Advanced Ceramic Technologies

Non-oxide ceramics

M. Stuer

Outline

- General aspects related to non-oxide ceramics
- Liquid phase sintering of carbides
- Ultra-high temperature ceramics
  - Potential of solid solution and high entropy ceramics
- MAX phases and their synthesis/sintering

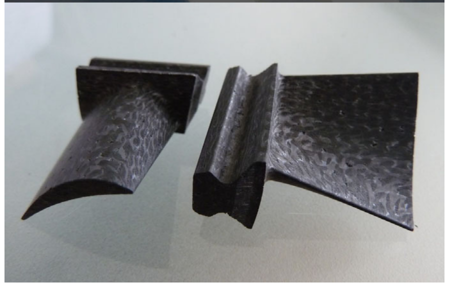
Learning objectives:

- Learn basic principles related to non-oxide ceramics
- Be able to select sintering additives based on theoretical grounds
- Learn basics on MAX phase synthesis/sintering illustrating the phase purity issue

Typical applications of non-oxide ceramics

Non-oxide ceramics play a **critical role** in **numerous application fields** such as

- **Cutting tools** due to wear resistance of
  - CerMets (i.e. carbides (ex. TiC), nitrides (ex. TiN) or carbonitrides (ex. TiCN) with Ni, Co, Mo-based binders)
  - Cemented carbides (i.e. carbides with mostly only Co binder (ex. WC/Co))
- **Hypersonic aerospace** due to high temperature resistance of
  - Refractory carbides and borides (i.e. ultra-high temperature ceramics (UHTCs))
- **Gas turbines** due to high temperature, toughness and creep resistance of
  - SiC/SiC ceramic matrix composites



Typical applications of non-oxide ceramics

Non-oxide ceramics play a **critical role** in **numerous application fields** such as

- **Jewelry** due to metallic luster and high hardness of
  - Certain interstitial carbides (e.g. WC, TiC) and nitrides (e.g. TiN, ZrN)
- **Heating elements in oxidizing atmospheres** due to electrical conductivity, high temperature resistance and formation of stable oxide layer of
  - $MoSi_2$ and SiC
- **Biomedical** due to high mechanical properties and osteoconductivity and antibacterial action of
  - Si_3N_4 (typically known as SiAlON due to sintering aids
- **Armour** due to extremely high hardness, low density and high energy dissipation due to microcracking of
  - Ultrahard lightweight B_4C

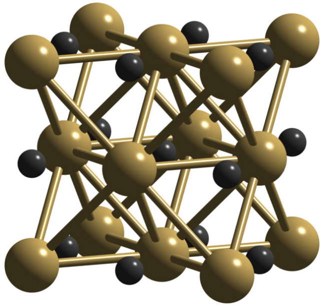
Interstitial vs Covalent non-oxide ceramics

Interstitial non-oxide ceramics

- TiC, NbC, VN, ZrB_2, HfH_2, $MoSi_2$, …
- Small non-metal atoms ($r_{NM}/r_M < 0.59$) occupy interstitial spaces of metal lattices
- Metal-metal bond dominate
  ➔ Good electrical conductivity
- Highly **non-stoichiometric** compounds

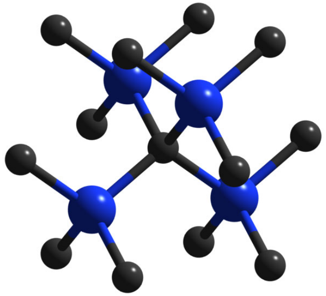
Covalent non-oxide ceramics

- SiC, B_4C, BN, AlN, Si_3N_4, diamond, …
- Secondary atoms are too large to fit into the interstitial spaces
- Oriented and hybridized covalent bonds
  ➔ Low electrical conductivity
- Typically hard, lightweight and refractory



TiC

Material	Type	Density [g cm^{-3}]	Melting point [°C]	Electrical resistivity [Ω cm]	⇔	Thermal conductivity [W m^{-1}K^{-1}]
TiC	Interstitial	4.9	3160	$\sim10^{-3}$	Non-stoichiometry (e.g. defects) ➔ **Phonon scattering**	20–30
ZrC	Interstitial	6.6	3540	$\sim10^{-3}$		~20
HfC	Interstitial	12.7	3900	$\sim10^{-3}$	Heavy metal atoms ➔ **Slow phonon velocity**	18–23
TaC	Interstitial	14.5	3880	$\sim10^{-3}$	Defects, d-orbitals and high DOS ➔ **Electron-phonon scattering**	22–27
TiN	Interstitial	5.4	2950	$\sim10^{-3}$		~30
SiC	Covalent	3.2	2830	10^5–10^8		120–270
B_4C	Covalent	2.5	2763	$\sim10^6$		30–60
h-BN	Covalent	2.3	2973	$\sim10^{14}$		~60
c-BN	Covalent	3.5	2973	10^5–10^6		200–400



SiC

Carbides and their sintering

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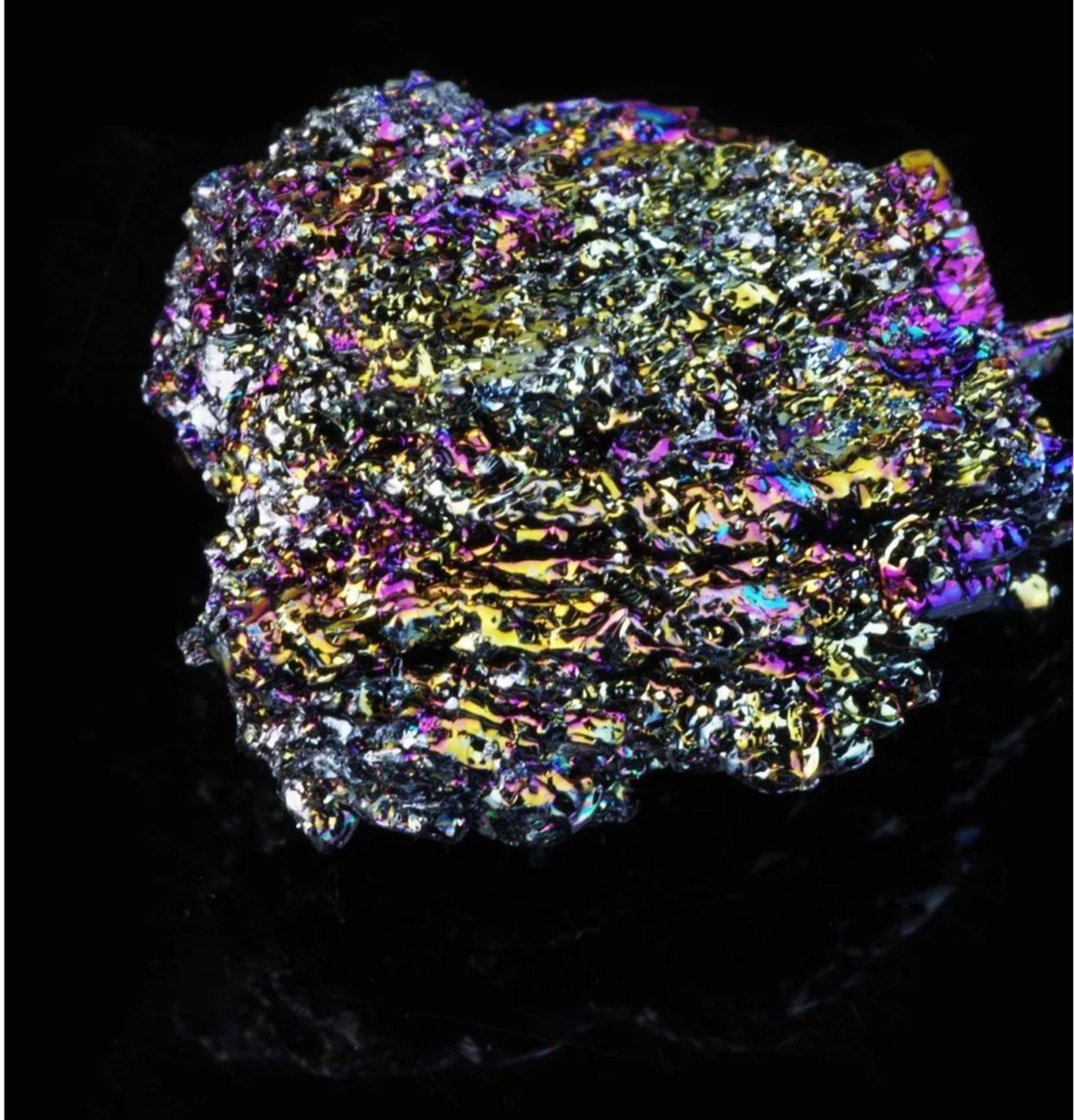


Sintering of carbides - Generalities

Interstitial carbides

- Less reaction risk with sintering aides
- Simple liquid forming metals (Ni, Co, Fe) wet carbide very well
  ➔ Good liquid phase sintering
- Native surface oxide layer hindering sintering less stable
  ➔ Easily removed during sintering
  ➔ Addition of reducing agents beneficial especially with nanopowders

Covalent carbides

- Covalent bonding reduces self diffusivity
- Wetting of carbide by liquid forming metals may be limited
  ➔ Risk of poor liquid phase sintering
- Native surface oxide layer hindering sintering very stable
  ➔ Difficult to remove during sintering
  ➔ Addition of strong reducing agents often necessary

- **Solid and/or liquid sintering aids typically used**
  - **Solid** sintering aid: Reduce the grain boundary versus surface energy to promote sintering
  - **Liquid** sintering aid: Promote sintering by forming liquid phase
    Wetting of powder required
    ➔ $\gamma_{sv} > \gamma_{sl} + v_{lv}$ (solid-vapor, solid-liquid, liquid-vapor)
- Sintering additives **must not decompose/react with the carbide**
  ➔ Must be **carefully selected** based on their reactivity

Case study: Liquid phase sintering of β-SiC – metal aids

Reminder: Chemical reaction occurs when

$$\Delta \boldsymbol{G_f^0(T)} = \Delta H_f^0 - T\Delta S_f^0 = \left(\Delta H_{f,298}^0 + \int_{298}^{T} \Delta C_p dT\right) - T\left(\Delta S_{f,298}^0 + \int_{298}^{T} \frac{\Delta C_p dT}{T}\right) < \mathbf{0}$$

Selection of metal sintering aids

- Upon addition of a metal M formation of metal carbide M_xC_y and/or metal silicide M_pSi_q can occur by reaction with $\beta - SiC$

$$\Delta G_2^0\text{: } \mathrm{a}SiC(s) + bM(s,l) \rightarrow cM_xC_y(s,l) + aSi(s,l)$$
$$\Delta G_3^0\text{: } \mathrm{a}SiC(s) + bM(s,l) \rightarrow dM_pSi_q(s,l) + aC(s)$$

- $\Delta G_2^0 = \Delta G_5^0 - \Delta G_4^0$ and $\Delta G_3^0 = \Delta G_6^0 - \Delta G_4^0$ with:

$$\Delta G_4^0\text{: } \mathrm{a}Si(s,l) + aC(s) \rightarrow aSiC(s)$$
$$\Delta G_5^0\text{: } bM(s,l) + aC(s) \rightarrow cM_xC_y(s,l)$$
$$\Delta G_6^0\text{: } bM(s,l) + aSi(s,l) \rightarrow dM_pSi_q(s,l)$$

source: 10.1016/j.ceramint.2016.09.022

Case study: Liquid phase sintering of β-SiC – metal aids

- Metal $\boldsymbol{M}$ **does not decompose** SiC if

  $\Delta G_2^0 = \Delta G_5^0 - \Delta G_4^0 > 0$ and
  $\Delta G_3^0 = \Delta G_6^0 - \Delta G_4^0 > 0$

  ➔ for appropriate $\boldsymbol{M}$

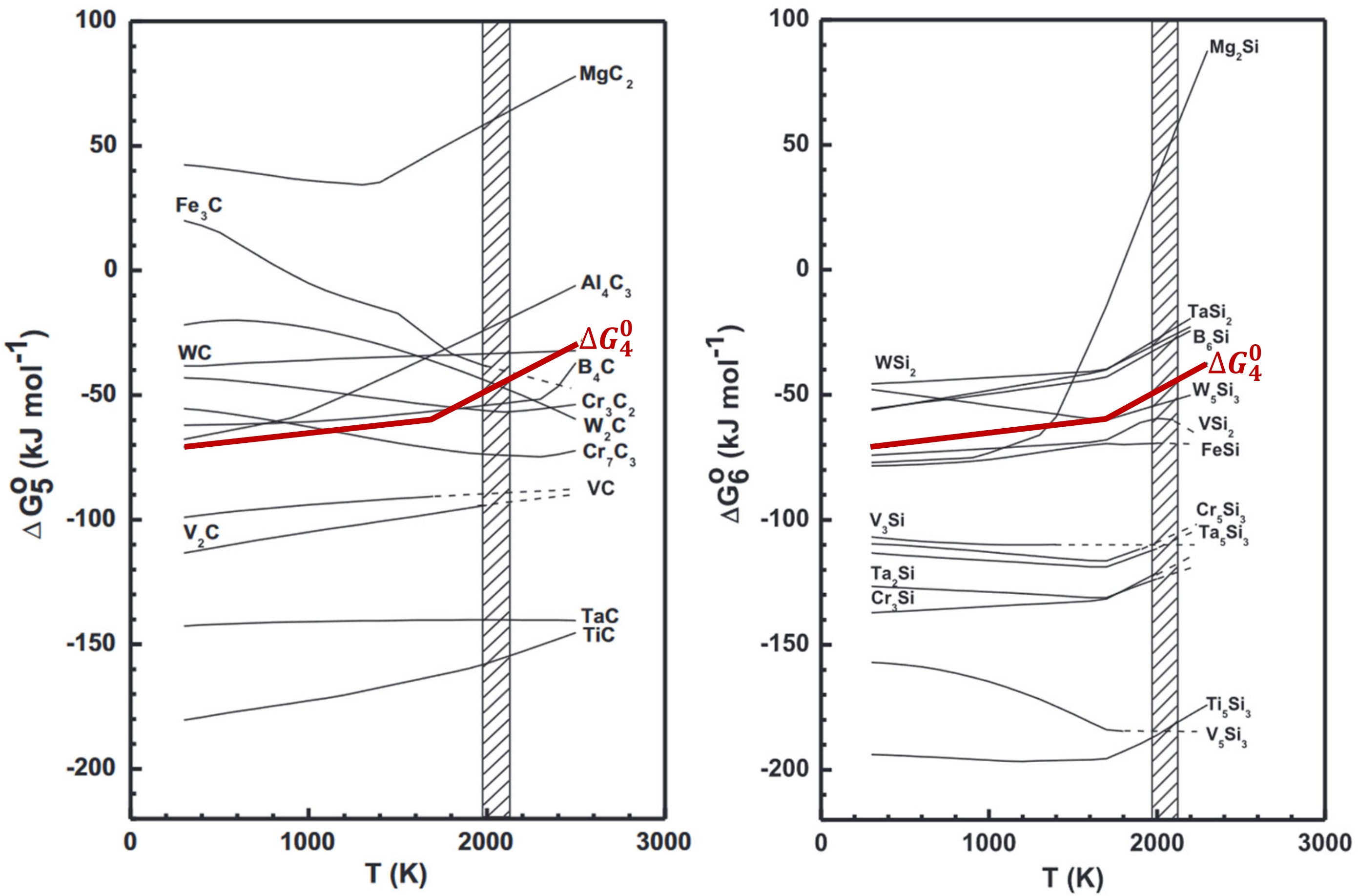
  $\boldsymbol{\Delta G_5^0 > \Delta G_4^0}$ **and**
  $\boldsymbol{\Delta G_6^0 > \Delta G_4^0}$

- **No carbide formation** from SiC degradation with:
  - Mg, Fe and Al
- **No silicide formation** from SiC degradation with:
  - Mg, Ta and B
  - Al silicide not possible at these conditions

➔ **Al and Mg suitable**

ΔG_5^0 vs. Temperature T for various metal carbides

ΔG_6^0 vs. Temperature T for various metal silicides



Hatched area: liquid phase hot pressing temperature range of β-SiC (1973–2123 K)

source: 10.1016/j.ceramint.2016.09.022

Case study: Liquid phase sintering of β-SiC – metal aids

Note: Sintering done at **very high temperatures**!

- For metal sintering aid to be effective it must also **not evaporate** during sintering

$$\mathrm{M(s)} \leftrightarrow M(v)$$
$$\Delta G = \Delta G^0 + RT\ln K$$

- Under equilibrium conditions $\Delta G = 0$

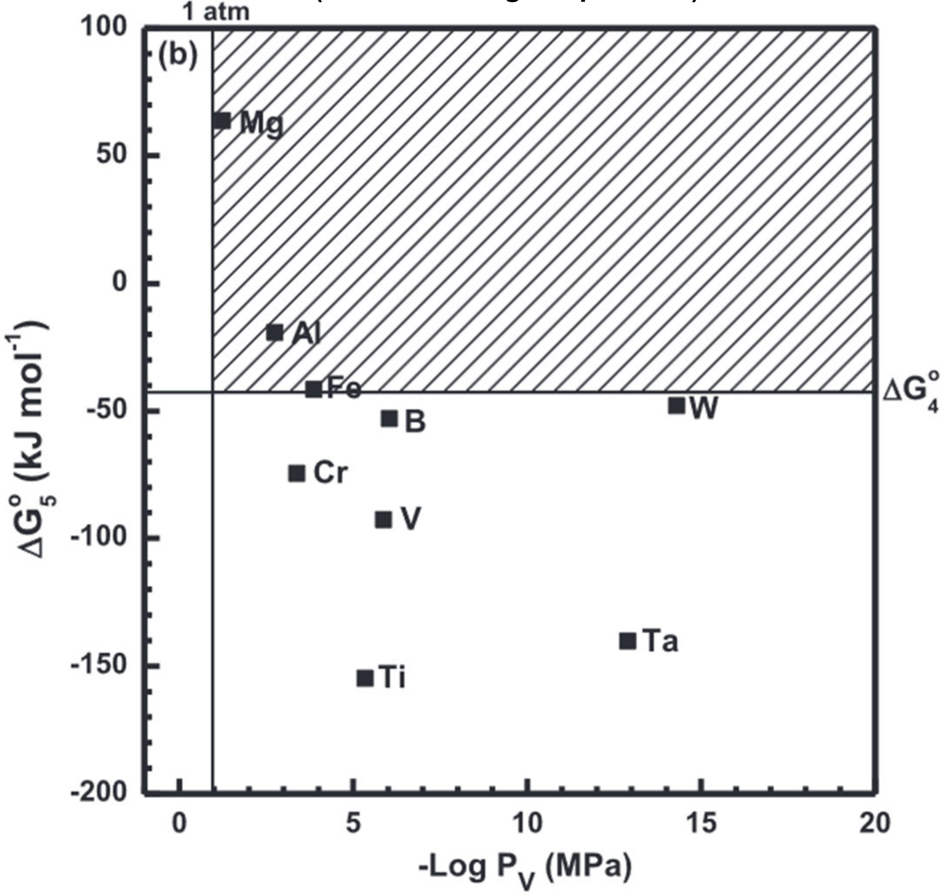
$$\Rightarrow \ln K = -\frac{\Delta G^0}{RT} \text{ with } K = P_v$$

- Evaporation **neglectable if**

$$\boldsymbol{P_v < 1\,atm \approx 1\,MPa}$$

➔ Mg and Al are suitable

ΔG_5^0 vs. vapor pressures P_v for metals at 2123 K (=max sintering temperature)



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Case study: Liquid phase sintering of β-SiC – metal aids

- **Carbon and/or boron** typically introduced as strong reducing agents to remove surface oxide layers
  - **Carbon:**

$$SiO_2\ (s) + 3C\ (s) \rightarrow SiC\ (s) + 2CO\ (g)$$

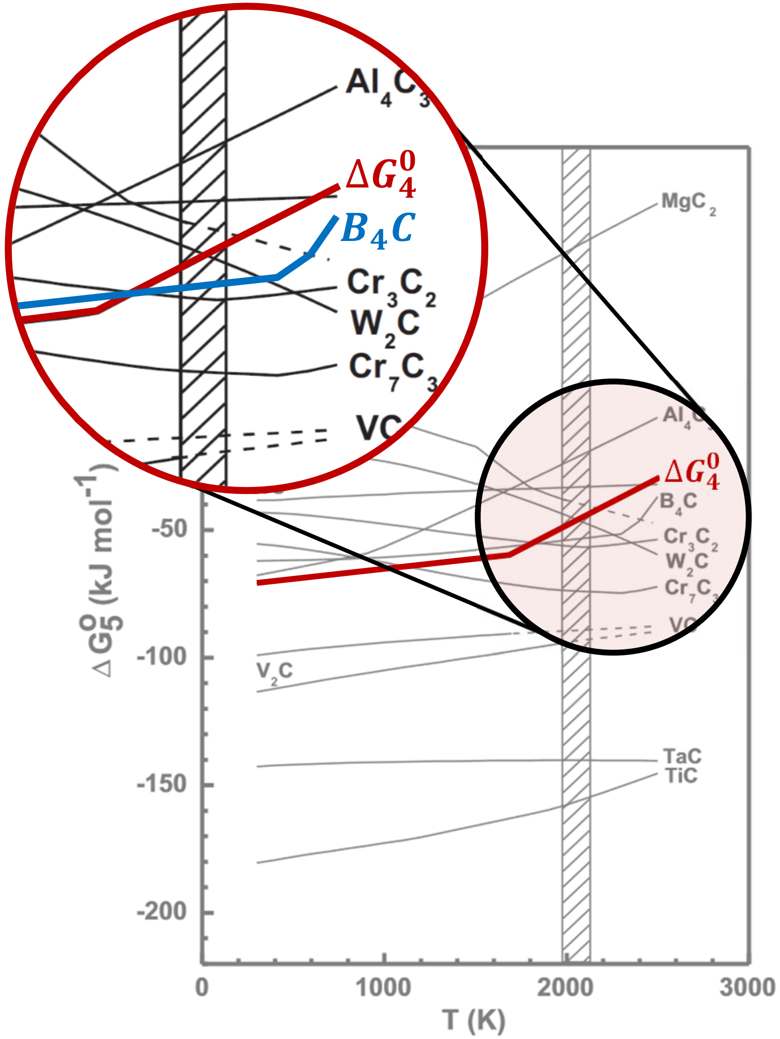
  - **Boron:**

$$2B\ (s) + 3SiO_2(s) \rightarrow B_2O_3\ (l) + 3SiO\ (g)$$

In presence of carbon boron is restored:

$$B_2O_3\ (l) + 3C\ (s) \rightarrow 2B\ (s) + 3CO\ (g)$$

- However, **B can also react with SiC** (see insert) to form B_4C
  ➔ Add B with excess C to "neutralize" B



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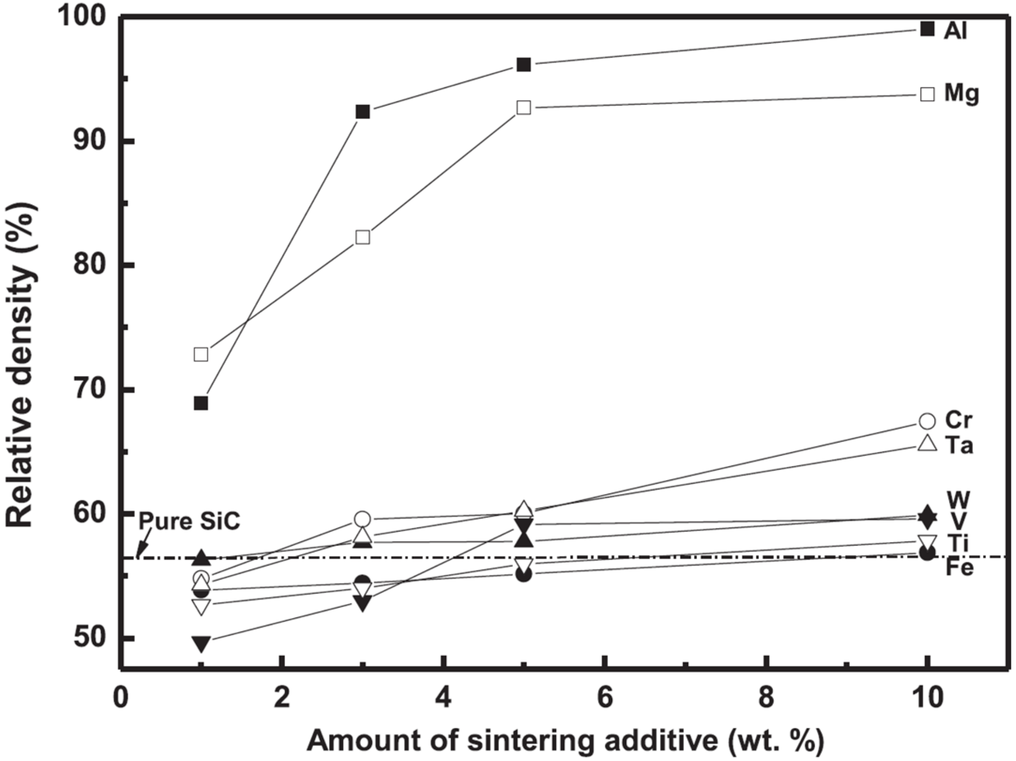
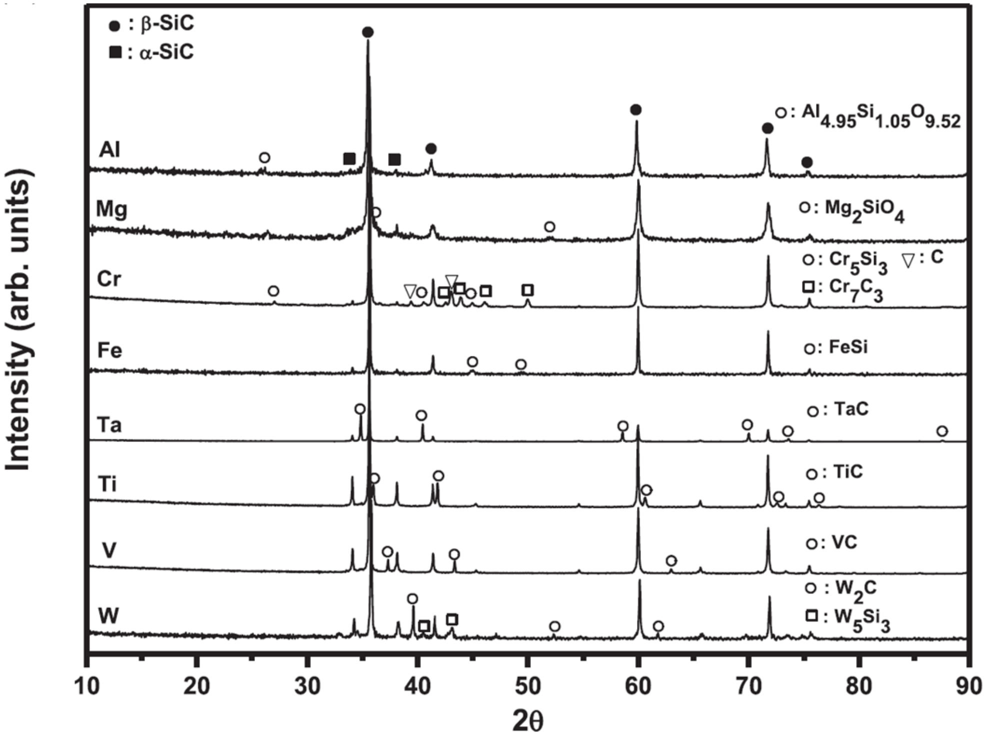
Case study: Liquid phase sintering of β-SiC – metal aids

- **Absence of reaction** during LPS yields **higher densities** (e.g. no gas formation)





- Amount of **additives limited** (ideally below 5 wt.%) to **preserve SiC properties**

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Case study: Liquid phase sintering of β-SiC – metal oxide aids

Selection of metal oxide sintering aids

- Upon addition of a metal M formation of metal carbide M_xC_y and/or metal silicide M_pSi_q can occur by reaction with $\beta - SiC$

$$\Delta G_{11}^0\text{: } {}^2/_3\, SiC(s) + bM_vO_w(s) \rightarrow {}^2/_3\, SiO_2(s,l) + aM(s,l) + {}^2/_3\, CO(g)$$
$$\Delta G_{12}^0\text{: } {}^2/_3\, SiC(s) + dM_vO_w(s) \rightarrow {}^2/_3\, SiO_2(s,l) + cM_xC_y(s,l) + eCO(g)$$
$$\Delta G_{13}^0\text{: } {}^2/_3\, SiC(s) + mM_vO_w(s) \rightarrow rSiO_2(s,l) + kM_pSi_q(s,l) + {}^2/_3\, CO(g)(s)$$

- $\Delta G_{11}^0 = \Delta G_{10}^0 - \Delta G_{14}^0$, $\Delta G_{12}^0 = \Delta G_{10}^0 - \Delta G_{15}^0$ and $\Delta G_{13}^0 = \Delta G_{10}^0 - \Delta G_{16}^0$ with:

$$\Delta G_{10}^0\text{: } {}^2/_3\, SiC(s) + O_2(g) \rightarrow {}^2/_3\, SiO_2(s,l) + {}^2/_3\, CO(g)$$

➔ most probable oxidation reaction of between 1700-1900°C

$$\Delta G_{14}^0\text{: } aM(s,l) + O_2(g) \rightarrow bM_vO_w(s)$$
$$\Delta G_{15}^0\text{: } cM_xC_y(s,l) + O_2(g) \rightarrow dM_vO_w(s) + eCO(g)$$
$$\Delta G_{16}^0\text{: } kM_pSi_q(s,l) + O_2(g) \rightarrow mM_vO_w(s) + rSiO_2(s,l)$$

- If $\Delta G_{10}^0 > \Delta G_{14}^0, \Delta G_{15}^0\ and\ \Delta G_{16}^0$ the M_vO_w oxide will not decompose the $\beta - SiC$ and may be suitable as a sintering additive

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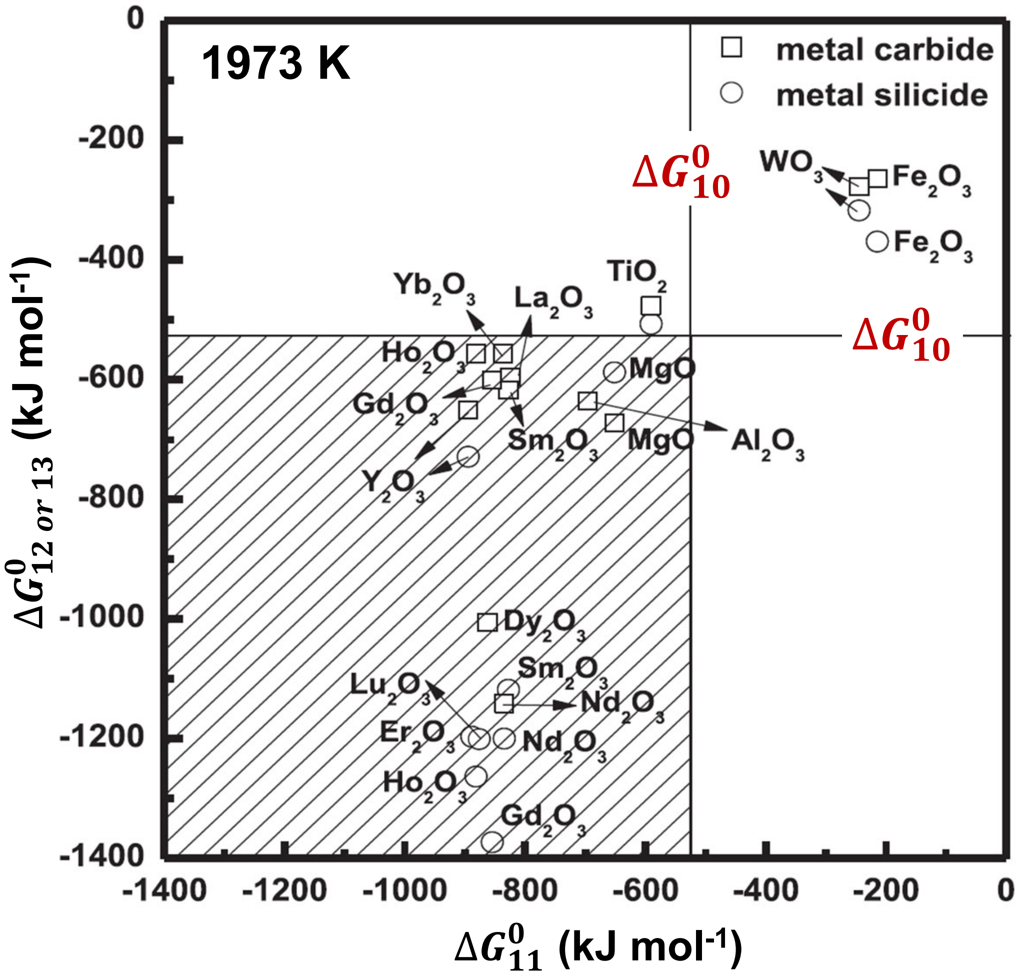
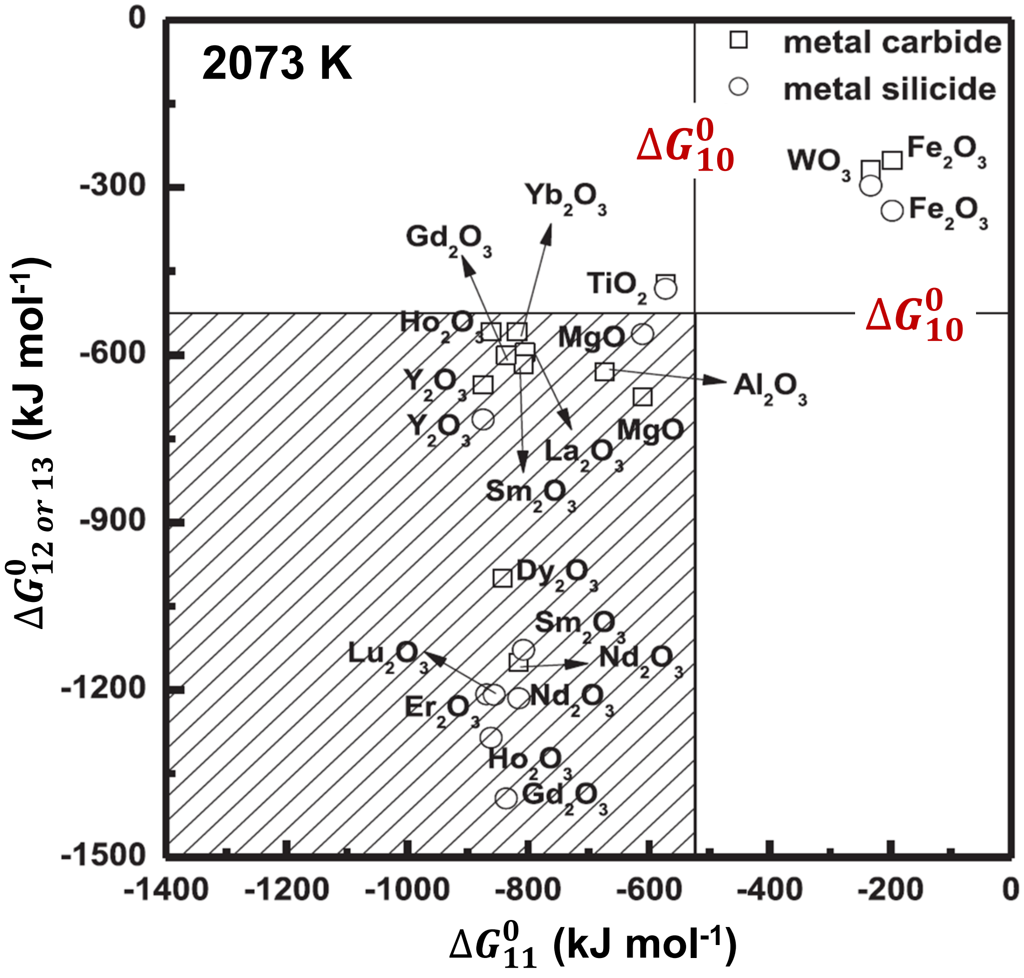
Case study: Liquid phase sintering of β-SiC – metal oxide aids





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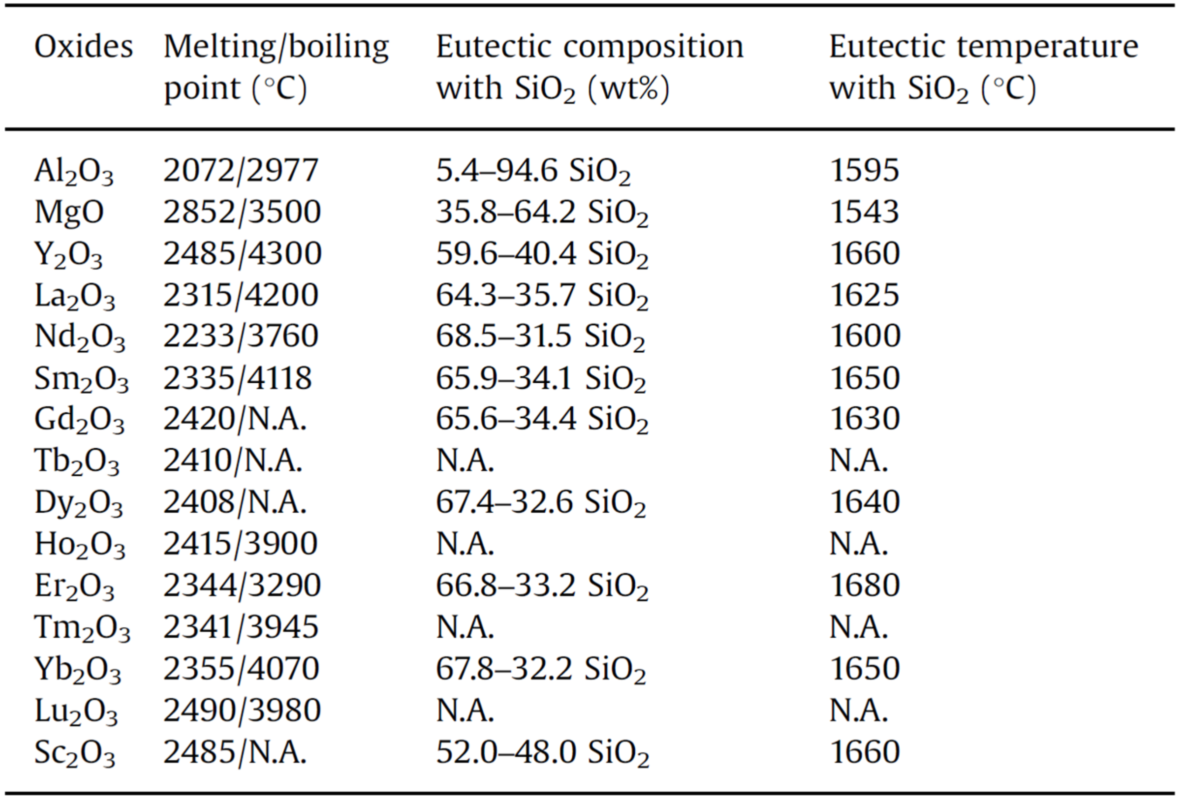
Case study: Liquid phase sintering of β-SiC – metal oxide aids

Note: Melting temperature of metal oxide additives high

- Need of liquid phase for LPS
- Native surface oxide (SiO_2) plays a significant role
  - **Eutectic** formation with metal oxide sintering aids
  - All **eutectic temperatures below** typical SiC sintering temperatures
- Contact and dihedral angle affect LPS performance and microstructural development

Melting/boiling temperatures of oxide sintering additives including eutectic composition and associated melting temperatures with SiO_2 (native surface oxide)



Oxides	Melting/boiling point (°C)	Eutectic composition with SiO_2 (wt%)	Eutectic temperature with SiO_2 (°C)
Al_2O_3	2072/2977	5.4–94.6 SiO_2	1595
MgO	2852/3500	35.8–64.2 SiO_2	1543
Y_2O_3	2485/4300	59.6–40.4 SiO_2	1660
La_2O_3	2315/4200	64.3–35.7 SiO_2	1625
Nd_2O_3	2233/3760	68.5–31.5 SiO_2	1600
Sm_2O_3	2335/4118	65.9–34.1 SiO_2	1650
Gd_2O_3	2420/N.A.	65.6–34.4 SiO_2	1630
Tb_2O_3	2410/N.A.	N.A.	N.A.
Dy_2O_3	2408/N.A.	67.4–32.6 SiO_2	1640
Ho_2O_3	2415/3900	N.A.	N.A.
Er_2O_3	2344/3290	66.8–33.2 SiO_2	1680
Tm_2O_3	2341/3945	N.A.	N.A.
Yb_2O_3	2355/4070	67.8–32.2 SiO_2	1650
Lu_2O_3	2490/3980	N.A.	N.A.
Sc_2O_3	2485/N.A.	52.0–48.0 SiO_2	1660

source: 10.1016/j.ceramint.2016.09.022

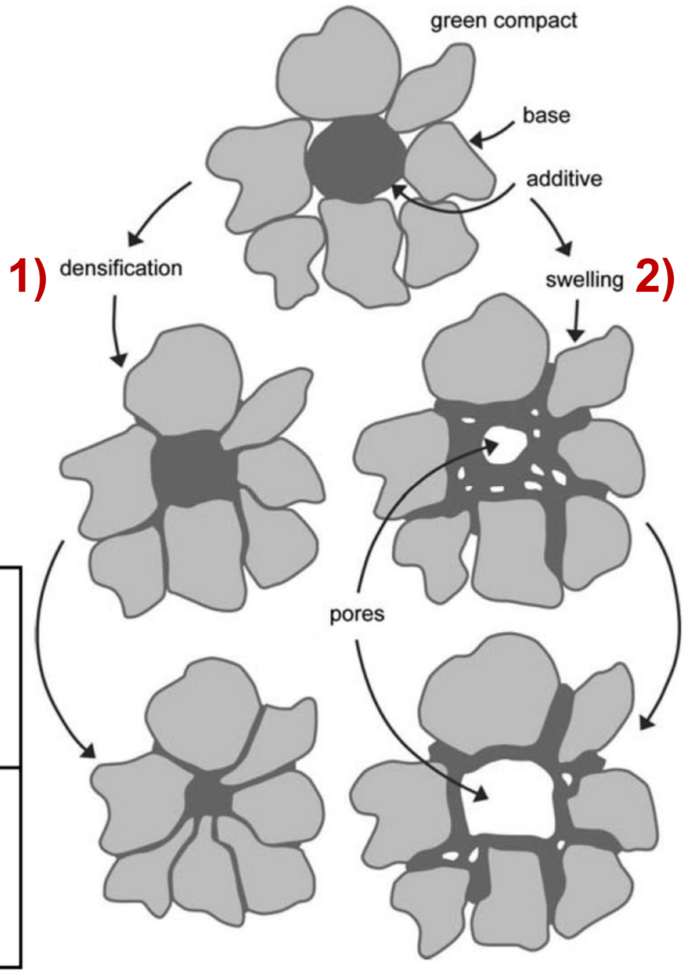
Case study: Liquid phase sintering – Solubility effect

- When liquid does not wet the solid, swelling and/or phase separation may occur during melt formation
  ➔ **Liquid needs to wet** the solid (here SiC)
- **Low dihedral angles** (20-60°) promote densification
  ➔ Large **solid-liquid contact area**
- **Mutual solubilities** of solid in liquid and vice versa **impact microstructural development**

1) **High** solubility of **solid in liquid** and **low** solubility of **liquid in solid**
➔ **Significant densification**
Grains grow into liquid via solution-reprecipitation

2) **Low** solubility of **solid in liquid** and **high** solubility of **liquid in solid**
➔ **No densification**
Swelling of grains via resorption of liquid with pore formation

liquid solubility in solid	solid solubility in liquid	
	low	high
low	limited densification, rearrangement	1) extensive densification
high	2) swelling, transient liquid	mixed effect swelling & densification



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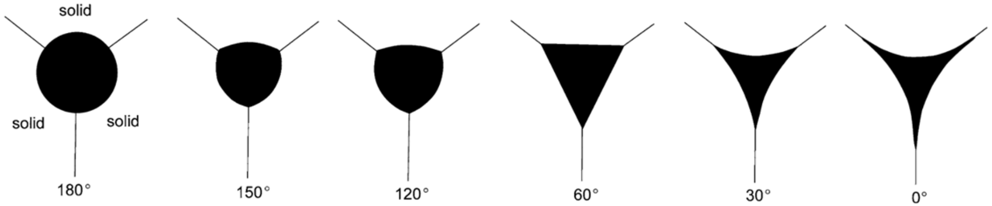
30/04/2025

source: 10.1007/s10853-008-3008-0

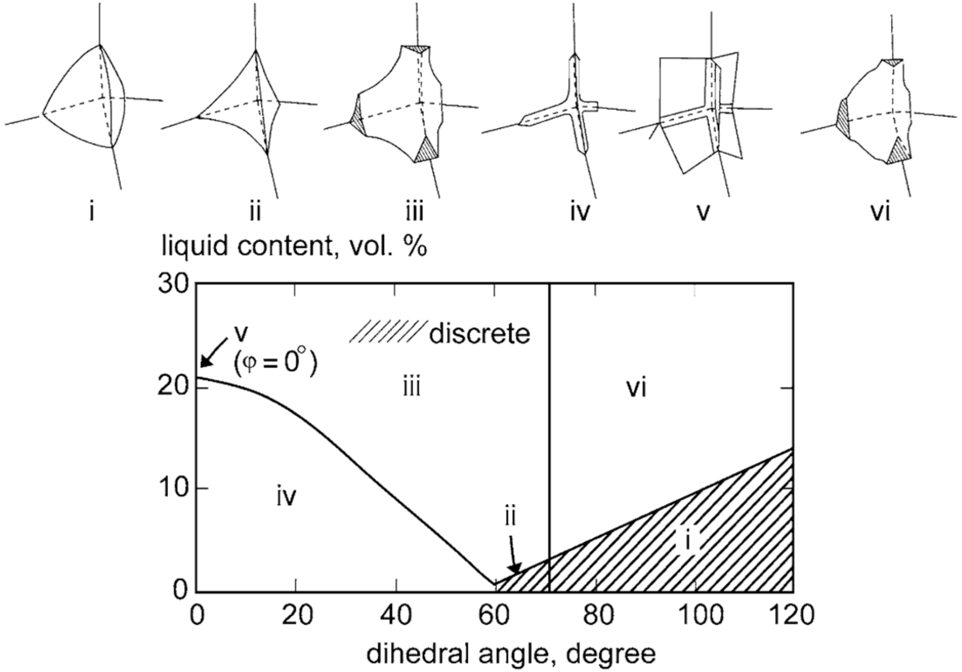
Case study: Liquid phase sintering – Dihedral angle effects

- ♦ **Low dihedral angles** promote wetting of the grain boundaries
  ➔ large **solid-liquid contact area**
  ➔ **facilitates solution-reprecipitation** reactions
- ♦ **Dihedral angles <20°** favor densification but **prevent solid-solid** grain boundaries
  ➔ **Weak mechanical properties**
- ♦ **Dihedral angles from 20-60°** are optimal for **densification and solid-solid GB** formation
- ♦ Dihedral angles >60° lead to discrete liquid pockets at GBs below critical liquid content

Liquid pocket shape at triple grain junction as a function of the dihedral angle at low liquid contents



Liquid shape and connectivity changes as a function of liquid content and dihedral angle



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Ultra-high temperature ceramics (UHTCs)

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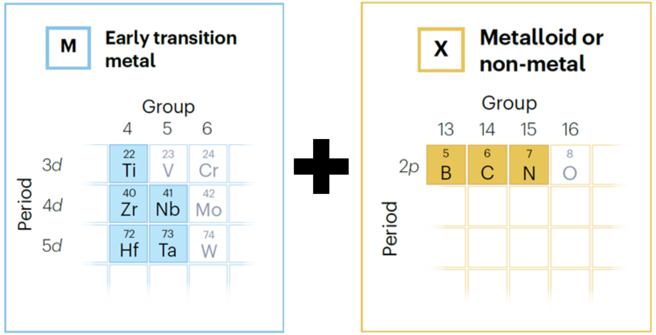
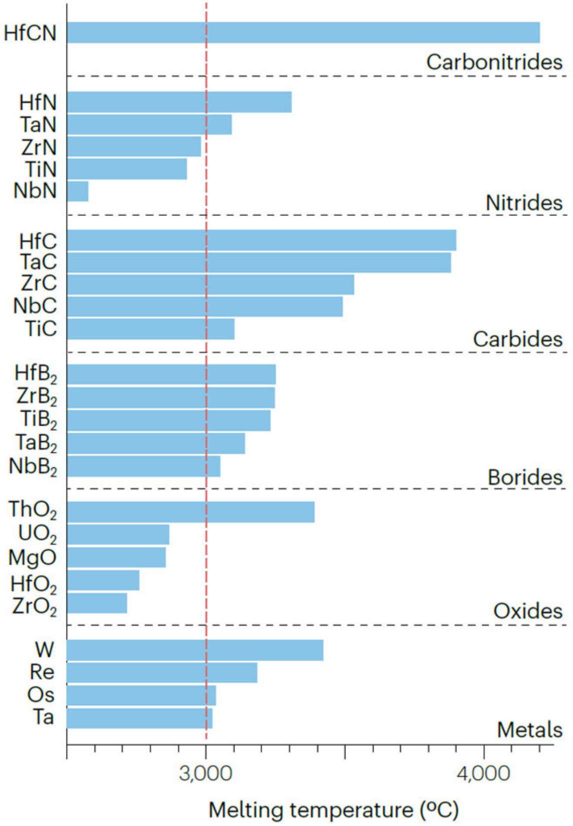
Ultra-high temperature ceramics - Definition

- Refractory ceramics with **melting points >3000°C**
- Typically **early transition metal** borides, carbides and nitrides (e.g. interstitial compounds)



- Why early transition?
  - **Interstitial** compounds:
    Mix of strong covalent (i.e. directional and rigid) and metallic (i.e. flexible) bonds ➔ structure **can absorb** a lot of energy before breaking
  - **Covalent** compounds:
    Very strong covalent bonds (i.e. directional and rigid) renders structure very brittle ➔ structure **cannot tolerate** a lot of thermal vibrations or thermal defects



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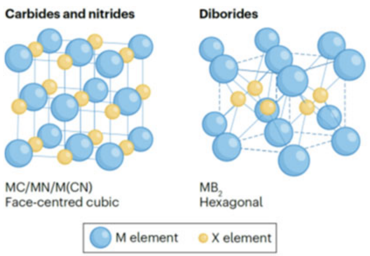
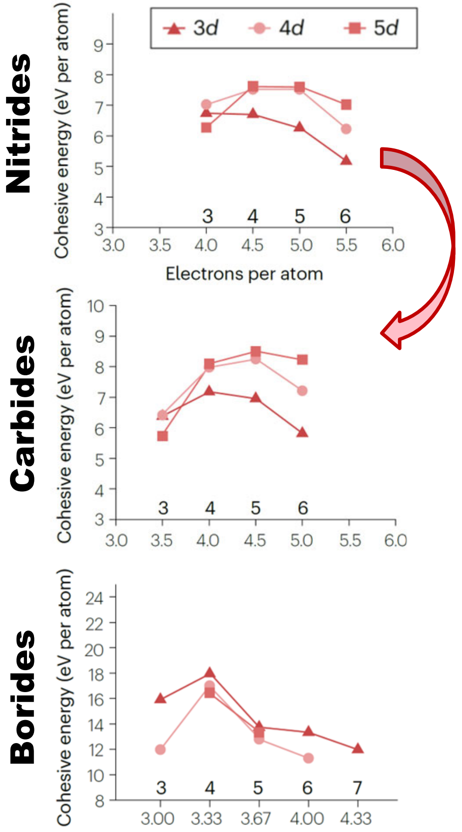
Ultra-high temperature ceramics – Cohesive energy

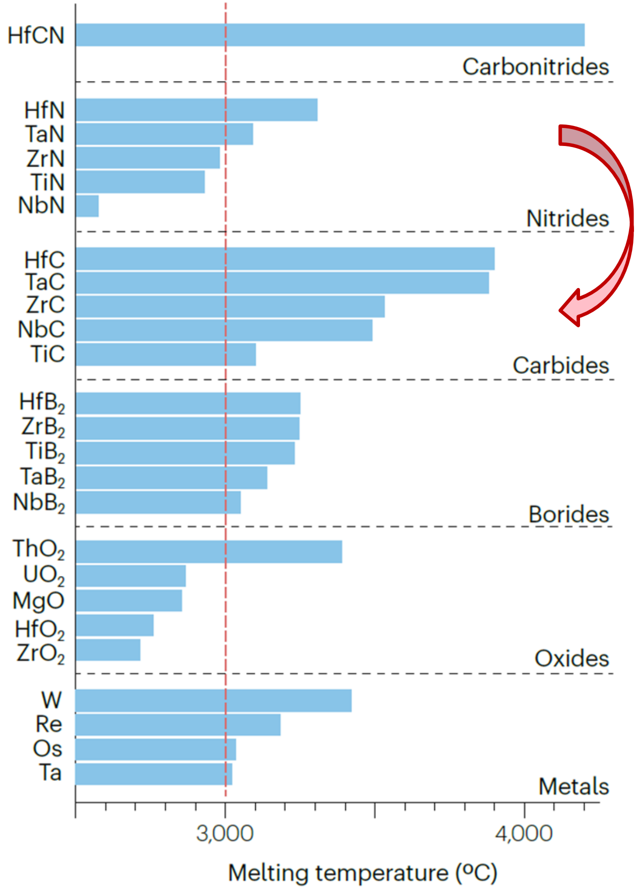
- **Melting temperature** related to **cohesive energy**
- For **nitrides and carbides** cohesive energy maximized for **group 4 and 5 elements**
- For **given crystal structure**, higher cohesive energy leads to higher melting temperatures (e.g. nitrides vs. carbides)
- For **borides**, cohesive energy maximized for **group 4 elements**



Note:
Different crystal structure for borides
➔ No direct comparison possible with carbides

Cohesive energy





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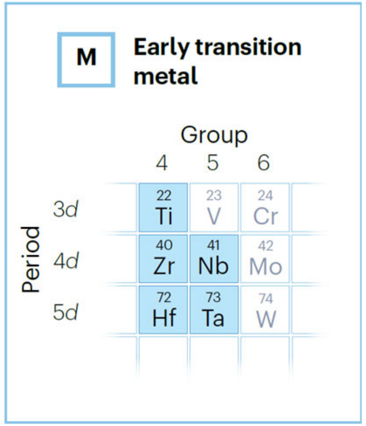
Ultra-high temperature ceramics – Cohesive energy

- **3** main **chemical bonds**
  - **Metal (M) to B/C/N (X)**
    ➔ M-X, mixed ionic and covalent bond
  - **Metal (M) to Metal (M)**
    ➔ M-M, metallic bond
  - **Non-metal (X) to Non-metal (X)**
    ➔ X-X, covalent bond
- **Additional valence electrons** by changing
  - **M** from group 4 to 5 to 6
  - **X** from C to N

reduce M-X bond length, increasing the M-X covalent and anti-bonding character

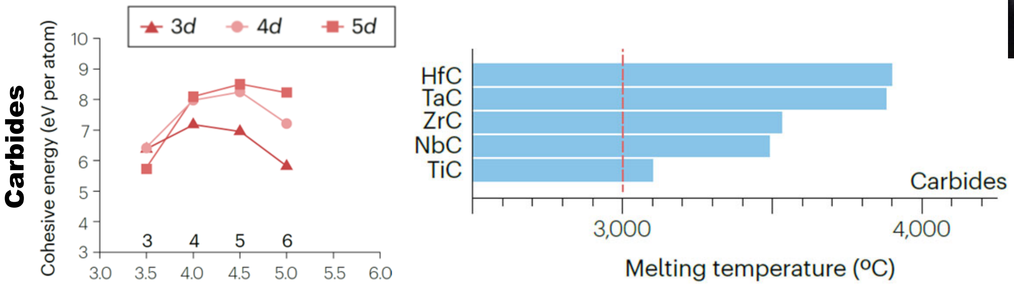
➔ **Cohesive energy** (i.e. thermal stability) **decreases**



Increasing number of **total electrons**
➔ **Increase of cohesive energy** (due to increased charge transfer in the M-X bond)

Increasing number of **valence electrons**
➔ **Reduction of cohesive energy** (due to increased covalent and M-X antibonding character)

Cohesive energy



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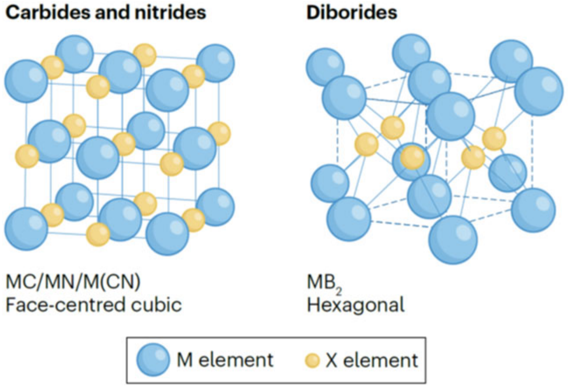
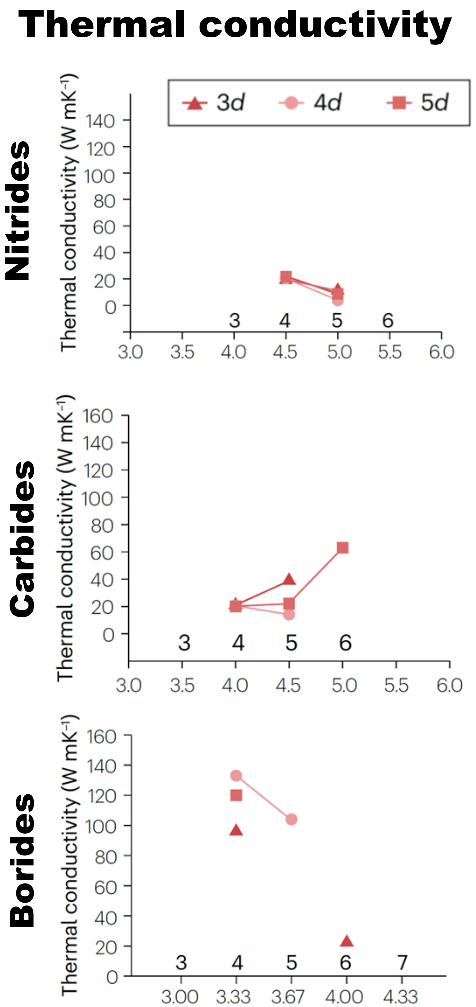
Ultra-high temperature ceramics – Thermal conductivity

- ♦ **Borides**
  electrons dominant contributors to **thermal conductivity** (due strong M-M bond in hexagonal system)
  - ➔ Higher energy required to move electrons as antibonding states filled
  - ➔ **Conductivity decreases** with increasing group number
- ♦ **Carbides and nitrides**
  lower electron contribution to **thermal conductivity** (due strong M-M bond in hexagonal system)
  - ➔ In **carbides**, **conductivity increases** with increasing group number
    (supposedly related to increase phonon contribution with reduced atomic size or antibonding states)

Opposing requirements for high **temperature** and high **thermal shock** resistance! ➔ **High-entropy systems may play here a significant role!**





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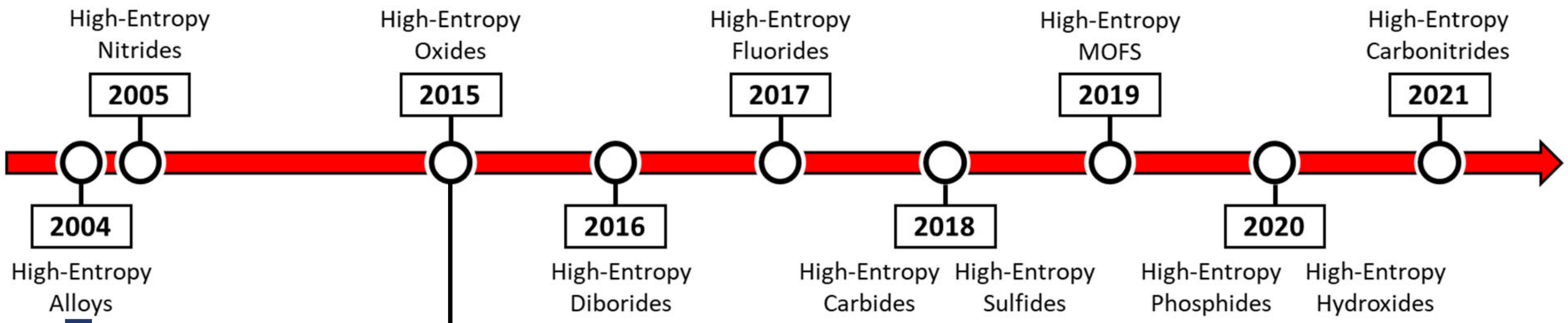
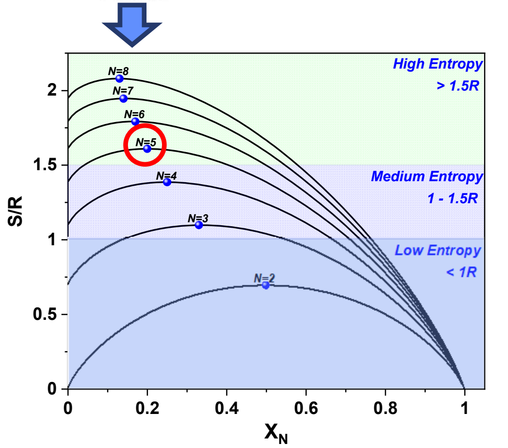
General aspects on high entropy ceramics – Timeline

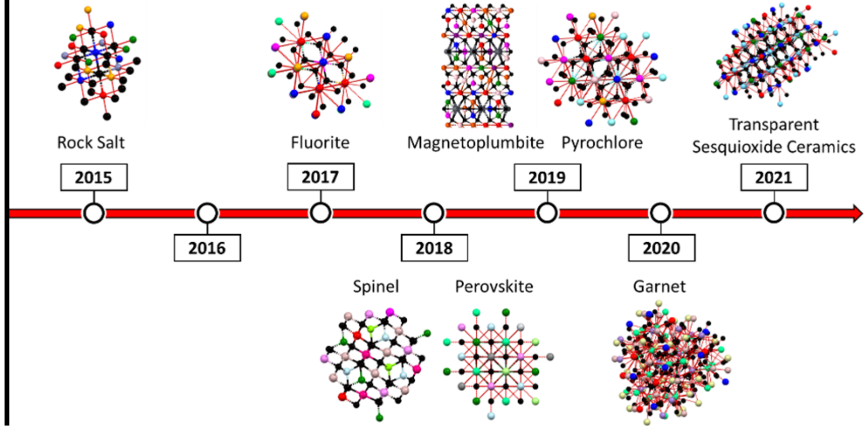
- High entropy ceramics are relatively novel material class



2004 High-Entropy Alloys
2005 High-Entropy Nitrides
2015 High-Entropy Oxides
2016 High-Entropy Diborides
2017 High-Entropy Fluorides
2018 High-Entropy Carbides
High-Entropy Sulfides
2019 High-Entropy MOFS
2020 High-Entropy Phosphides
High-Entropy Hydroxides
2021 High-Entropy Carbonitrides



In metals (equivalent atomic sites)
➔ 5+ elements = high entropy



General aspects on high entropy ceramics – Entropic metric

- Entropy and enthalpy of mixing important parameters:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} = \Delta H_{mix} + RT\sum_{i=1}^{n} X_i \ln(X_i)$$

If $\Delta G_{mix} < 0$, then:

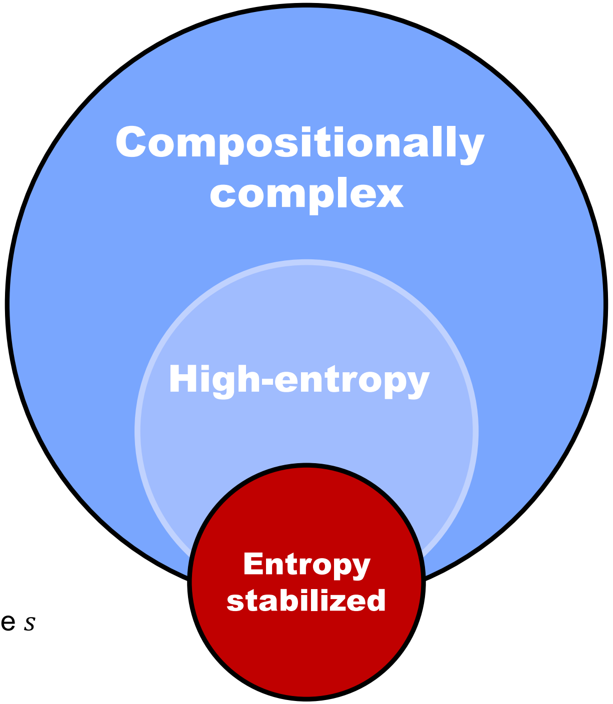
  - $\boldsymbol{\Delta H_{mix} \geq 0}$ ➔ (high) entropy stabilized
  - $\boldsymbol{\Delta H_{mix} < 0}$ ➔ high entropy

- Unless in alloys, not all sites are equivalent:

➔ Entropic metric (sublattice model): $\boldsymbol{EM = \frac{S_{SL}^{Config}}{R} * L}$

$$S_{SL}^{Config}(\Delta S_{mix}) = \frac{-R\sum_s \sum_i a^s x_i^s \ln(x_i^s)}{\sum_s a^s}$$

- a^s: number of sites on sublattice s
- L: number of sublattices
- R: universal gas constant
- x_i: mole/atomic fraction of i



$EM < 1$	$1 \leq EM < 1.5$	$EM \geq 1.5$
Low entropy	**Medium entropy**	**High entropy**

source: 10.1016/j.scriptamat.2021.113974

MAX phases

M. Stuer

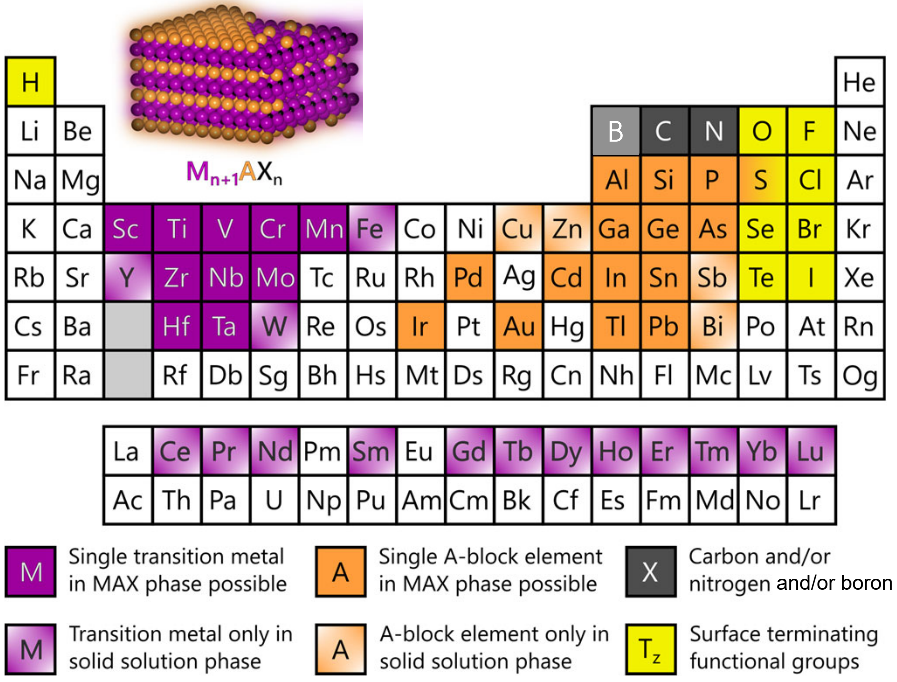
What are MAX phases?

- **Nanolaminated** ternary carbide/nitride/boride ceramics with general chemical formula

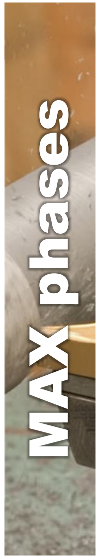
$$M_{n+1}AX_n \quad \text{with } n = 1, 2 \text{ or } 3$$

M = early transition metal
A = (semi-)metallic A-group element
X = carbon and/or nitrogen

- Metallic **M-A** bonds and covalent **M-X** bonds result in unique **part metallic part ceramic material properties**
  - Machineability
  - Thermal shock and damage tolerance
  - Good electrical and thermal (12-60 $Wm^{-1}K^{-1}$) conductivity
  - High-temperature mechanical properties
  - Resistance to oxidative (especially with $Al \rightarrow Al_2O_3$), corrosive, and irradiating environments

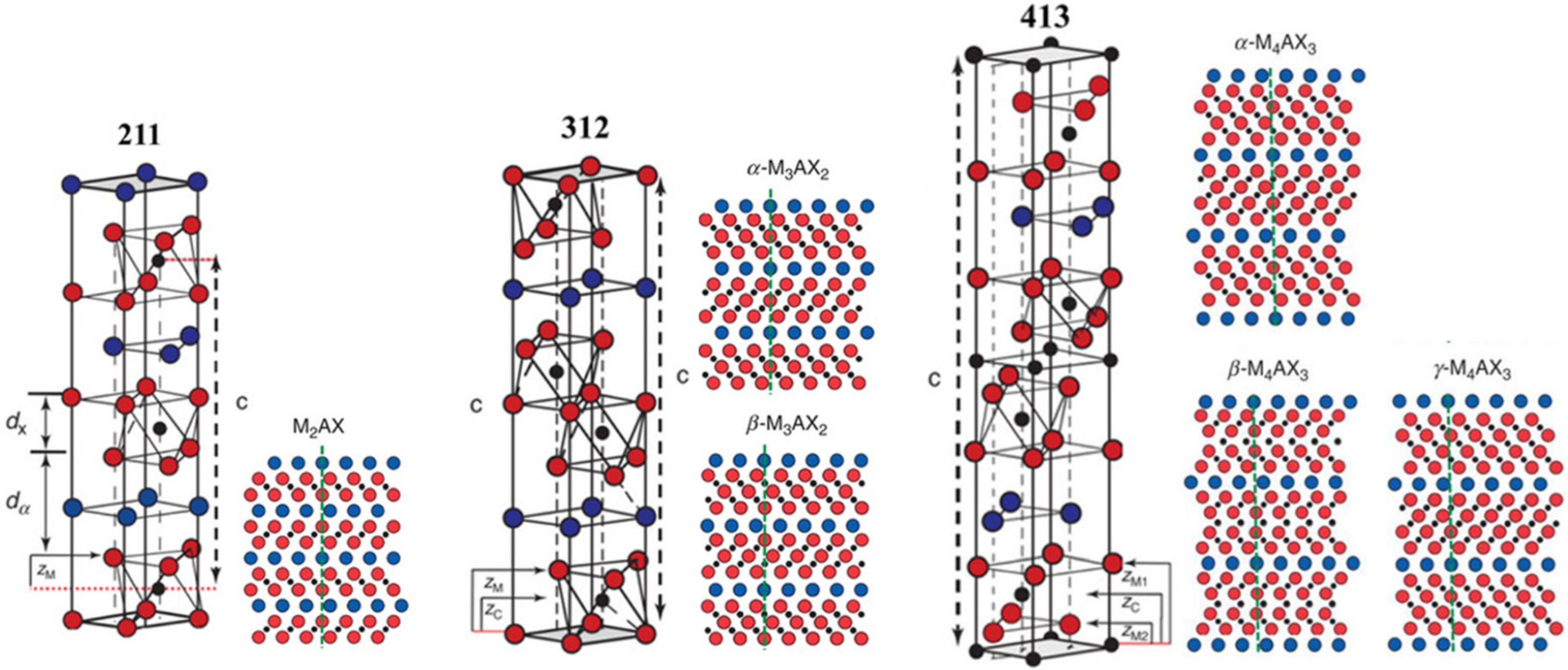


Single transition metal in MAX phase possible
Single A-block element in MAX phase possible
Carbon and/or nitrogen and/or boron
Transition metal only in solid solution phase
A-block element only in solid solution phase
Surface terminating functional groups



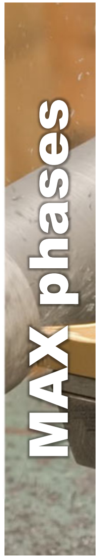
MAX phase types and polymorphs

- MAX phases typically produced via **liquid phase-assisted reactive sintering** of (near-)elemental powders (see next slides)
- **Properties** tuned via **chemical composition and microstructure** (e.g. synthesis strategy dependent)
- For **higher order** MAX phases different **polymorphs** exist



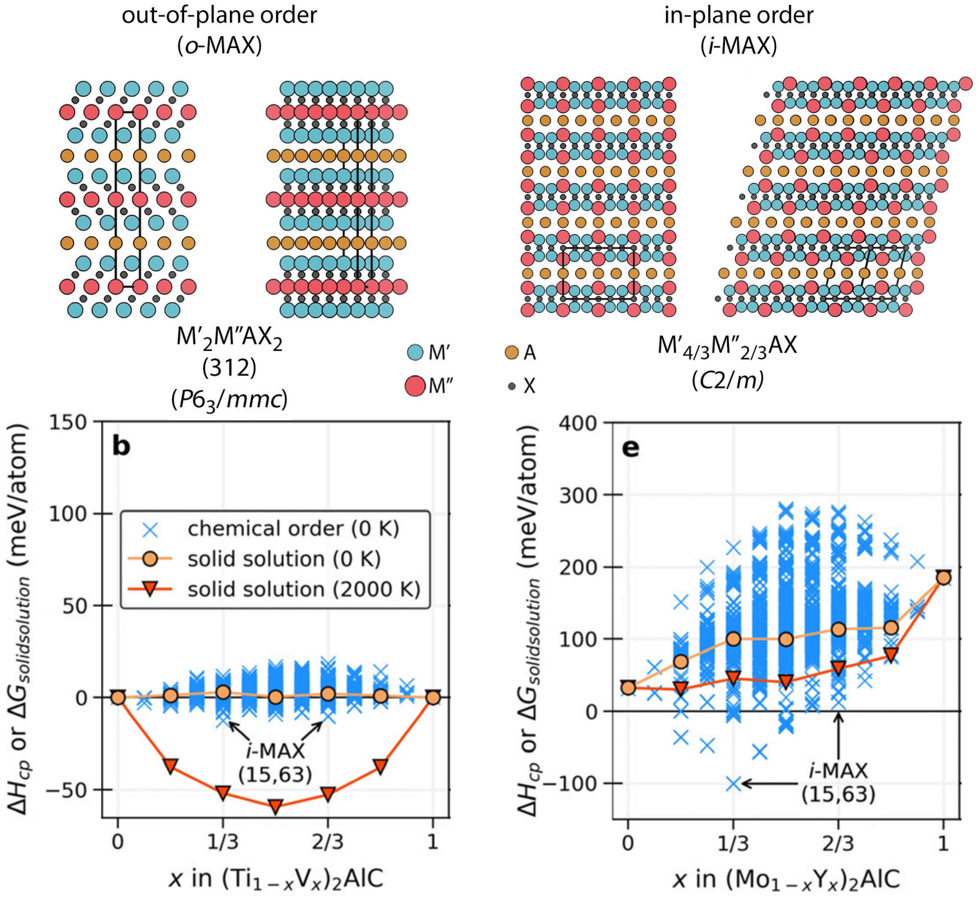
M_6X-layer ≡ d_x

A-layer ≡ d_α



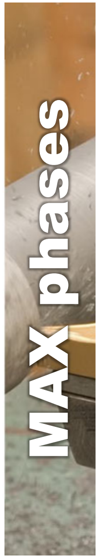
MAX phase solid solutions (complex and high entropy)

- **Solid solution** MAX phases allow extensive **chemistry and property tailoring**
- Solid solution can be:
  - **Disordered** due to “high” ΔS_{mix} and low enthalpic ordering driving force
  - **Ordered** due to “low” ΔS_{mix} and strong enthalpic ordering driving force
- **Ordering** results from steric/physical incompatibilities between atoms (c.f. Hume-Rothery rules for metal alloys)
  - If n ≥ 2, dissimilar electronegativity and M-A interaction energy causes M-atom separation into adjacent planes
    ➔ **out-of-plane (o-MAX) ordering**
  - Lattice strains due to dissimilar atom radii get relaxed by **in-plane (i-MAX) ordering** and crystal symmetry changes
    Note: REE-based i-MAX phases exhibit magnetism



ΔH_{order} (×) << $T\Delta S_{disorder}$ (▼)
➔ **Disordered SS**

ΔH_{order} (×) >> $T\Delta S_{disorder}$ (▼)
➔ **Ordered (i-MAX) SS**



sources: 10.1016/j.mattod.2023.11.010, 10.1039/D2NR02414D

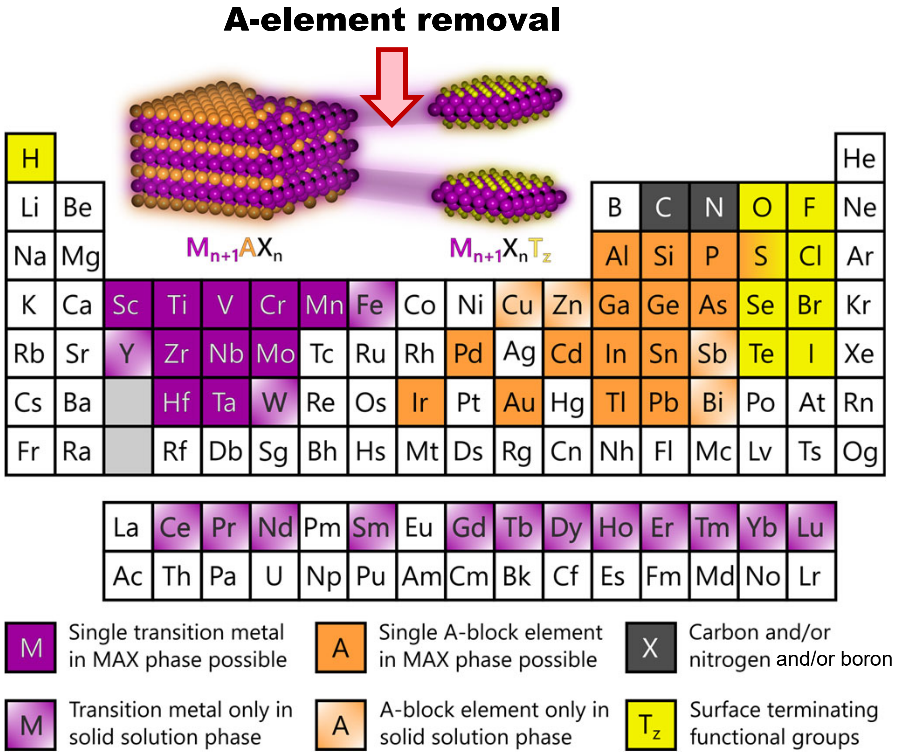
MXenes by exfoliation of MAX phases

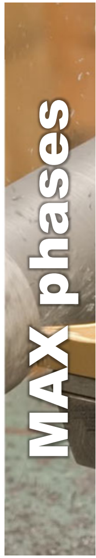
- Exfoliation of MAX phases (in HF or molten salts) lead to MXene formation (2D material)

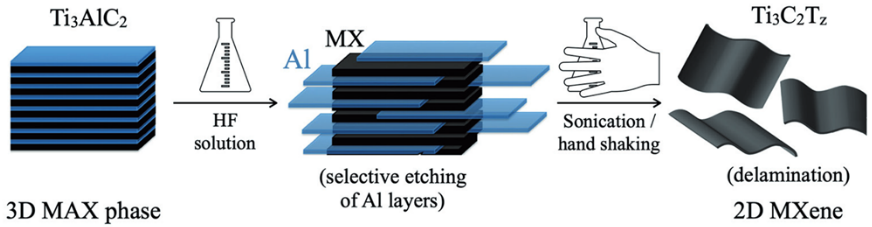
  $M_{n+1}X_nT_z$ n = 1, 2, 3 or

  $M_{1.33}XT_z$ z = degree of functionalisation

- MXene surface chemistry T_z depends on reaction of **M**-~~**A**~~ dangling bonds with (electronegative) anions during exfoliation
  - in HF/LiF+HCl → –F/-O/-OH
  - in NaOH → –O/-OH
  - in molten salts → -Cl/-Br/-I (e.g., $ZnCl_2$, $CdBr_2$ or CuI)



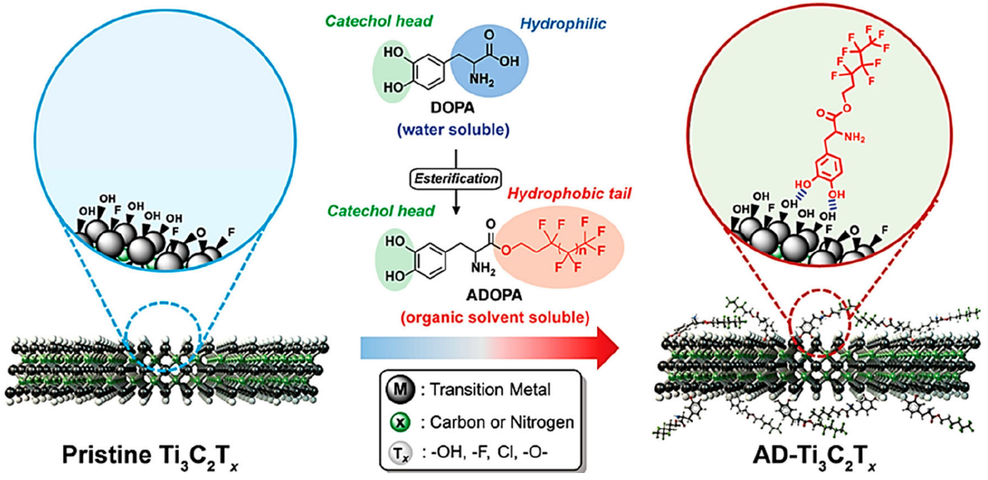


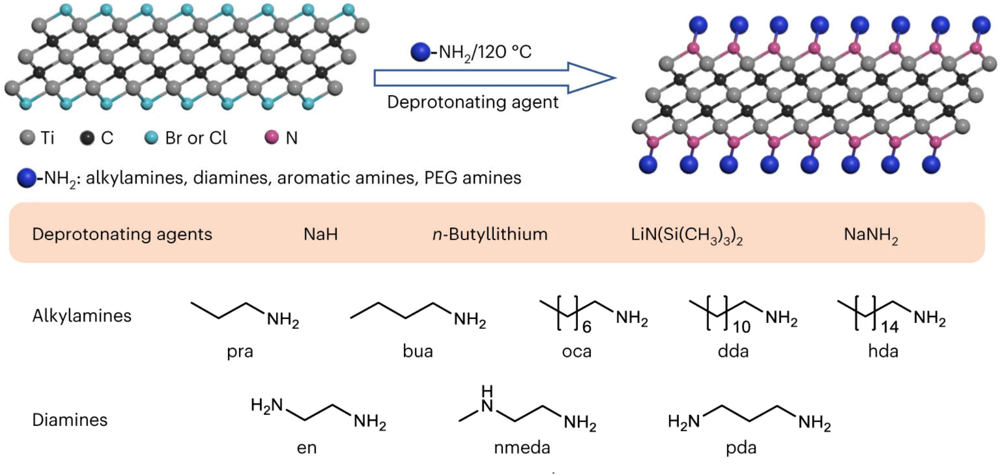


source: Champagne, Chimie nouvelle 135 (2020)

Subsequent MXene surface functionalization (for information)

- Chemical replacement of weaker surface groups with chalcogens (-S, -Se, -Te) or grafting organic functional groups allows further property tuning
  - Hydrophilic ↔ hydrophobic behavior
  - Specific molecular affinity
    ➔ sensing applications
  - Band structure engineering
    ➔ electrical properties
- Electronegative MXene surface attracts cations
  - Facilitates charge storage (Li$^+$, Na$^+$, K$^+$ from electrolyte)
    ➔ capacitors
  - Redox activity
    ➔ pseudocapacitance (e.g. quick charge transfer)
  - Enable decoration with metallic nanoparticles
    ➔ catalysis (Pt, Ni, Pd), biosensing (Au), electromagnetic shielding

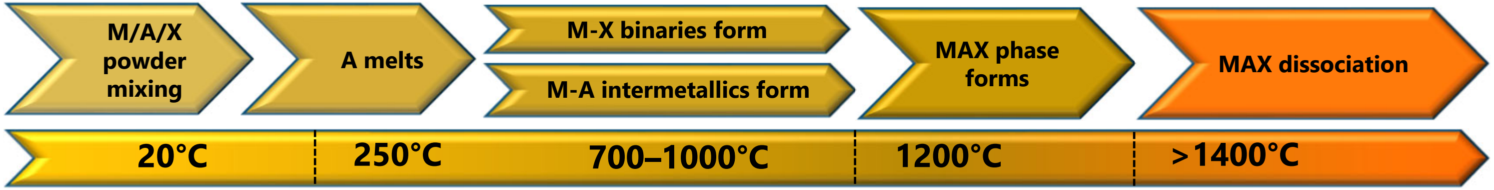




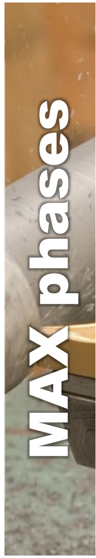
sources: 10.1021/acsnano.2c08209, 10.1038/s41557-023-01288-w

Synthesis of MAX phases: Overview

- MAX phases form in a **sequential and diffusion-controlled** powder metallurgical process



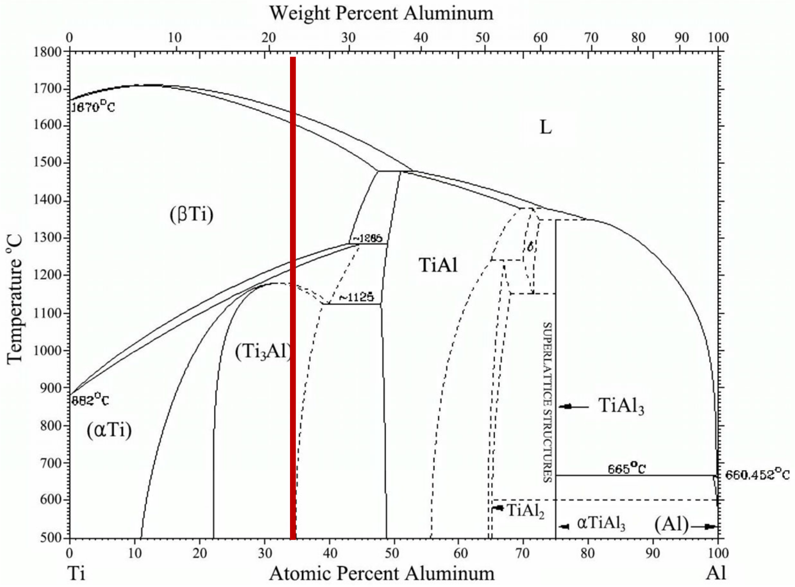
- Liquid phases form due to **low melting temperature** of the **A-element** and **(eutectic) intermetallic compounds (IMCs)**
- Liquid phases can be **introduced on purpose** by
  - ➔ introducing alloying elements (Zn, Fe, Co) ➔ bulk MAX phases
  - ➔ non-reacting molten salts (usually alkali metal halides) ➔ MAX phase powders
- Quantity and reactivity of liquid phase set processing limits (Consult phase diagrams)
  - **Small** volumes ➔ Pressure-assisted sintering possible
  - **Large** volumes ➔ Pressureless sintering required
  - **Low reactivity** ➔ **Reduced heating rate** and increased dwell time **required** (**HP** > SPS)
  - **High reactivity** ➔ **Increased heating rate** and reduced dwell time **possible** (**SPS** > HP)

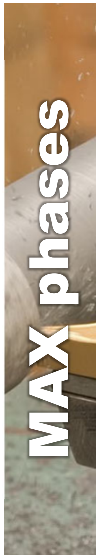


Synthesis of MAX phases: Process selection examples

- **Ti_2AlC:**
  - A-element:
    $T_m(Al) = 660°C$ **high**
  - Ti-Al intermetallic compounds
    - Melting points: **high**
    - Reactivity: **high**
- **Low risk of liquid formation** (A-element and/or IMCs) before reaction of IMCs with carbon to form MAX phase
- Suitable synthesis approaches
  - SPS **OK**
  - HP **OK**
  - pressureless sintering **OK**

Ti-Al binary phase diagram

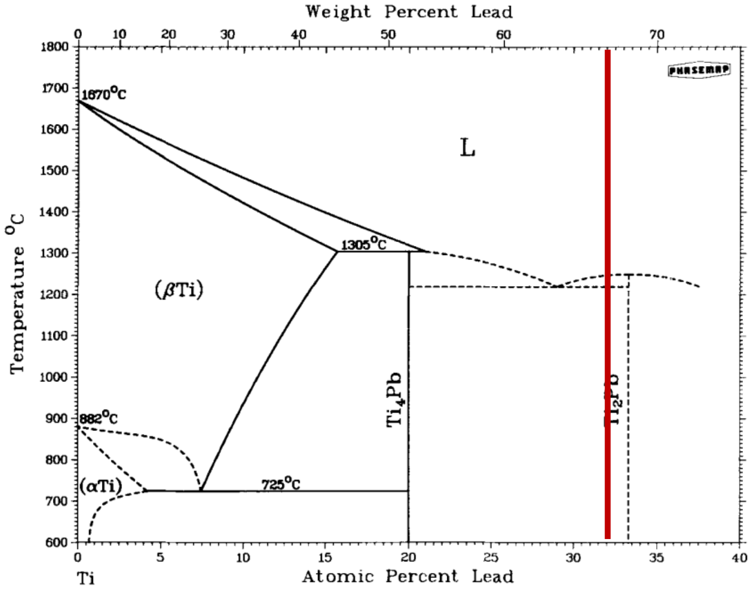


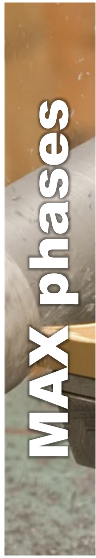


Synthesis of MAX phases: Process selection examples

- **Ti_2PbC:**
  - A-element:
    $T_m(Pb) = 327°C$ **low**
  - Ti-Pb intermetallic compounds
    - Melting points: **moderate**
    - Reactivity: **low**
- **Guaranteed substantial liquid formation** (A-element or IMCs) before reaction of IMCs with carbon to form MAX phase
- Suitable synthesis approaches
  - SPS **KO**
  - HP **KO**
  - pressureless sintering **OK**

Ti-Pb binary phase diagram

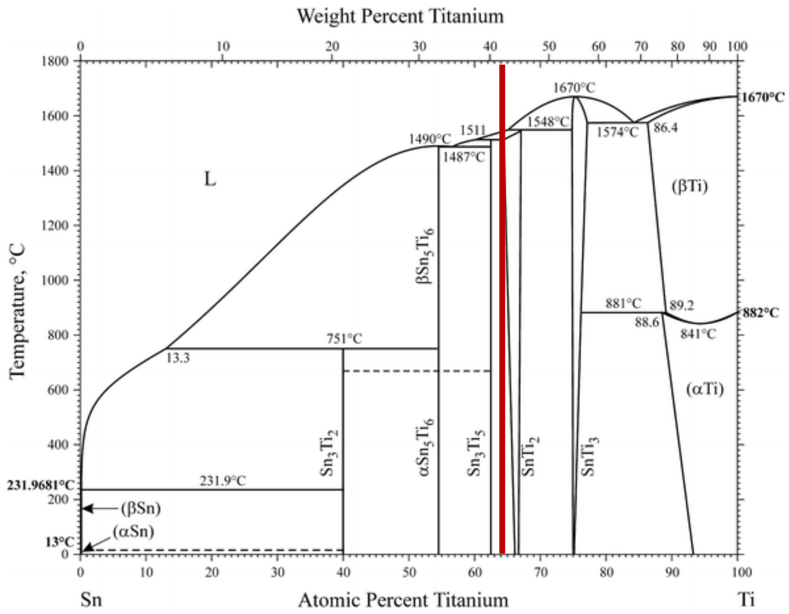


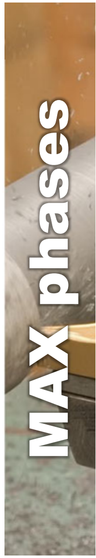


Synthesis of MAX phases: Process selection examples

- **Ti_2SnC:**
  - A-element:
    $T_m(Sn)$ = 232°C **low**
  - Ti-Sn intermetallic compounds
    - Melting points: **moderate**
    - Reactivity: **high**
- **Guaranteed liquid formation** (A-element or IMCs) before reaction of IMCs with carbon to form MAX phase
- Fast heating to critical temperature for MAX phase formation limits liquid amount or liquid loss risk
- Suitable synthesis approaches
  - SPS **OK**
  - HP **KO**
  - pressureless sintering **OK**

Sn-Ti binary phase diagram





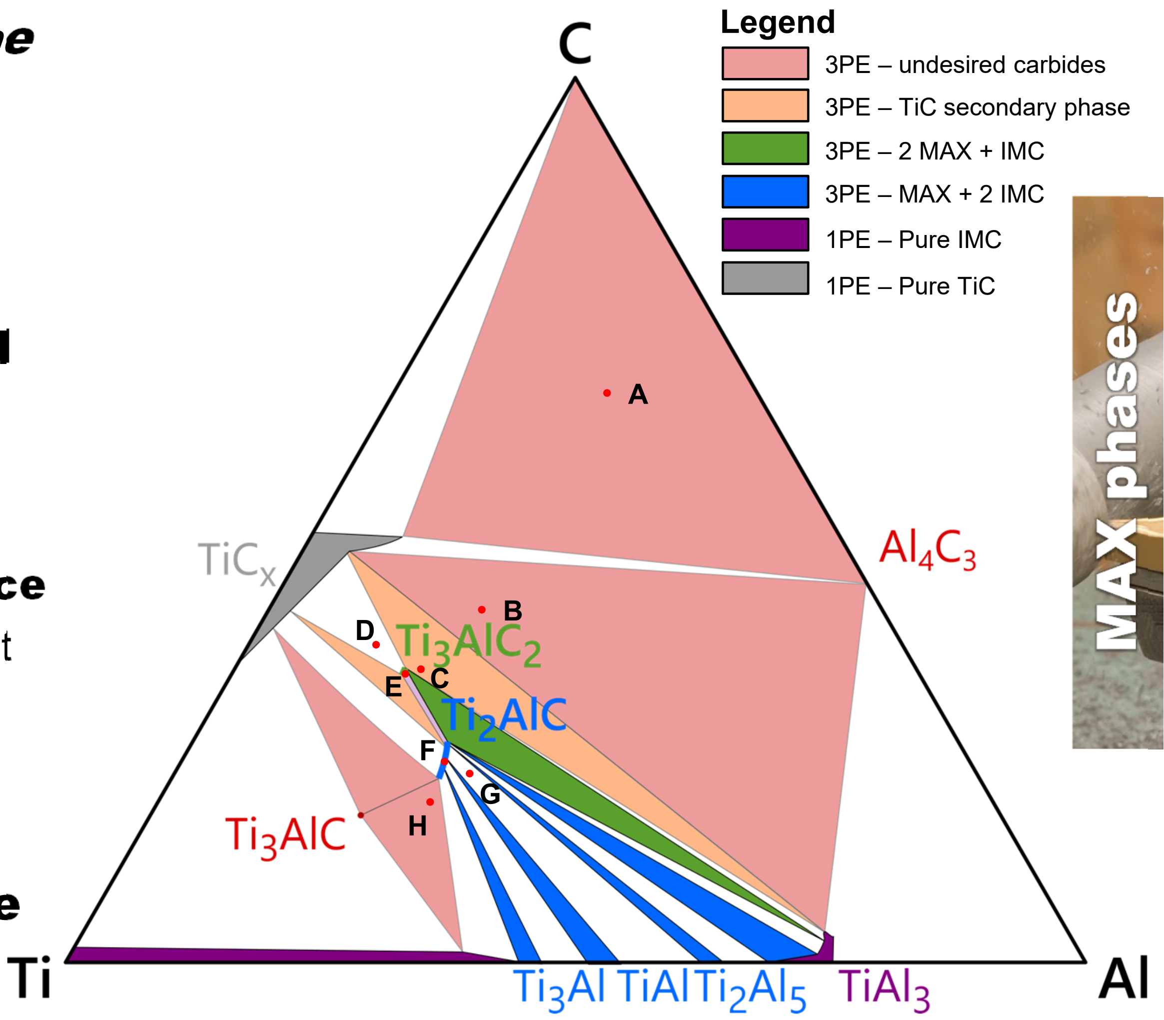
Synthesis of MAX phases: Composition selection

- MAX phases are **non-stoichiometric *line* compounds**
  ➔ Achieving **high purity** is **compositional and processing challenge**

In practice:

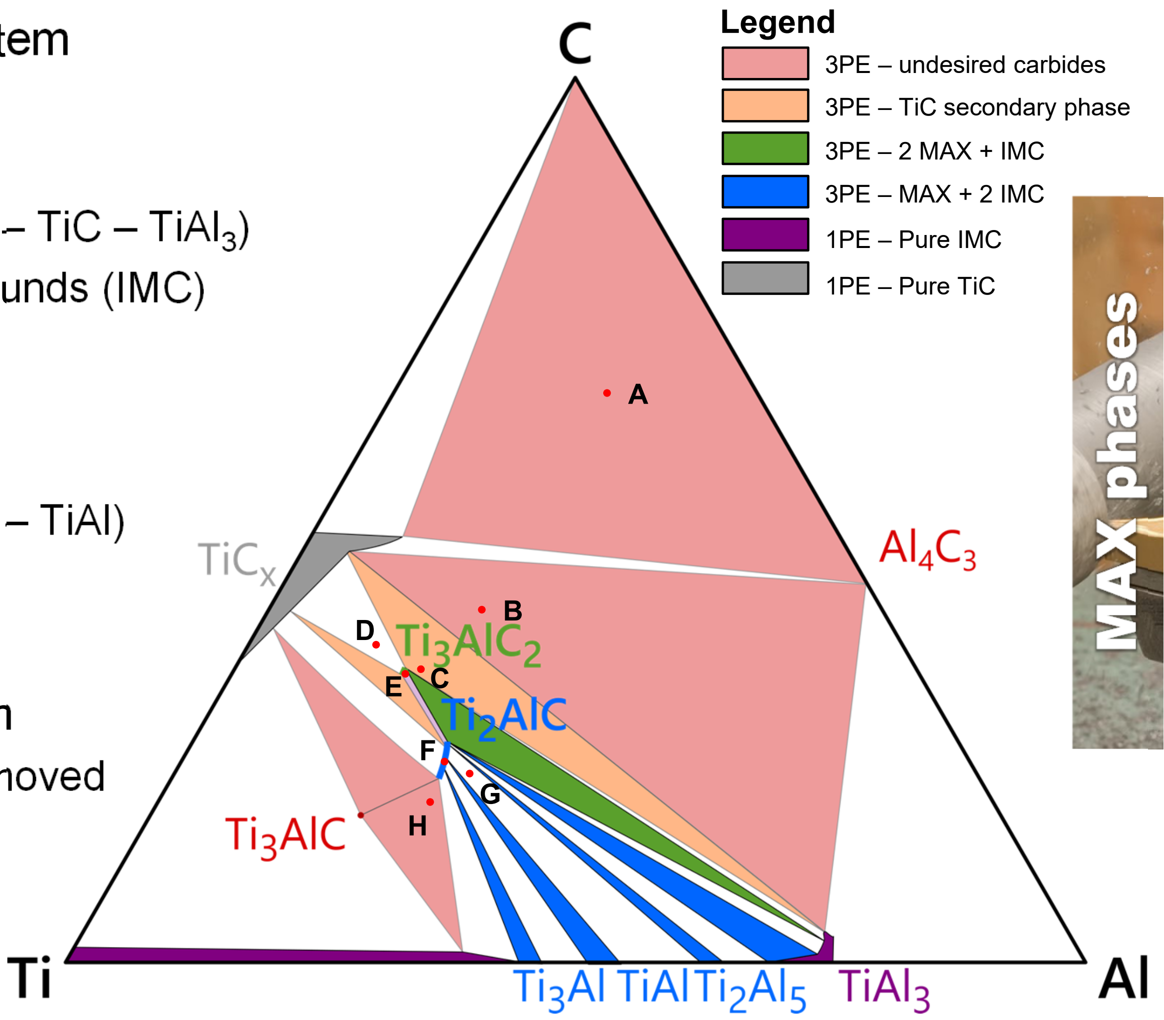
- Control **type of secondary phases and microstructure**
- Problem:
  - Availability of **system-specific thermodynamic data extremely scarce**
  - Kinetics vs thermodynamic equilibria (e.g. fast SPS)

➔ **Ideal chemical composition and process** typically determined by **trial & error / knowledge database**

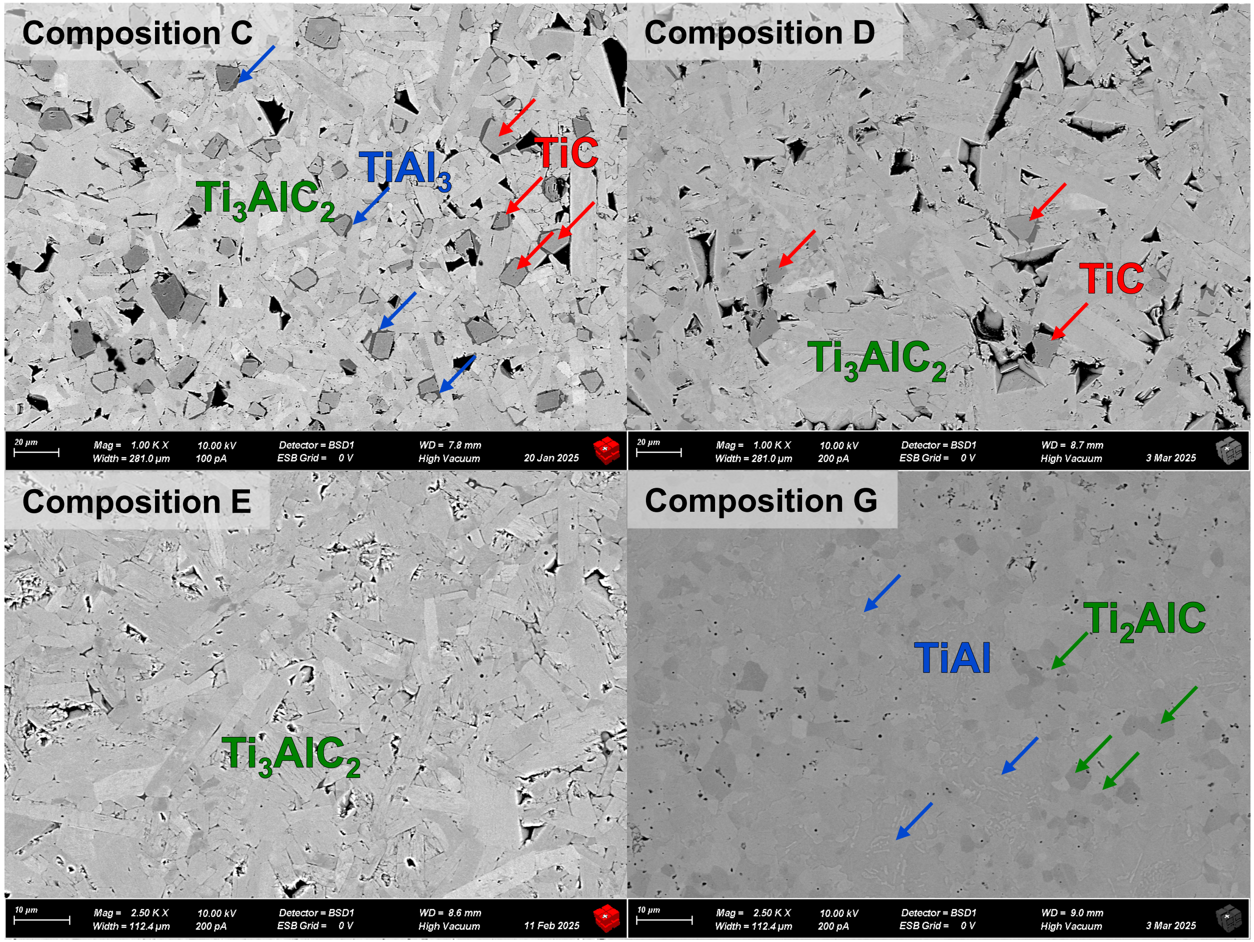


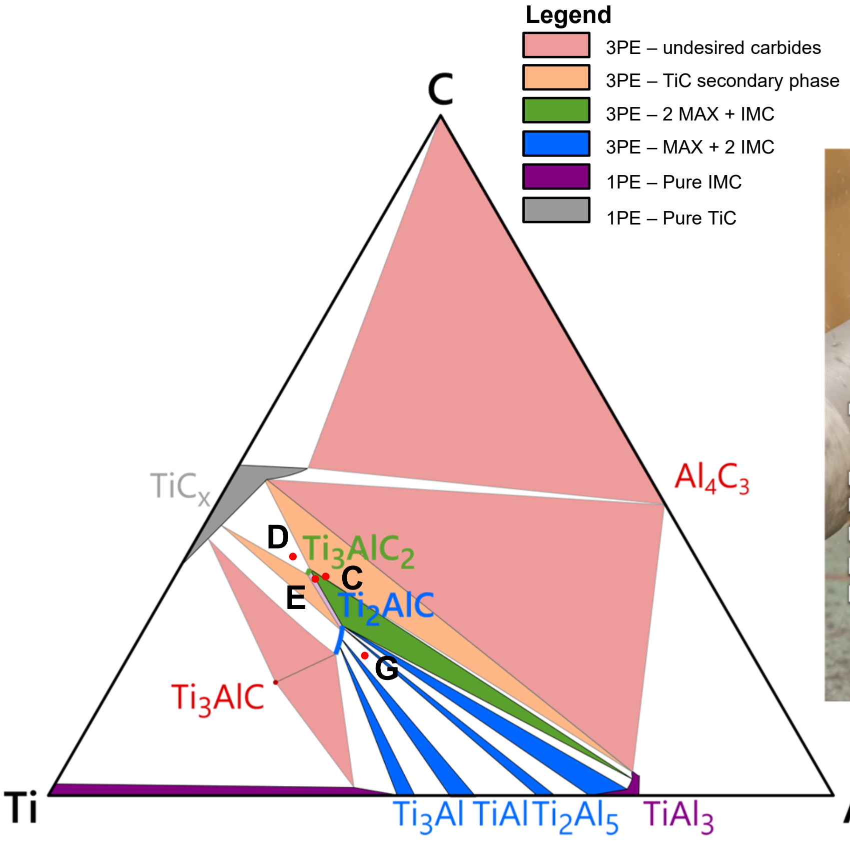
Synthesis of MAX phases: Composition selection

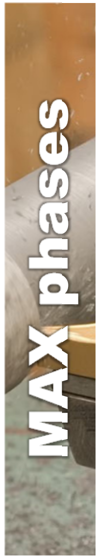
- Example: Phase equilibria in the Ti-Al-C system
  - A: No MAX phases (TiC – Al_4C_3 – Graphite)
  - B: No MAX phases (TiC – Al_4C_3 – $TiAl_3$)
  - C: Excess C causing TiC formation (Ti_3AlC_2 – TiC – $TiAl_3$)
  - D: Insufficient Al to form intermetallic compounds (IMC) (Ti_3AlC_2 – TiC)
  - **E: Phase-pure Ti_3AlC_2**
  - **F: Phase-pure Ti_2AlC**
  - G: Excess Al causing IMC formation (Ti_2AlC – TiAl)
  - H: Ternary ***non-MAX phases*** due to strong off-stoichiometry (Ti_2AlC – Ti_3AlC – Ti)
- Example: MAX phases for MXene production
  - IMC chemically soluble but TiC cannot be removed
    - ➔ Only pure MAX or MAX/IMC tolerated
    - ➔ Compositions C/D/H should be avoided
    - ➔ Compositions E/F/G are acceptable



Synthesis of MAX phases: Composition selection







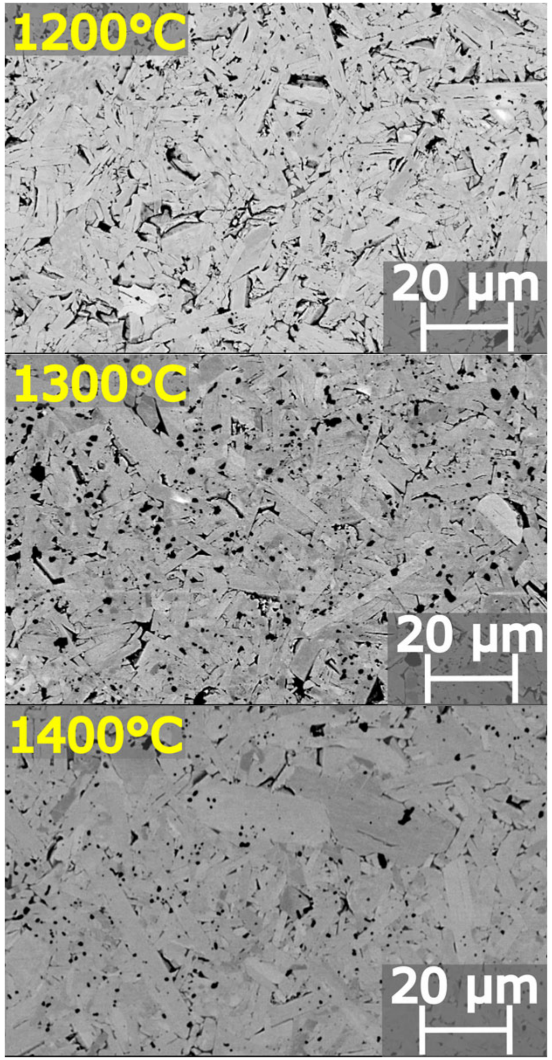
Synthesis of MAX phases: Effect of sintering conditions

- **Pressure** application and **short** processing **times** at minimum temperature for complete reaction favor **fine microstructures**, and inversely!

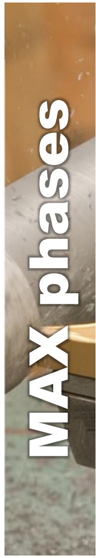
Examples:

- **SPS of Ti_3AlC_2 ceramics**
  (P_{ext} = 30 MPa, 50°C/min heating, 15 min dwell time)
  - Higher **sintering temperatures (and times)** promote grain **coarsening**
  - To produce (ultra)fine microstructures minimization of diffusion required
    - Reduce sintering temperature to **critical temperature** required to maximize (or complete) reaction
    - Apply **pressure** to boost formation kinetics (e.g. contact) without enhancing grain growth

Note: Multi-element diffusion in (complex) solid solutions further limits grain boundary movement

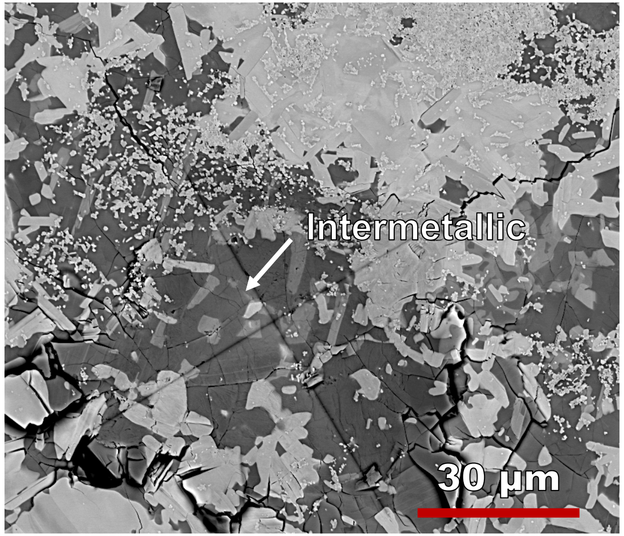


Synthesis of MAX phases: Effect of sintering conditions



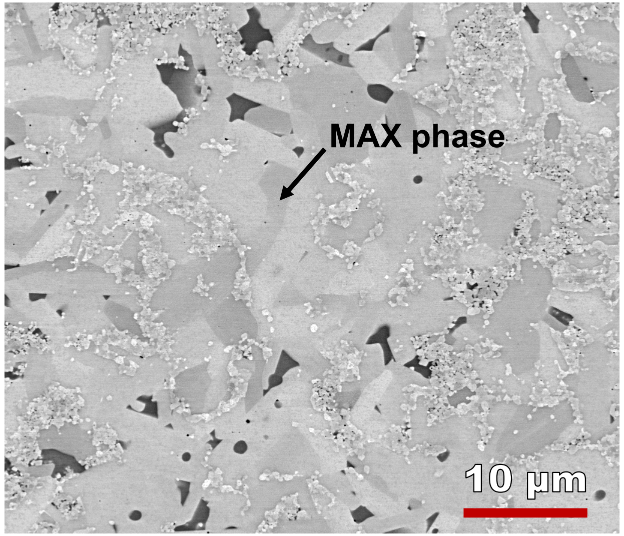
- **HP of Hf_3AlC_2 ceramics**
  (P_{ext} = 30 MPa, 50°C/min heating, sintering at 1500°C)
  - **Too short sintering** times result in **incomplete reactions**!
    - Dark zones (images) show crystallized unreacted $HfAl_2$/Hf_2Al_3 intermetallics upon cooling
  - **Excessive sintering times** result in microstructural coarsening (and may induce decomposition)

30 min dwell time

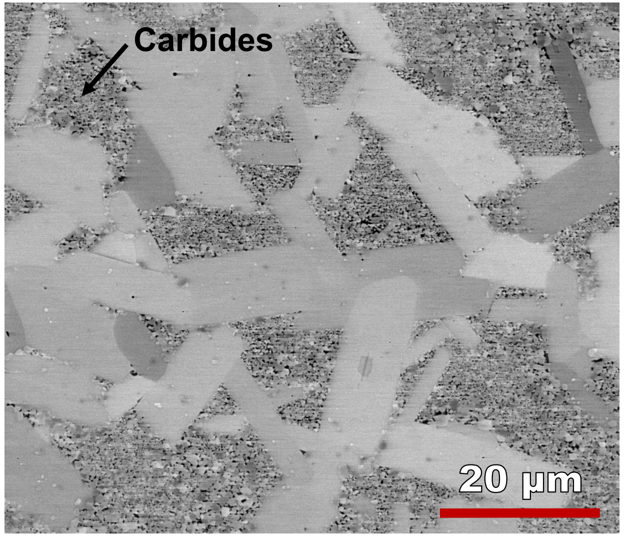


Dark zones: unreacted $HfAl_2$/Hf_2Al_3 intermetallics

60 min dwell time



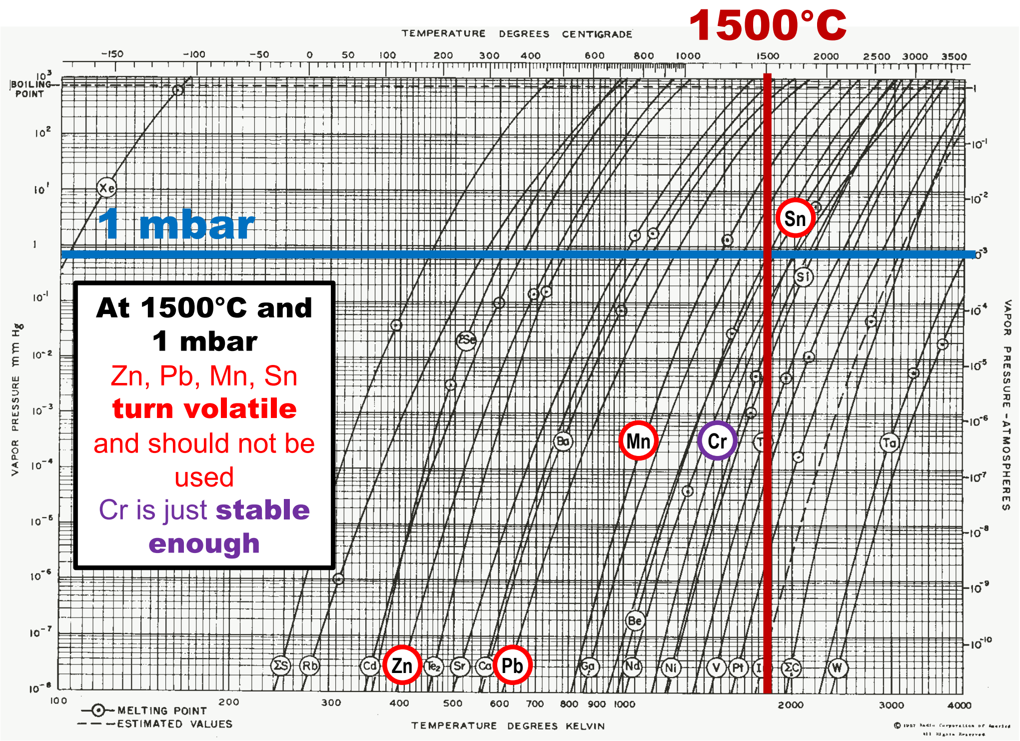
120 min dwell time



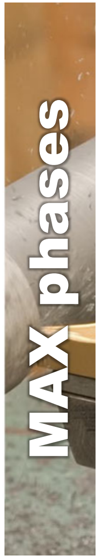
Note: Decomposition of MAX phase to carbides can occur due to excessive dwell times (A-element evaporation) or temperatures

Synthesis of MAX phases: Effect of sintering atmosphere

- Metals, carbides and nitrides can (easily) oxidize
  ➔ **Protective atmosphere required**
- Inert gases (Ar, N_2) typically contain trace amounts of O_2
  ➔ **Vacuum is preferred**
- Metallic and various oxide compounds volatilize in vacuum
  ➔ **Compositional changes**
  ➔ **Toxicity danger!**



At 1500°C and 1 mbar
Zn, Pb, Mn, Sn **turn volatile** and should not be used
Cr is just **stable enough**



Synthesis of MAX phases: Effect of sintering atmosphere

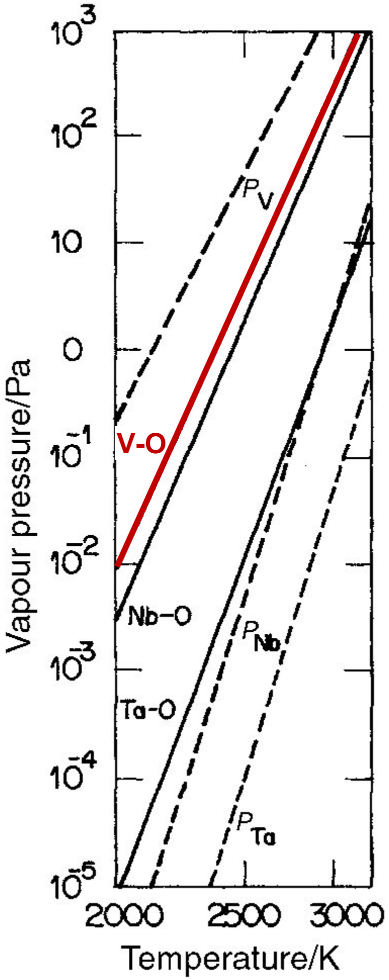
Beware of suboxides

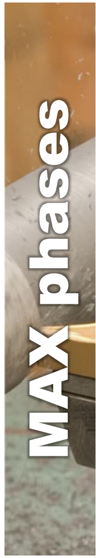
- Transition metals like V, Ti, Nb, Ta appear sufficiently stable in vacuum under typical synthesis temperatures
- However, even purest **metallic powders** are likely **partially (surface) oxidized**
  ➔ Necessary to check **volatility of (sub)oxides**
- The evaporation rate $\dot{m}$ is given by

$$\dot{m} = \alpha \frac{P_v - P}{\sqrt{2\pi MRT}}$$

- α: evaporation coefficient ($0 < \alpha \leq 1$)
- P_v: equilibrium vapor pressure
- P: ambient partial vapor pressure
- M: molar mass of evaporating species
- R: universal gas constant
- T: absolute temperature

- **Note:** Certain (sub)oxides such vanadium (sub)oxides are very toxic
- **Example:**
  At a "vacuum" pressure below 0.1 Pa V-suboxides will form gases above 2000 K





Emerge of Si_3N_4 as bioceramic

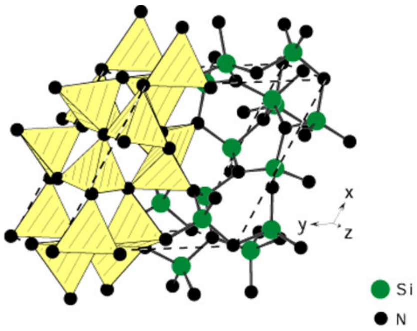
General Si_3N_4 aspects

Sintering of Si_3N_4

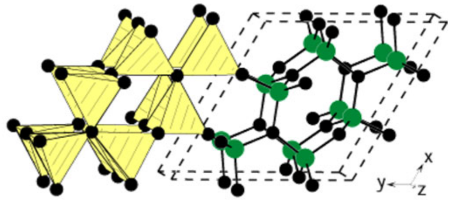
- Si_3N_4 typically sintered with few weight % of Al_2O_3 as a sintering aids
  ➔ referred to as SiAlON
- Pressure assisted sintering and UHS allow sintering of pure Si_3N_4 which may be expanding in future

Crystal structure

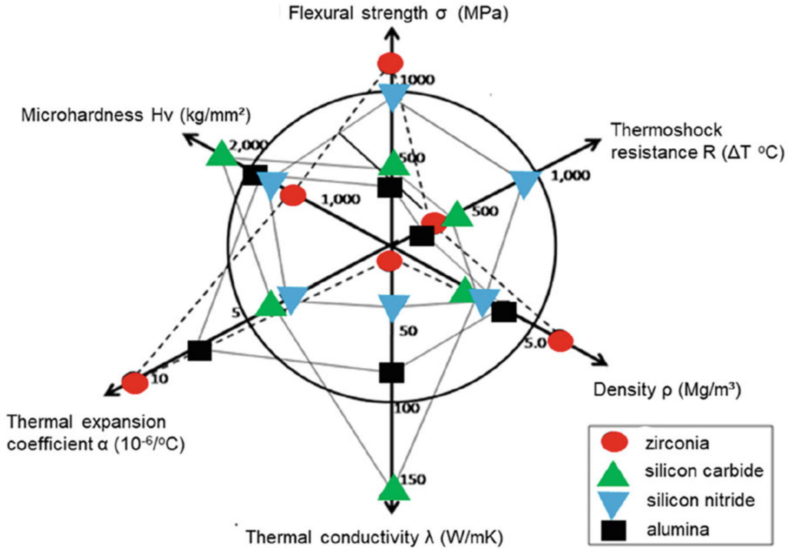
- Si_3N_4 can exist in different crystal structures. Most common:
  - Trigonal-α (lower density, stable up to 1300°C)
  - Hexagonal-β (higher density, stable up to 1900°C)



Trigonal α-Si_3N_4



Hexagonal β-Si_3N_4



source: Classic and Advanced Ceramics. From Fundamentals to Applications

Relevance of Si_3N_4 for medical applications

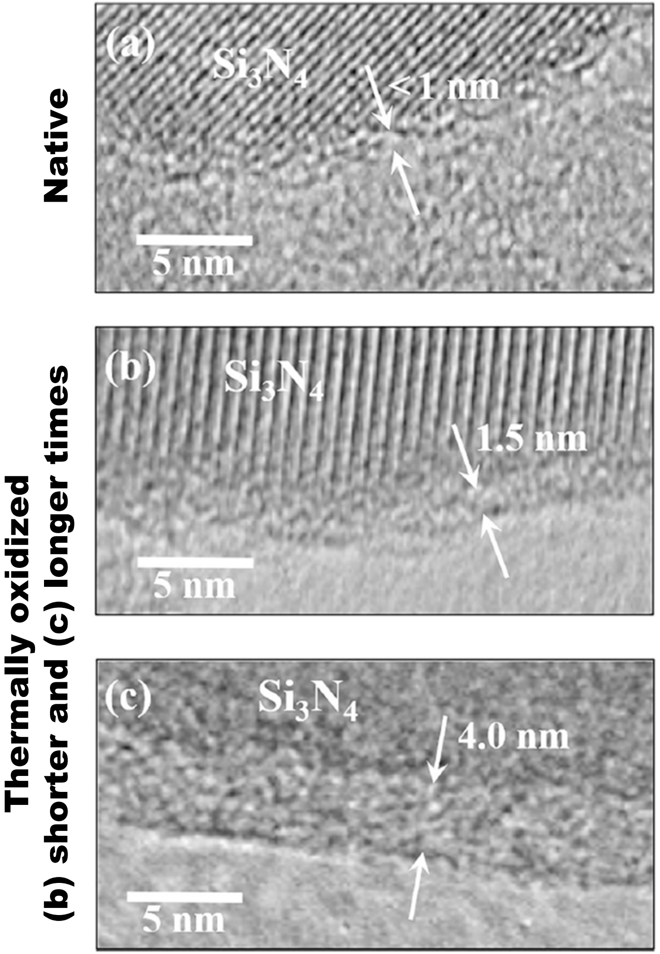
Osteoconductivity and osteostimulation

$$Si_3N_4 + 12H_2O \rightarrow 3Si(OH)_4 + 4NH_4^+ + 4OH^-$$

- ♦ $Si(OH)_4$ (othosilicique acid) stimulates collagen synthesis and upregulates osteogenic genes, mild pH increase also favorable
  - – Thermal or plasma oxidation allows tuning density of ≡Si–OH
    ➔ more ≡Si–OH ➔ more $Si(OH)_4$ release
  - – Doping with CaO (and MgO) may additionally lead to Ca^{2+}/Mg^{2+} release
    ➔ hydroxyapatite formation promoted

Fracture toughness

- ♦ Elongated grains in β-Si_3N_4 as well as residual glassy phase from Al_2O_3+Y_2O_3 sintering aids (e.g. liquid phase sintering) provide good fracture toughness



source: 10.1016/j.ceramint.2018.05.081

Relevance of Si_3N_4 for medical applications

Antibacterial effect

- Antipathogenic action due to surface hydrolysis
  - In water: $Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3$
  - In vivo: $Si_3N_4 + 12H_2O \rightarrow 3Si(OH)_4 + 4NH_4^+ + 4OH^-$

  ➔ In vivo NH_3 is protonated to NH_4^+ buffering the local pH to 8-10
  ➔ Basic pH (e.g. OH^- release) unfavorable to many bacteria
- Reactive nitrogen species (RNS) formed damage lipid membranes, proteins and nucleic acids
  ➔ Lethal for microbes
- Electrostatic and competitive binding effects compete with host-cell receptors
  ➔ Prevent microbial adhesion

source: 10.1016/j.ceramint.2018.05.081

The end

What was on the

- MENU -

today ?

- **Summary**
  - Technical relevance of non-oxide ceramics
  - Selection of sintering aids, example SiC
  - Fundamentals about UHTCs and potential for HECs
  - MAX phase synthesis/sintering approach and challenges
  - Si_3N_4/SiAlON for biomedical applications

- **Questions**