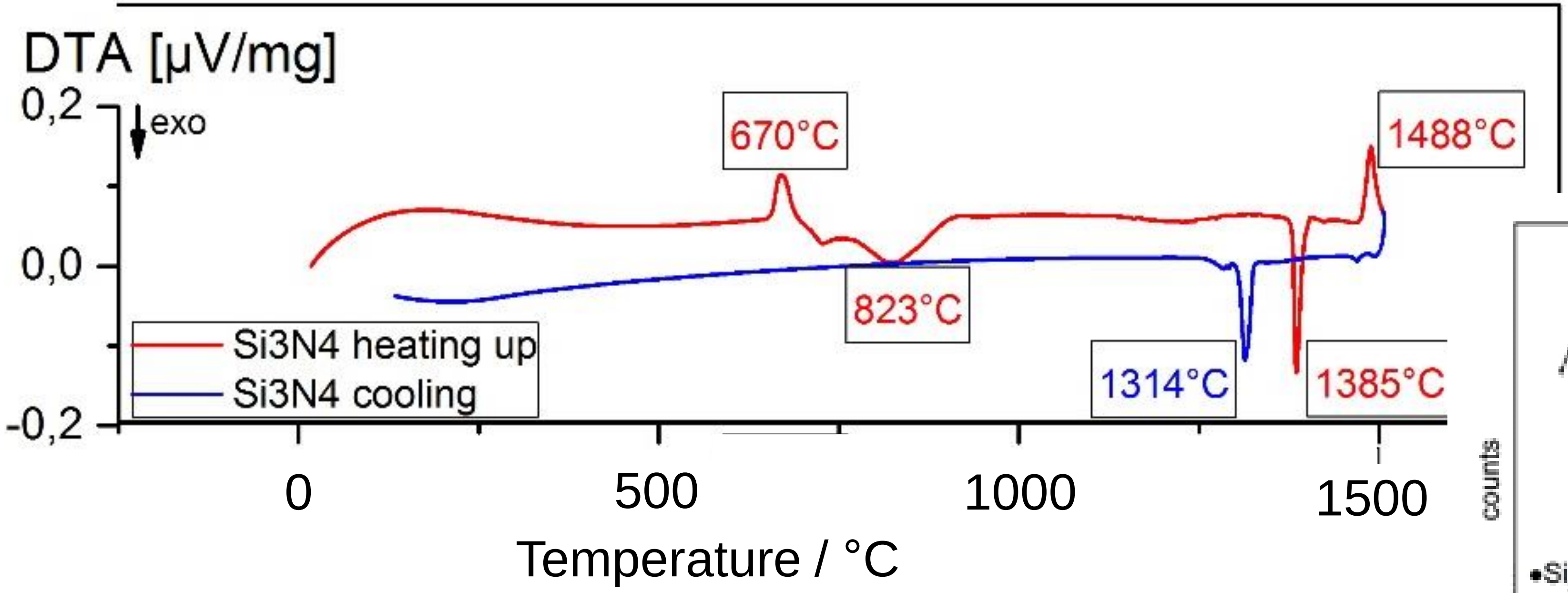
- Al
- Ti_3SiC_2

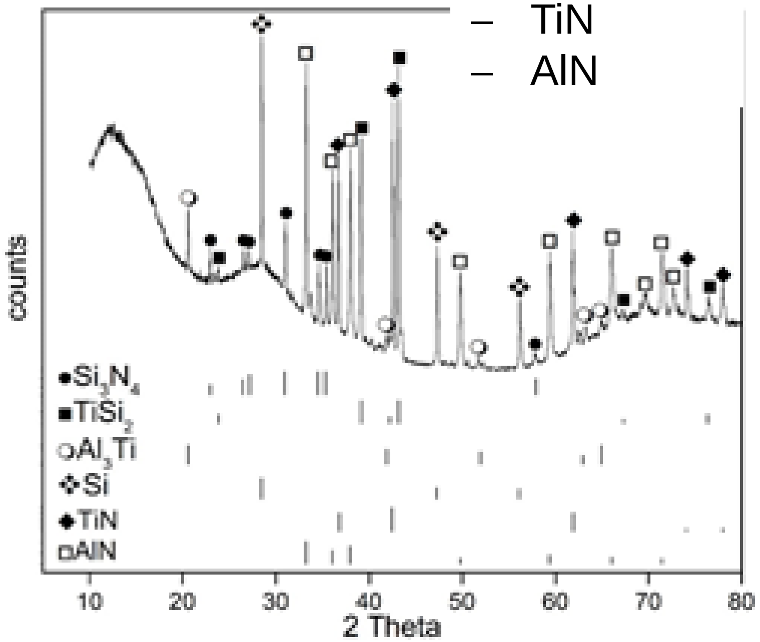


Ti + Al + SiC

Basic investigations

DTA and XRD analysis





Formation of:

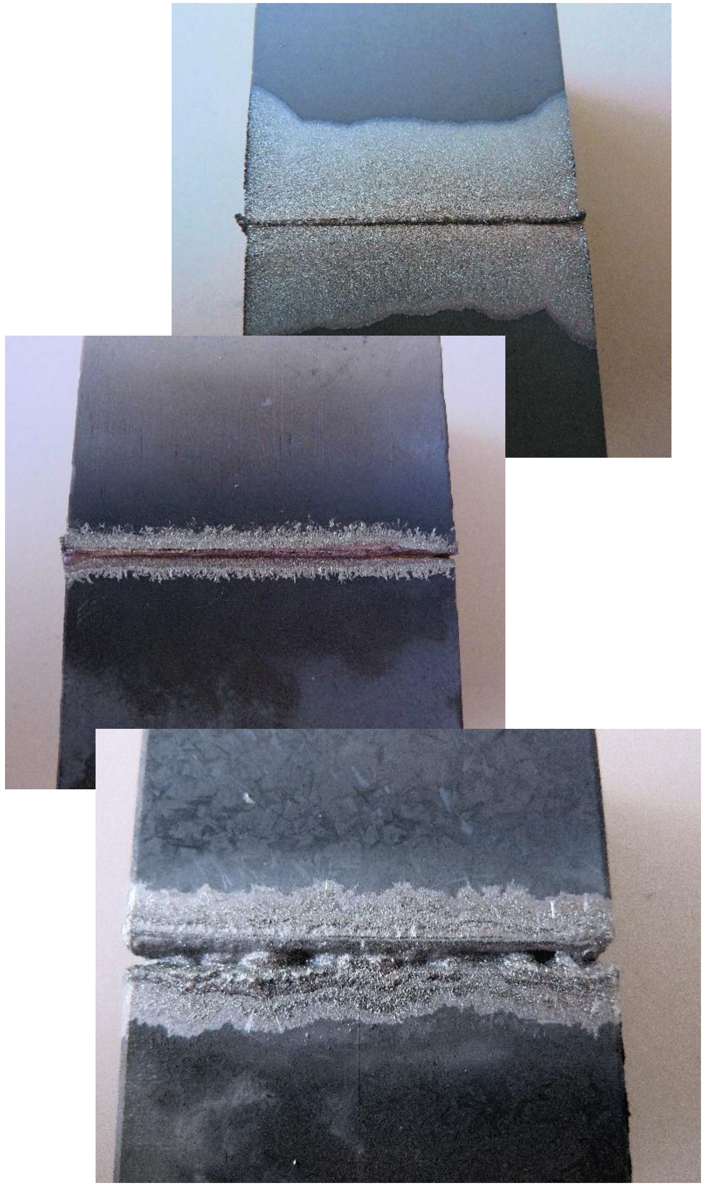
- Al_3Ti
- $TiSi_2$
- TiN
- AlN

$$Ti + Al + Si_3N_4$$

Joining experiments

pretesting after brazing procedure

Brazing temperature /°C	**ceramic**	hammer test result
< 1400 °C brazing temperature all samples failed by hammer test		
1400	**Al_2O_3**	failed
1400	**SiC**	passed
1400	**Si_3N_4**	passed
1450	**Al_2O_3**	passed
1450	**SiC**	failed
1450	**Si_3N_4**	failed
1500	**Al_2O_3**	passed
1500	**SiC**	failed
1500	**Si_3N_4**	passed

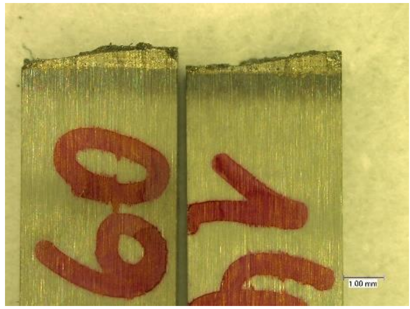


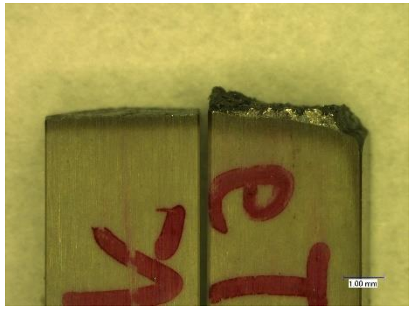
Joining experiments

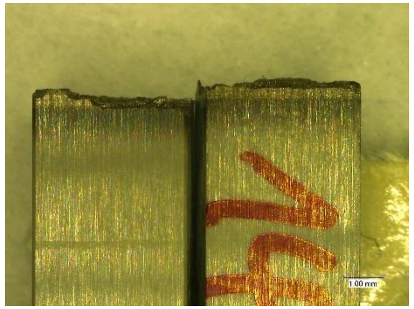
mechanical strength of joined ceramic

Brazing at:	Ceramic type	4 point – bending - strength MPa
1400 °C	SiC	39 ±
1400 °C	Si_3N_4	10 ±
1450 °C	Al_2O_3	44 ±
1500 °C	Si_3N_4	27 ±
1500 °C	Al_2O_3	69 ±

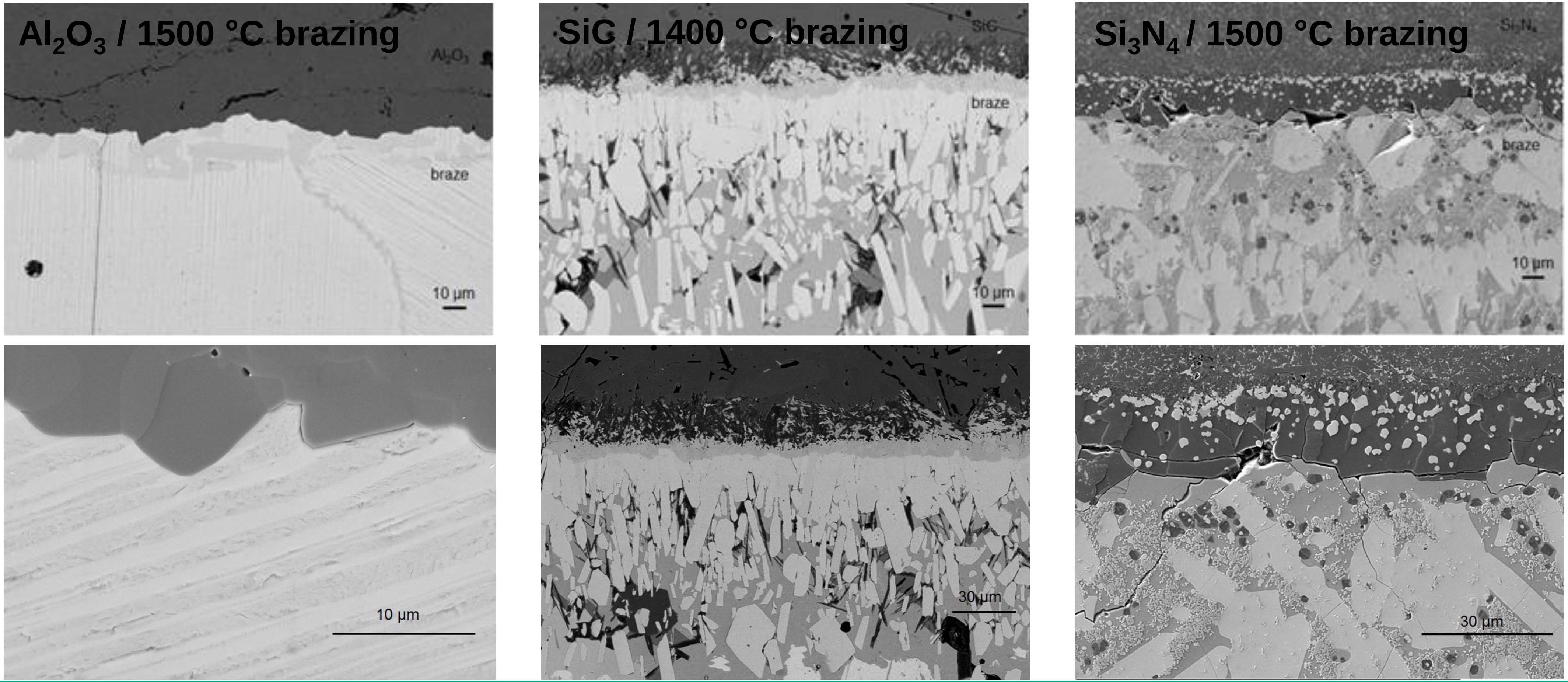
		4 point – bending - strength at 800 °C MPa
1500 °C	Si_3N_4	177





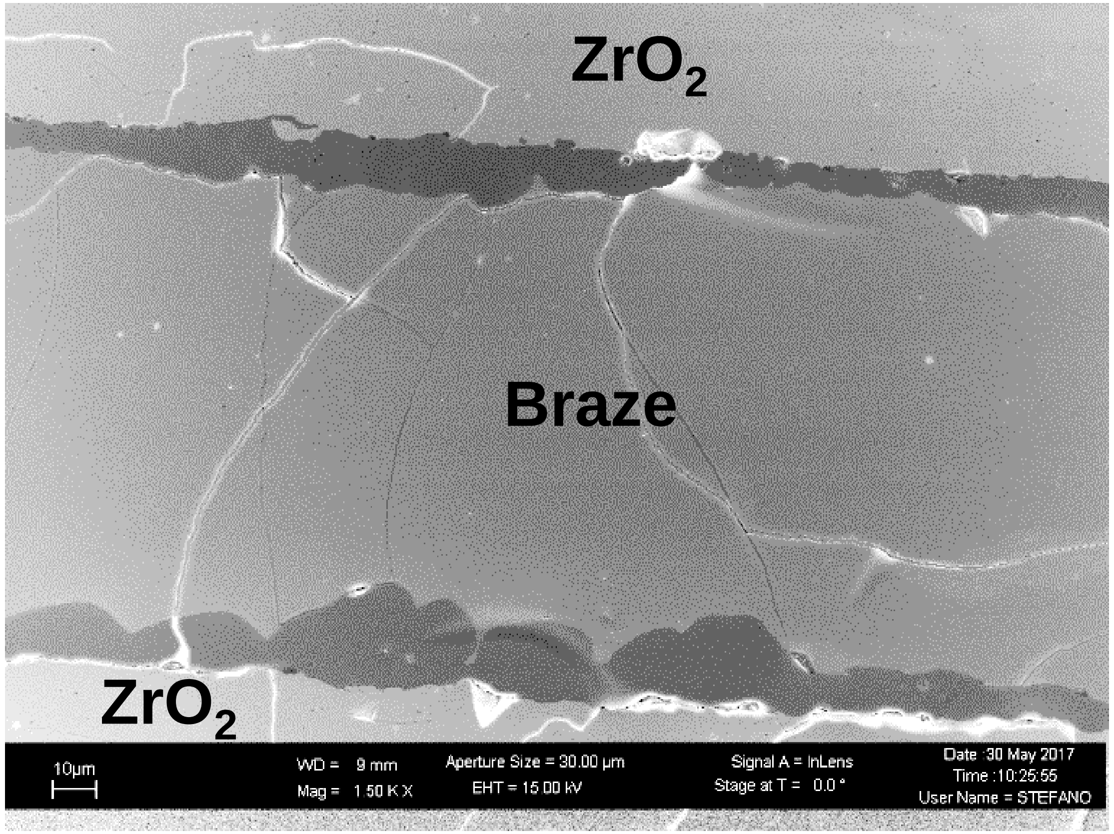


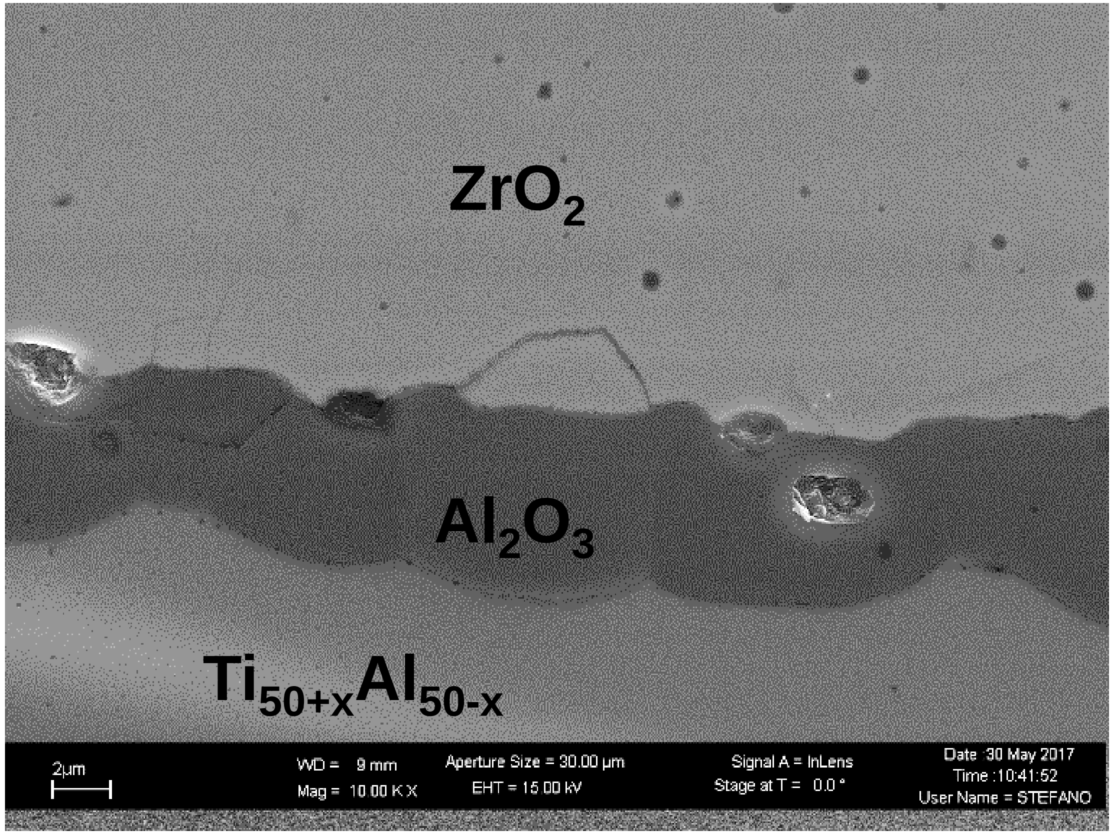
Joining experiments
microstructure of joining zone by FESEM



Joining experiments
microstructure of joining zone by FESEM

ZrO_2 + $Ti_{50}Al_{50}$ / 1700 °C brazing





Summary and outlook TiAl braze alloys

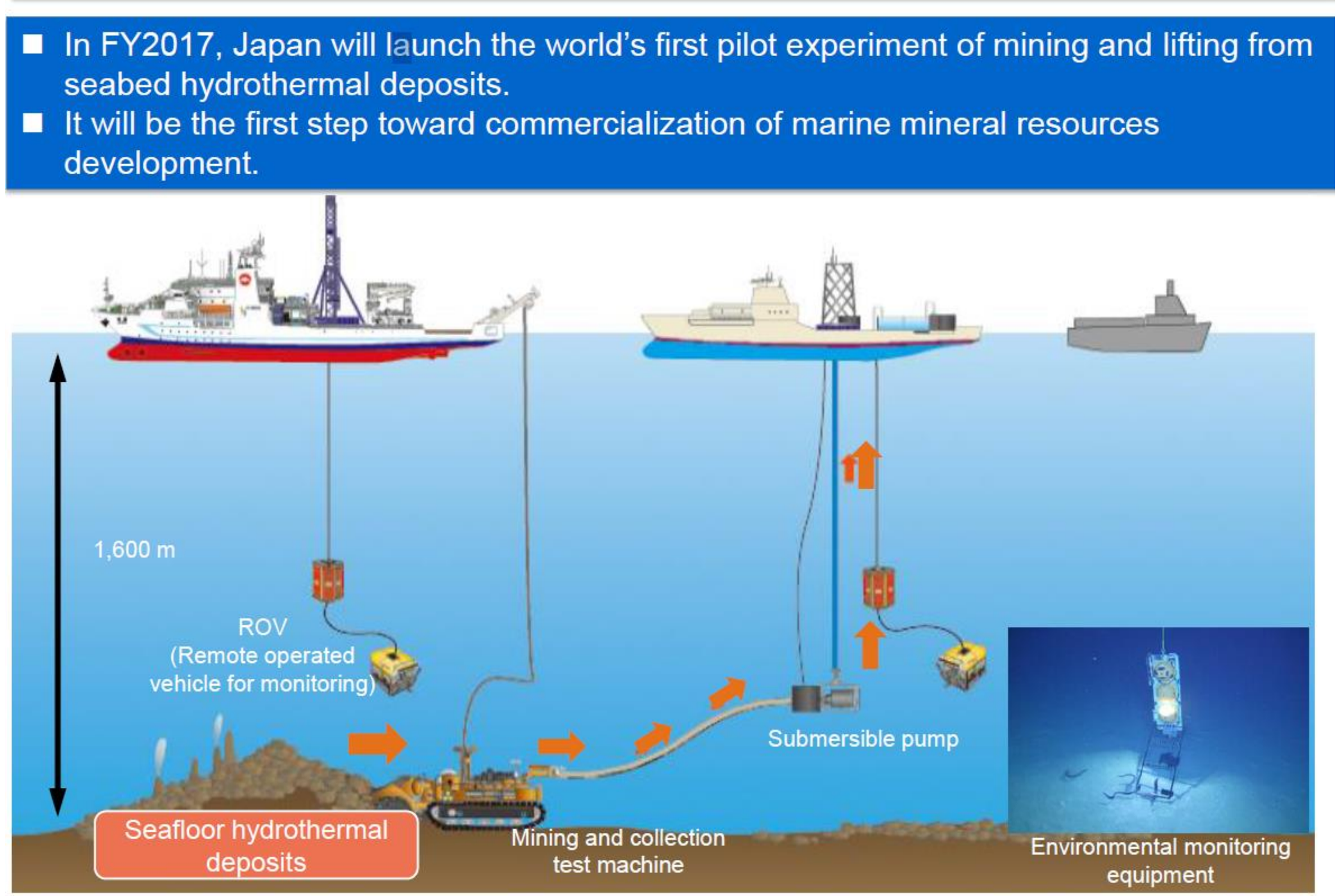
- Strong chemical interactions occur between TiAl braze and SiC / Si_3N_4 ceramics while a medium reaction occurs with ZrO_2 and no chemical interaction occurs with Al_2O_3
- the optimum joining temperature depends on the found interactions between braze and ceramic
- reliable ceramic joining can be reached, particularily outstanding high temperature strength was obtained
- Specific investigations need to be done for tuning the process parameters

  → Polito: 700 °C up to 1400 °C powder mixtures of braze ceramic 1:1

  → CNR Genova: arc melting, rolling of foils, wetting angles

Further projects

- Braze alloys or for Super High working temperature up to 1600 °C (systems TaZr, TiZr, WZr, WTi, NiZr)
- Braze alloys or for sub sea systems (crofer, Inconel, SiC, H_2S corrosion)
- Innovative glueing of ceramics up to 1000 °C working temperature



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