Self-Healing in $M_{n+1}AX_n$ Phase Ceramics

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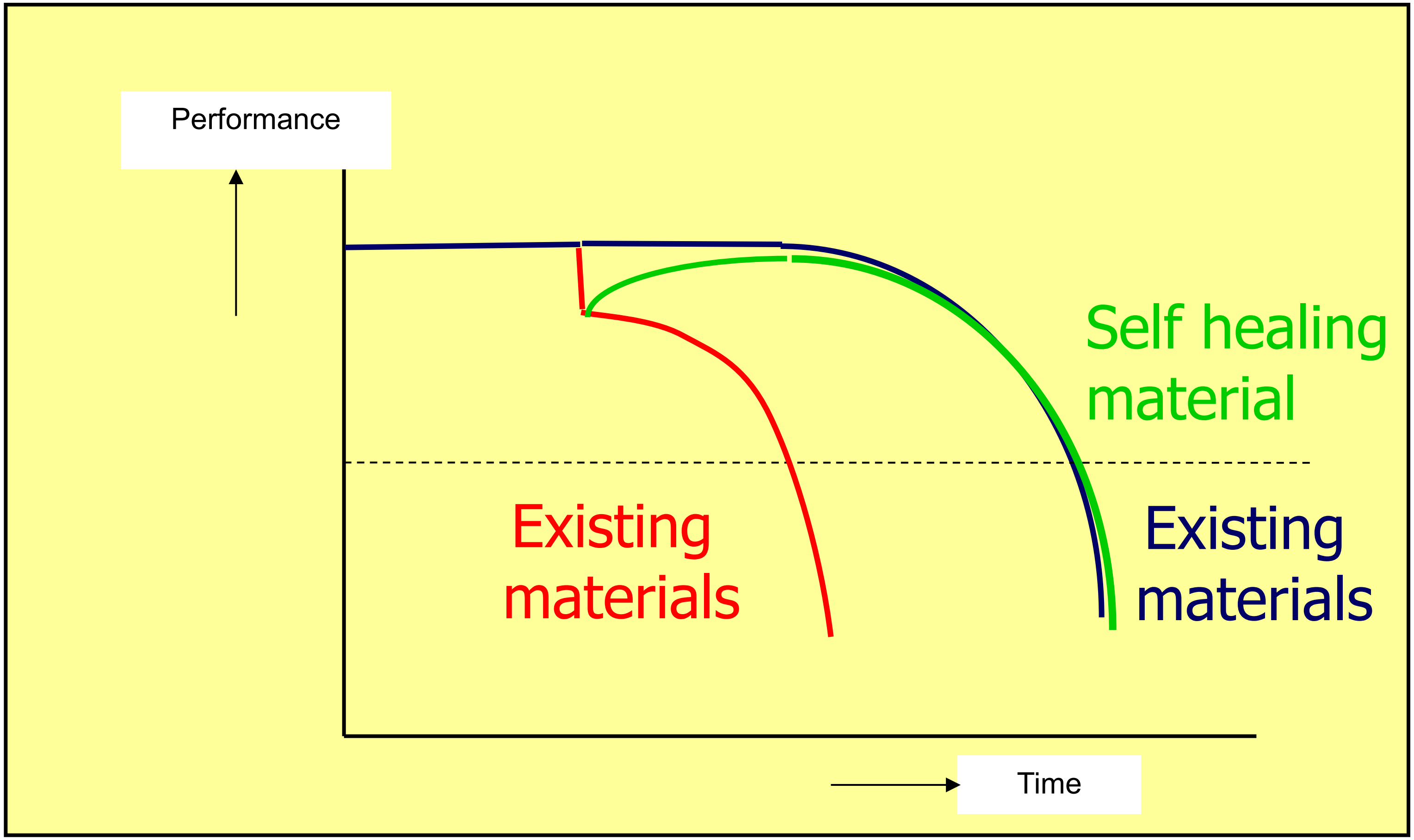
Outline

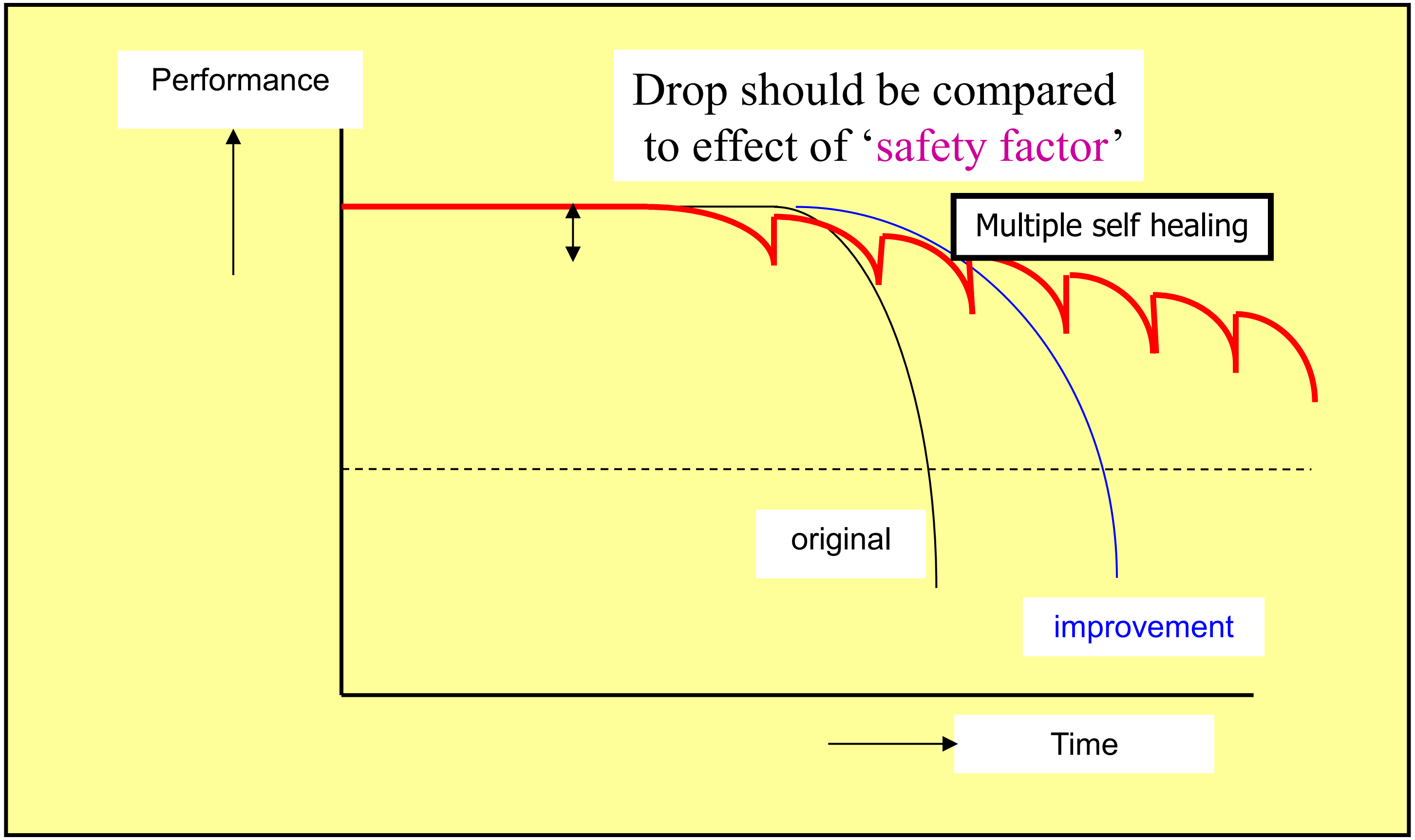
- Concept of Self-Healing Materials
- MAX-Phase Ceramics
- Self-Healing in Ti_2AlC & Ti_3AlC_2
- Other Self-Healing MAX-Phases?
- Summary

Concept of Self-Healing Materials

Self-Healing Ambitions
single event

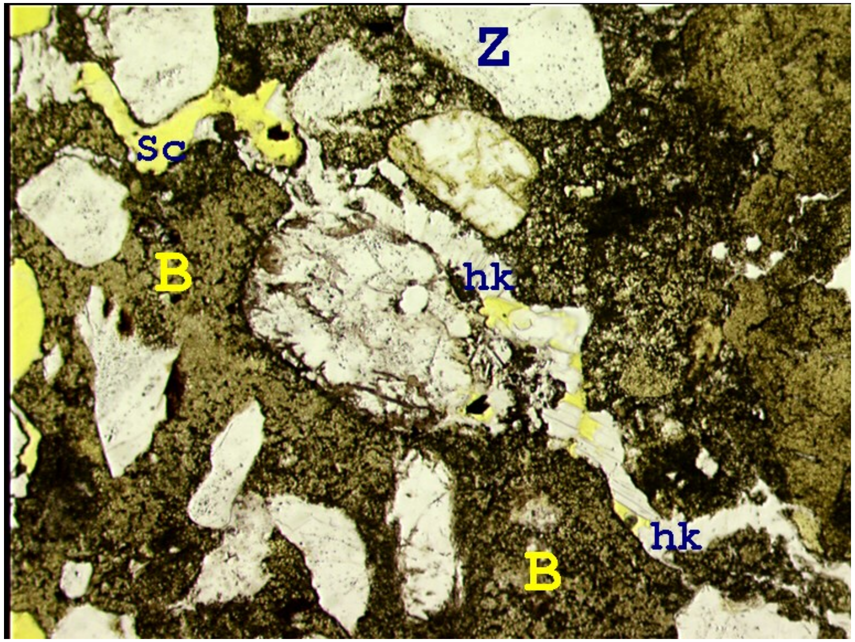


Self-Healing Ambitions
multiple healing



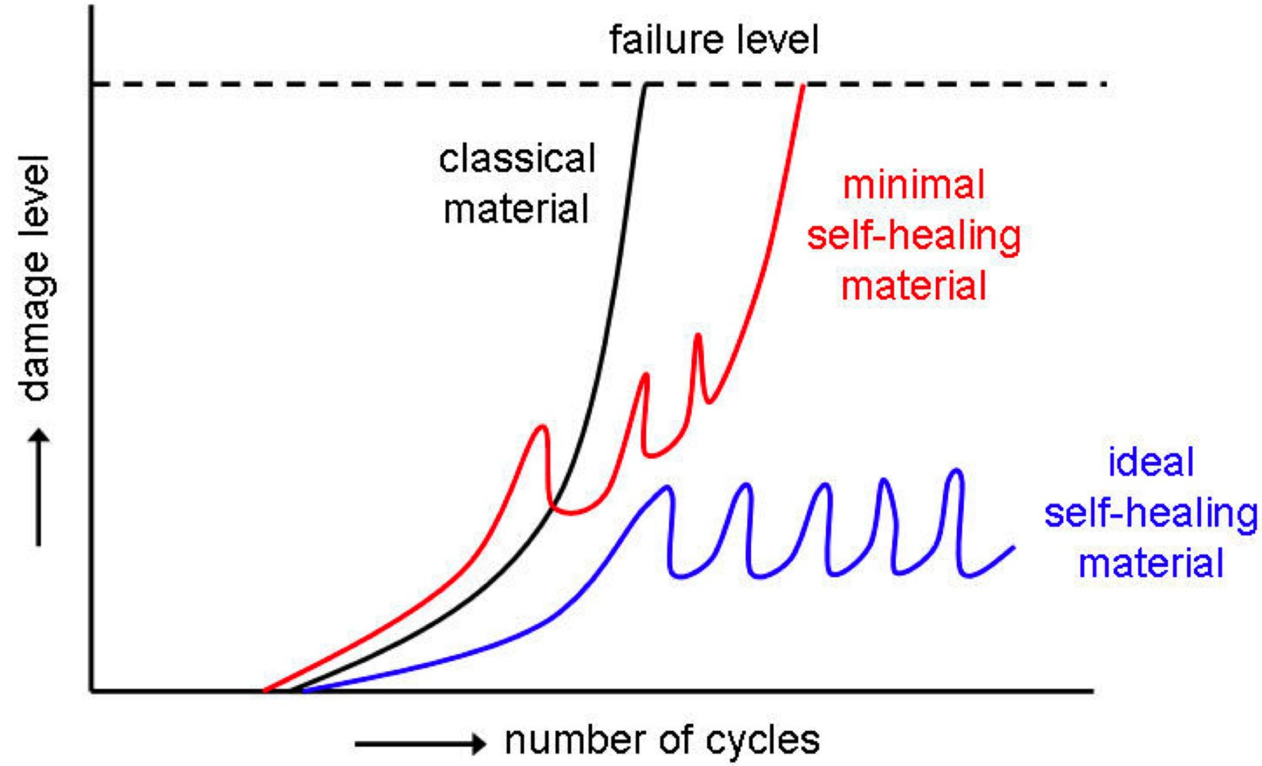
Concrete bridge less than 50 years old

Self-Healing Bridge in Amsterdam
multiple healing



Nearly 300 years old

Concept of Self-Healing Materials



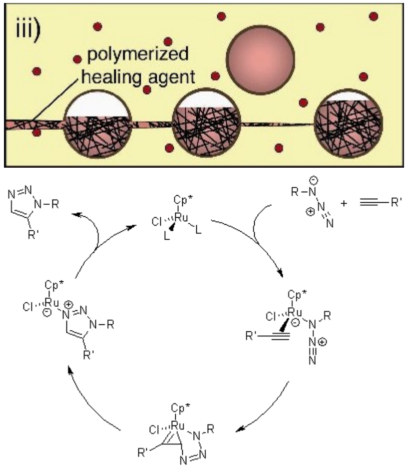
Schematic illustration of the damage development in a classical material (black line), an ideal self-healing material (blue line), and a realistic self healing material (red line)

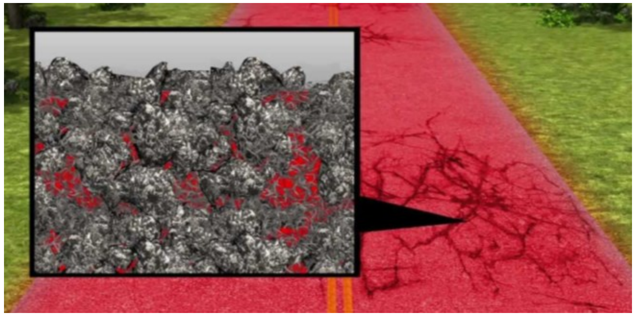
Design your Self Healing Material

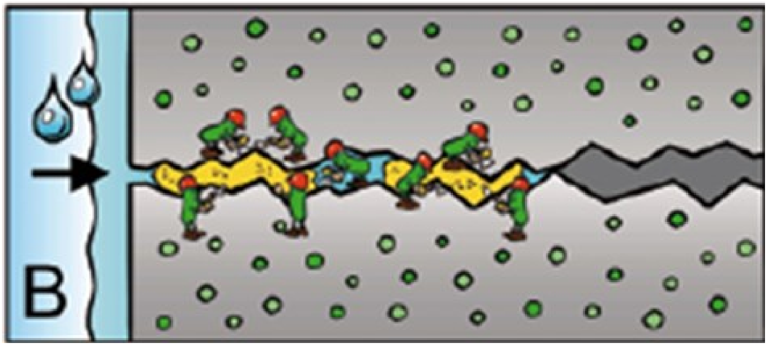
Requirements

- Flow to the crack
- Crack filling
- Bonding to crack faces

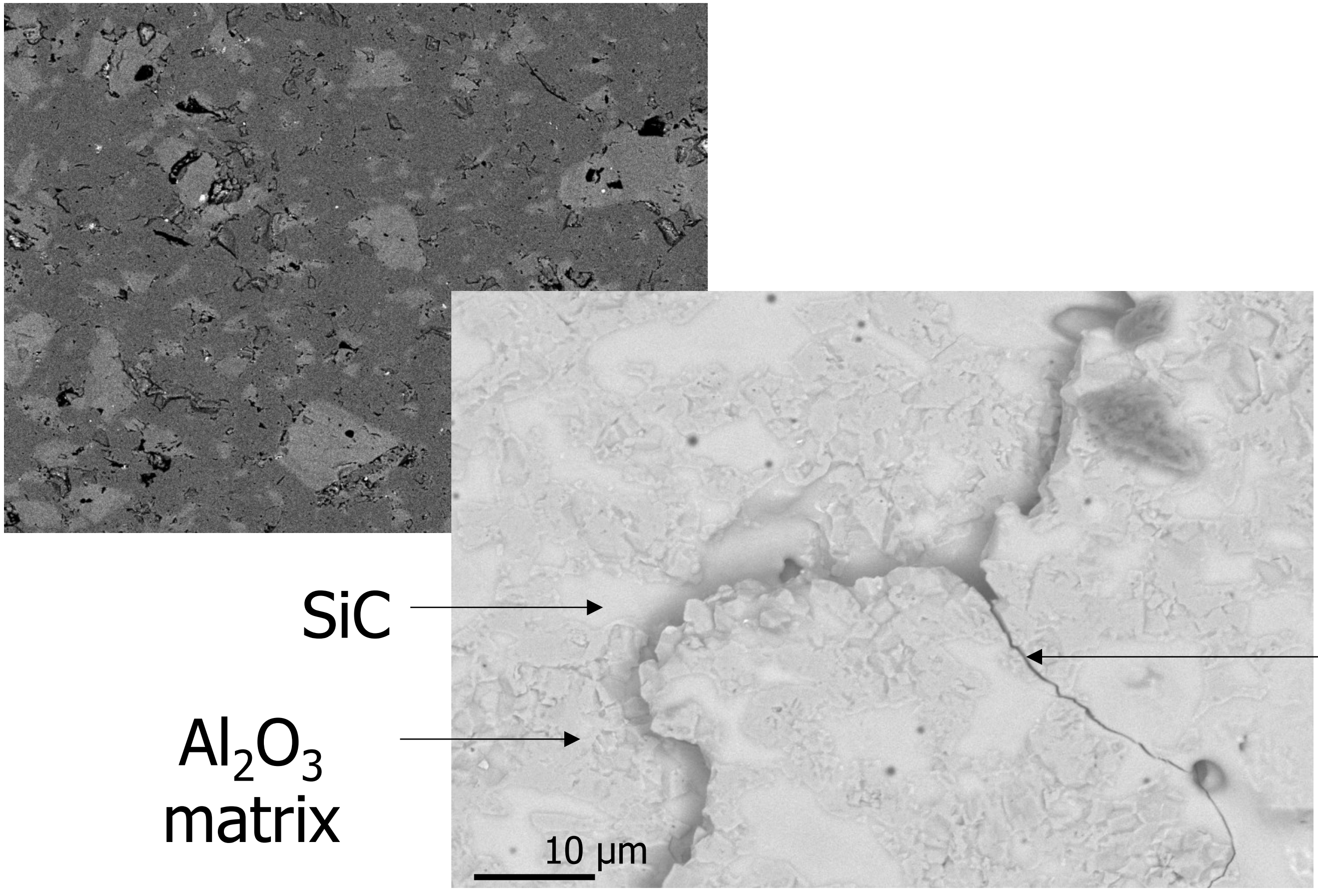
- **Polymers**: Micro-capsules or chemical reactions
- **Asphalt**: Induction heating
- **Concrete**: bacteria
- **Ceramics**: ???



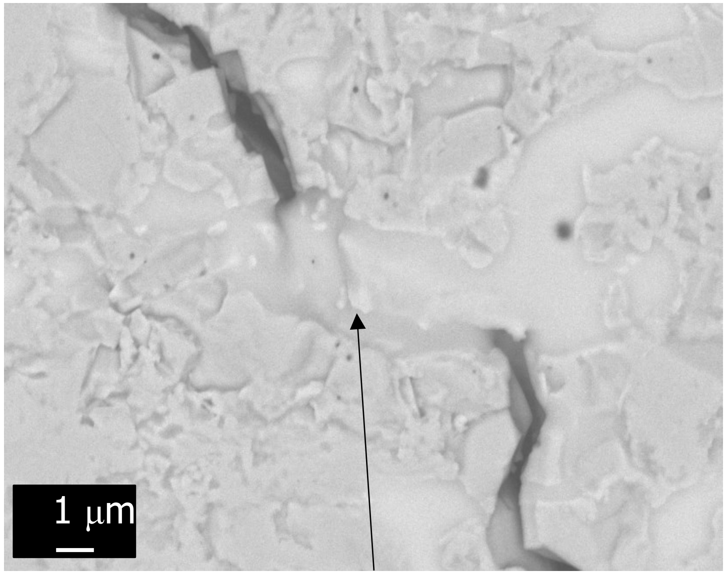




Self-Healing of Oxide Ceramics with (inter-)metallic Particles

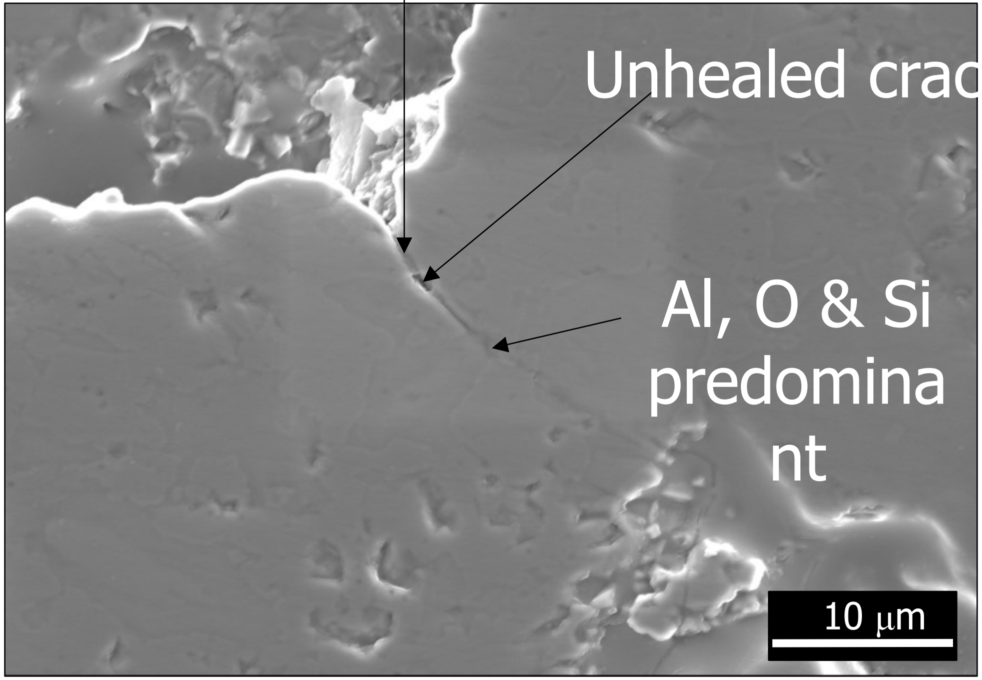


Self-Healing of Oxide Ceramics with (inter-)metallic Particles



SiO_2 by X-ray Micro Analysis (EDS) 1300 °C in Air for 6 hrs

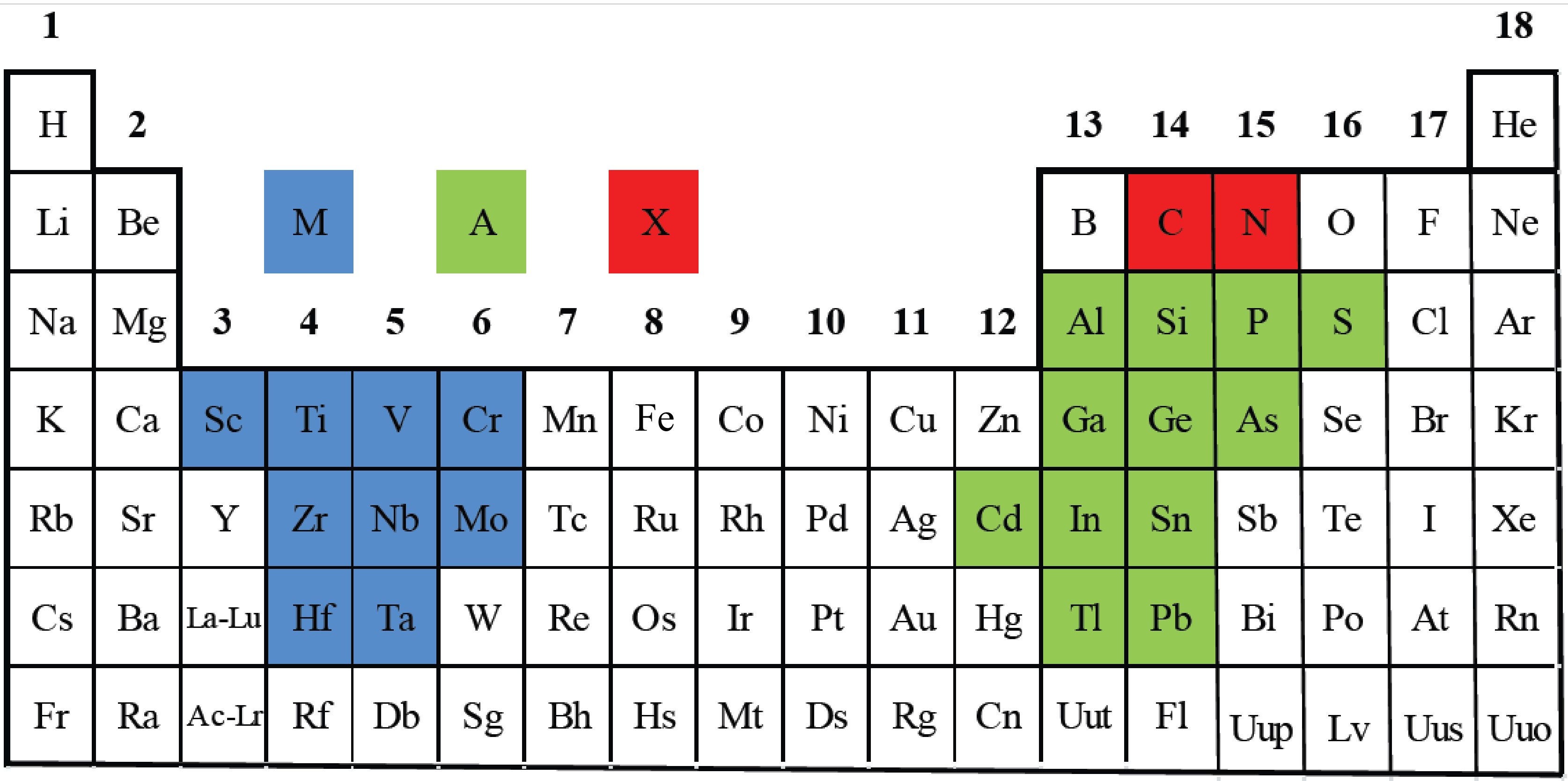
Al and Oxygen, small content of Si



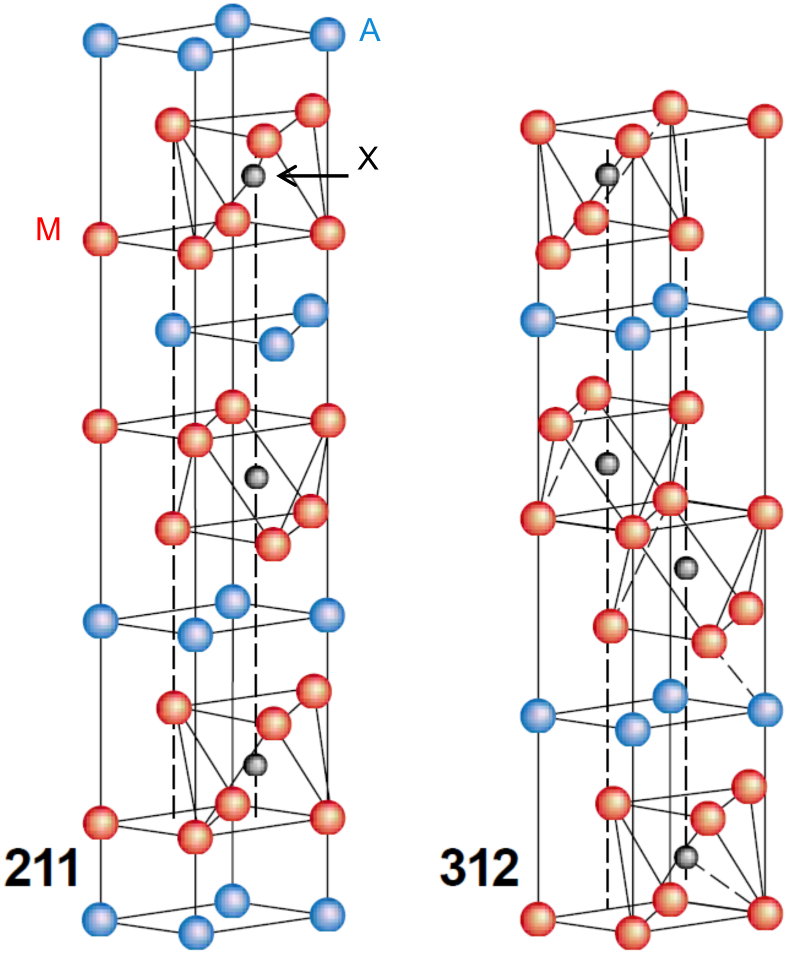
Synthetic Air, 1300C for 18h

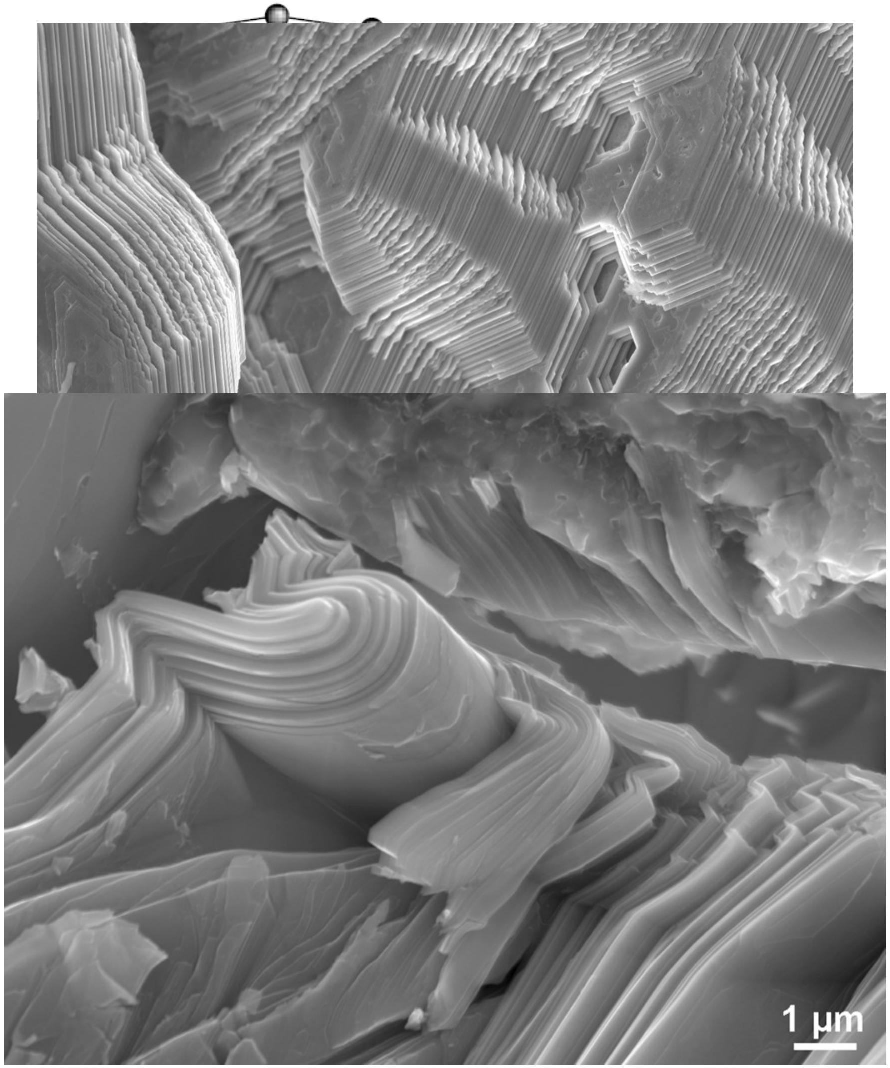
MAX Phase Ceramics

$M_{n+1}AX_n$ Phase Ceramics

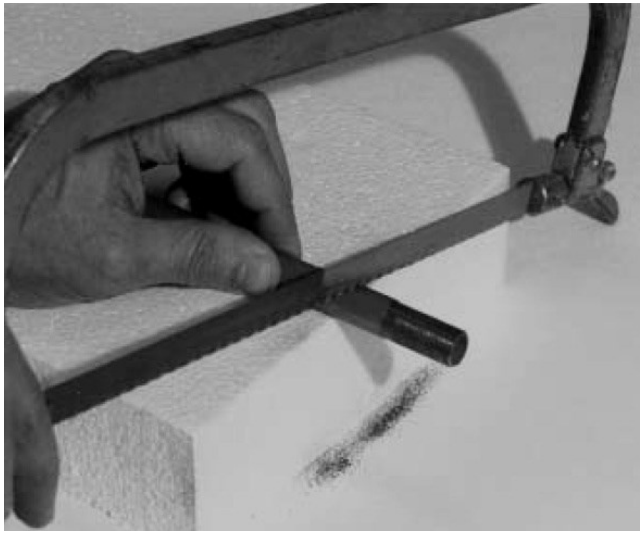


$M_{n+1}AX_n$ Phase Ceramics





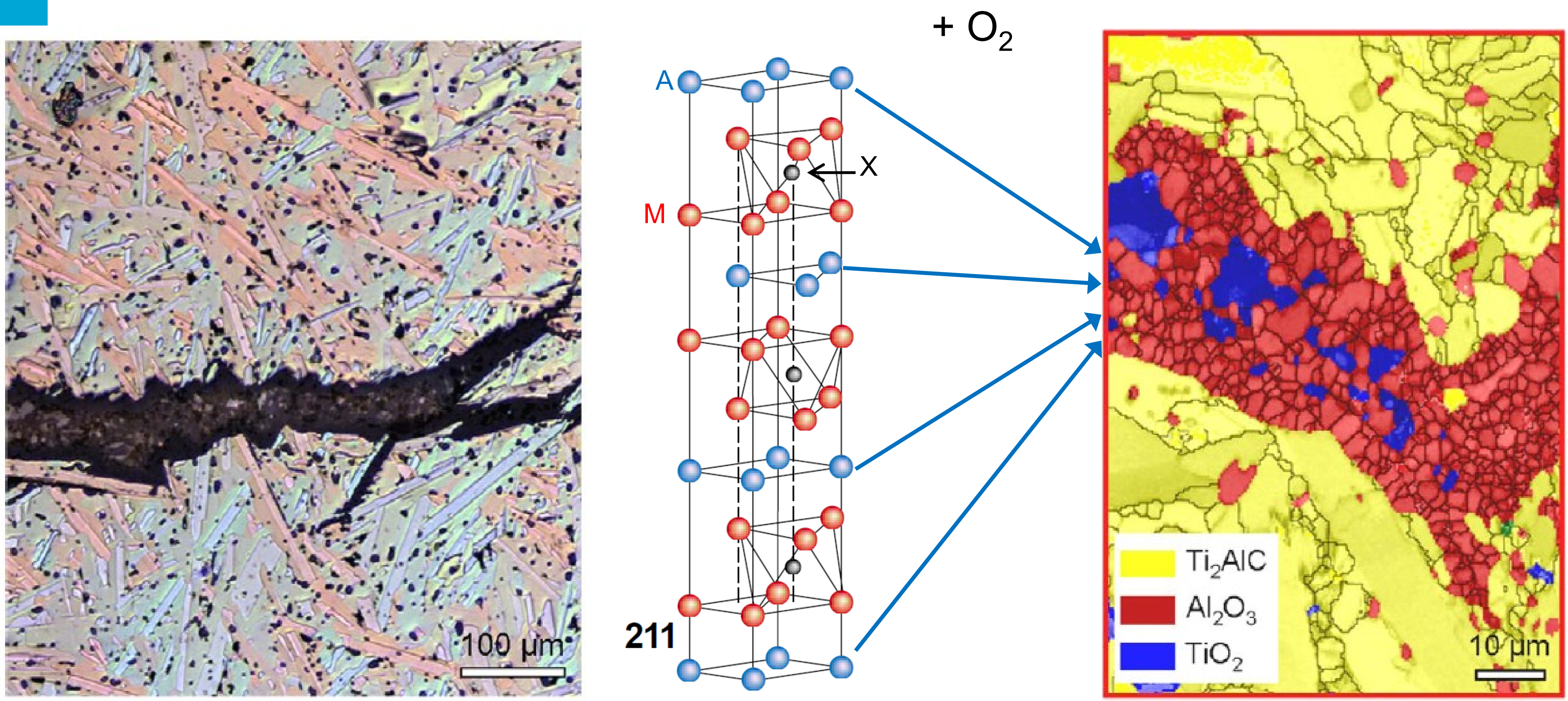
$M_{n+1}AX_n$ Phase Ceramics



- Thermodynamically stable nanolaminates
- Combine favourable properties of metals & ceramics
  - Good electrical & thermal conductivity*
  - Easily machinable
  - High temperature strength

* Electrical resistivity: 0.2-0.7 μΩm (298K)
Thermal conductivity: 12-60 W/mK

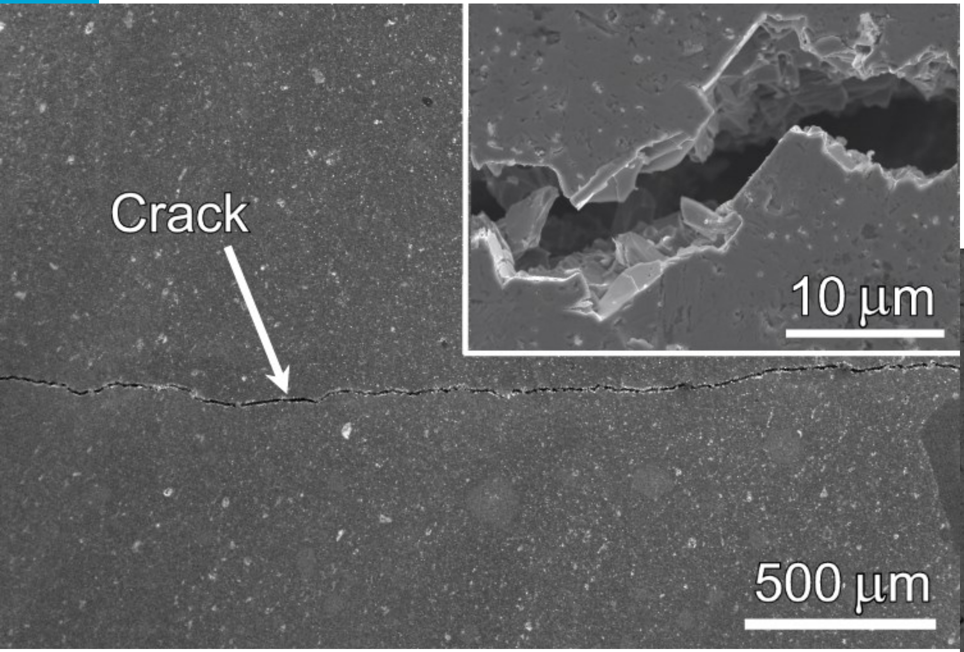
Crack-Healing in MAX Phases



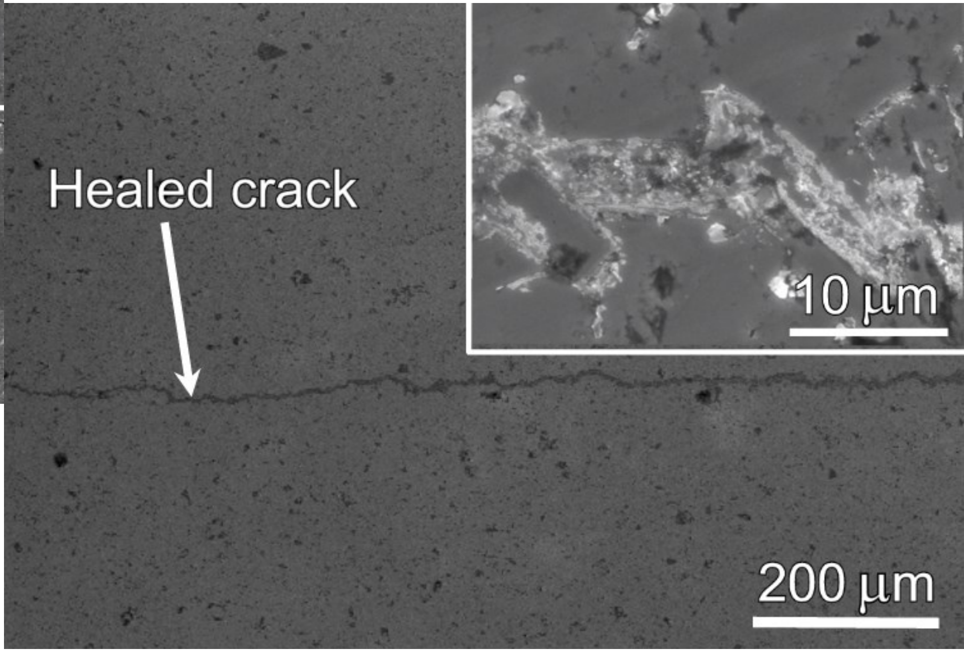
Self-Healing in Ti_2AlC & Ti_3AlC_2

Oxidation induced crack-healing in Ti_3AlC_2

proof of principle



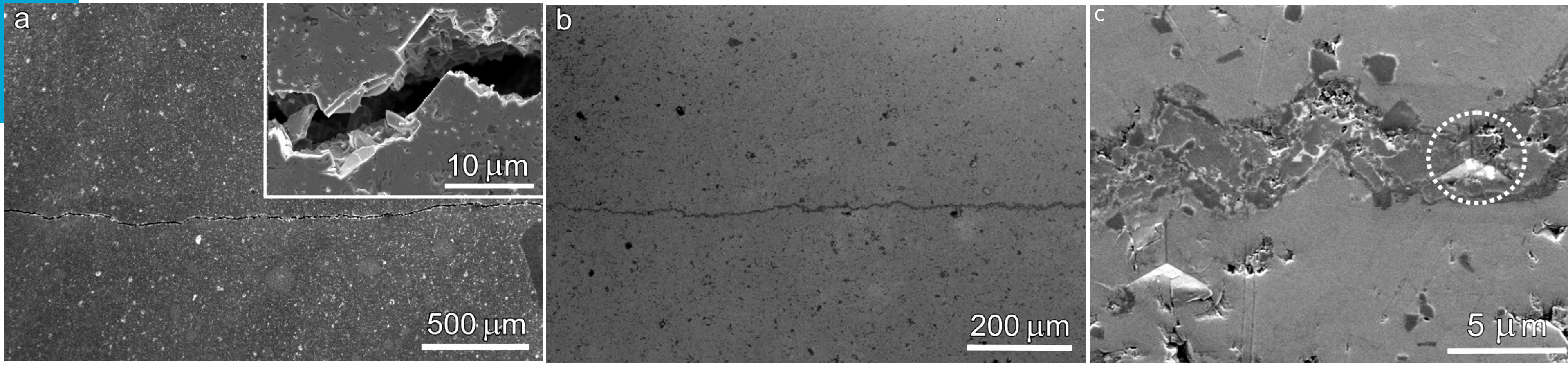
Selective oxidation of Al
2h @ 1100 °C in air



Healing product has similar properties as matrix

G.M. Song et al. Scripta Mat. 58 (2008) 13-16

Autonomous crack healing in MAX phase ceramics

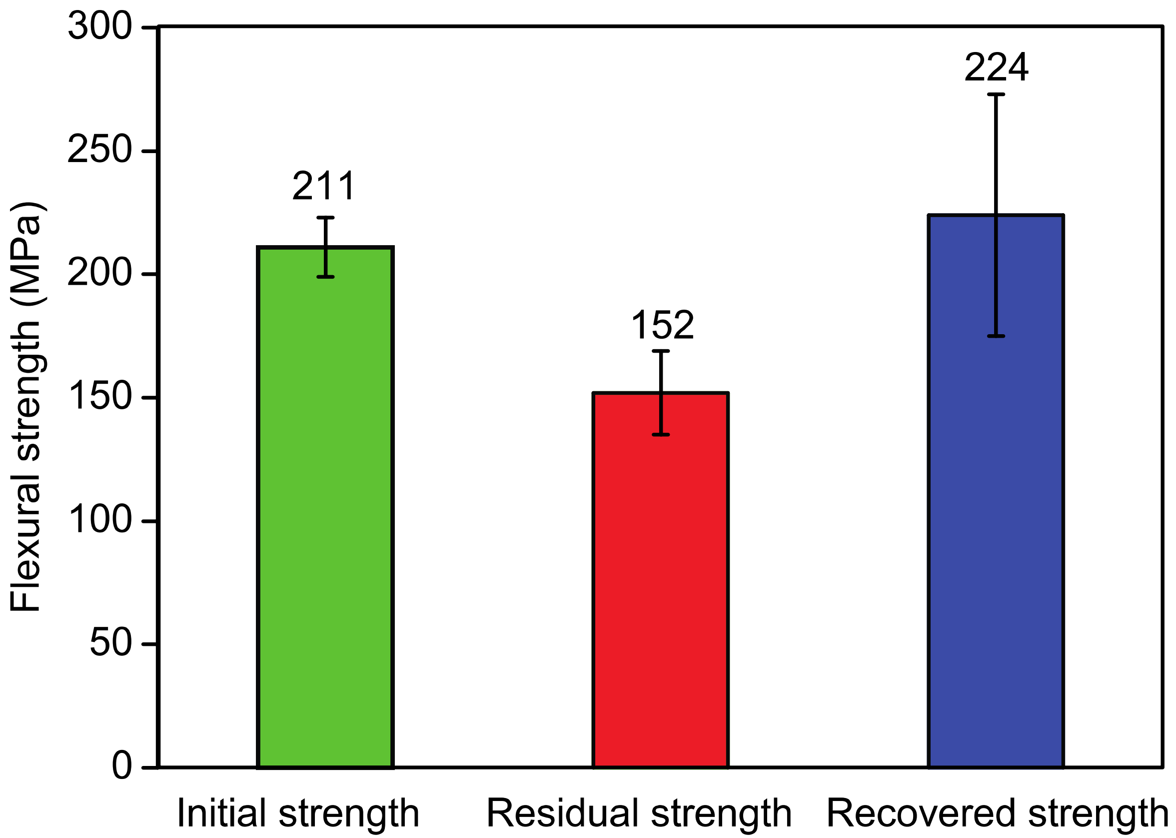


a. Crack with length of ~7 mm and average width of 5 microns
b. Crack healed after oxidation at 1100 ºC in air for 2 h
c. Healed zone: hardness $H = 13.3 \pm 2.1$ GPa and
   Young's modulus $E = 305 \pm 38$ GPa
   Base materials: $H = 11.7 \pm 1.6$ GPa and $E = 296 \pm 15$ GPa

➡ Cracks in Ti_3AlC_2 can be healed via oxidation with healing product having similar properties

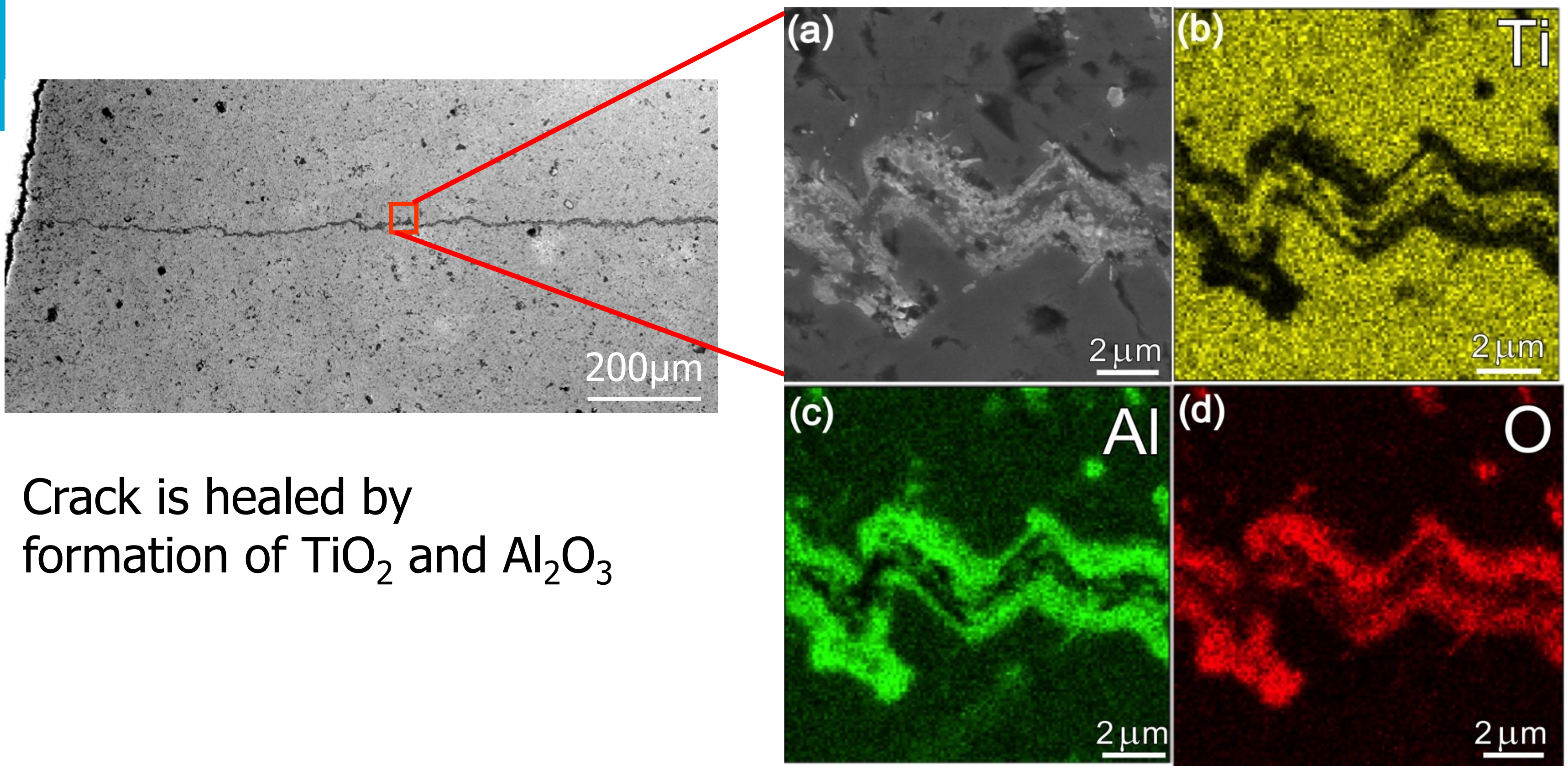
G.M. Song et al. Scripta Mat. 58 (2008) 13-16

Strength recovery after oxidation induced crack healing



Oxidized for 2 h in air @ 1200 ^{o}C

Element distribution in healed crack region of Ti_3AlC_2

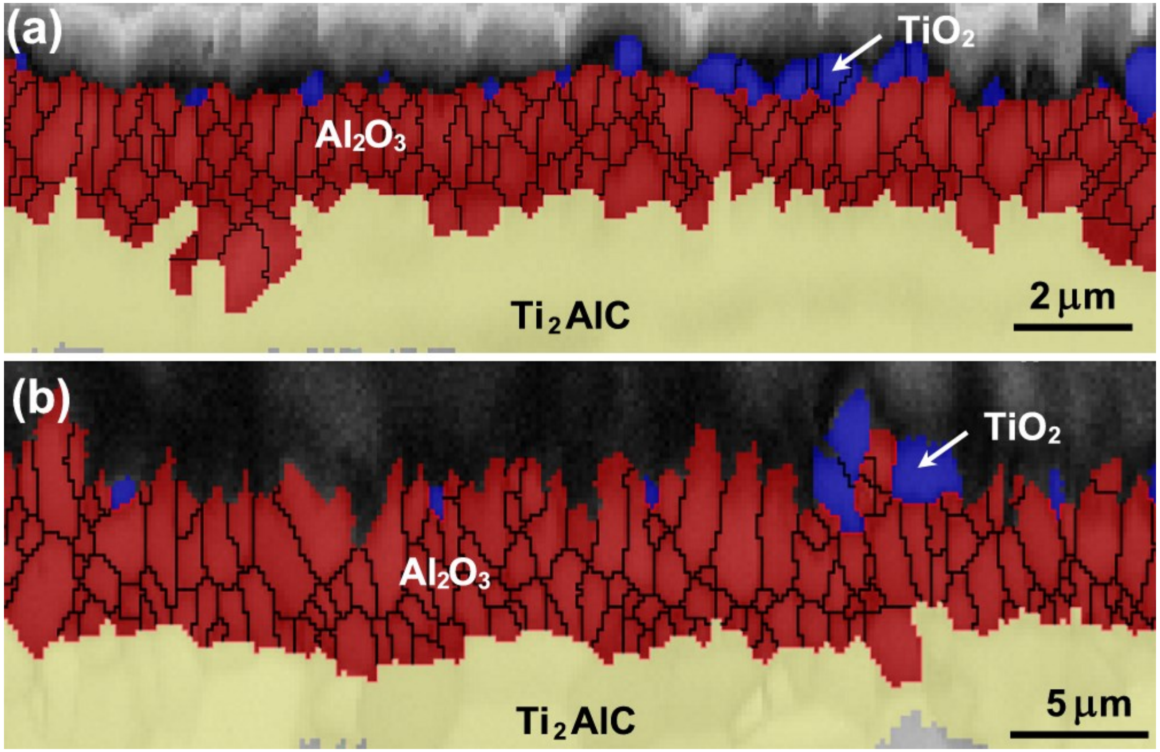


Crack is healed by formation of TiO_2 and Al_2O_3

→ Next, to reduce the amount of TiO_2 in the healing product, crack healing of Ti_2AlC is studied

G.M. Song et al. Scripta Mat. 58 (2008) 13-16

Oxidation behaviour of Ti_2AlC



Oxidation in air:

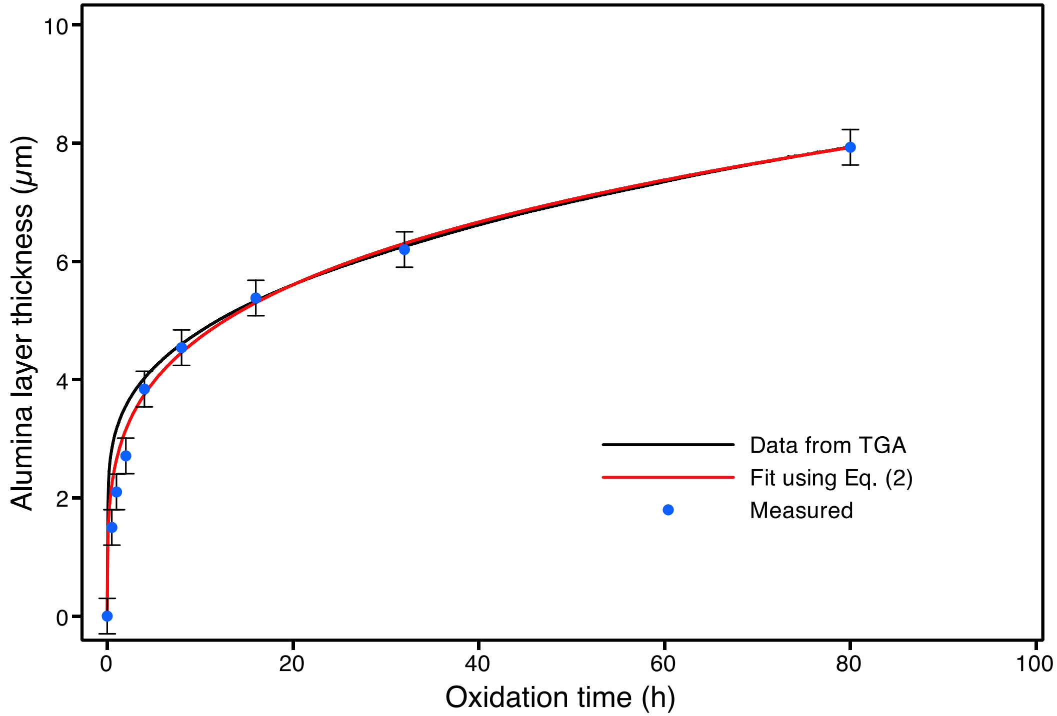
1 h @ 1200 ° C

16 h @ 1200 ° C

- Oxidation product is mainly α-Al_2O_3
- Only at the beginning minor amount of TiO_2 is formed
- Oxide grain size increases with oxidation time: $d_t = d_0 \sqrt{t}$

TUDelft G.M. Song et al. Mat. at High Temp. 29 (2012) 205-209

Oxidation behaviour of Ti_2AlC



Oxidation kinetics can be described with:

$$X = 2\sqrt{k_n} \, t^{\frac{1}{4}}$$

Where X is the alumina layer thickness, k_n is a rate constant and t is the oxidation time

Primary selective oxidation reaction:

$4Ti_2AlC + 3x\, O_2 = 4Ti_2Al_{1-x}C + 2x\, Al_2O_3$

Fast initial growth and slow subsequent growth of α-Al_2O_3 due to reduction of fast diffusion paths, i.e. oxide grain growth

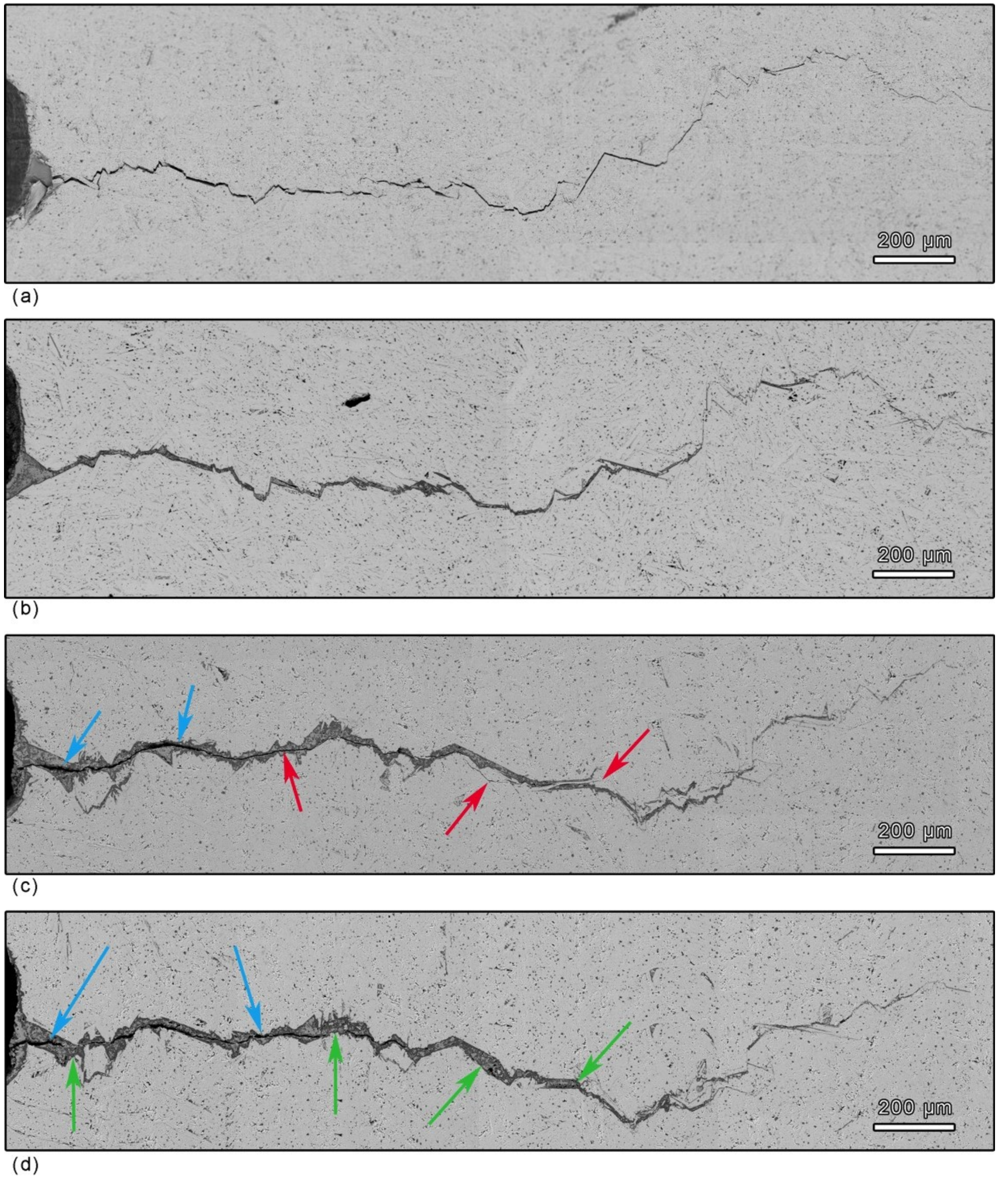
Multiple crack healing Ti_2AlC

(A) A through-thickness crack with a length of about 2.5 mm and gap of about 8 μm introduced after loading in 3-point bending (sample width ≈ 4 mm)

(A) Subsequent crack healing of first fracture at 1200 ° C for 2 hours in air

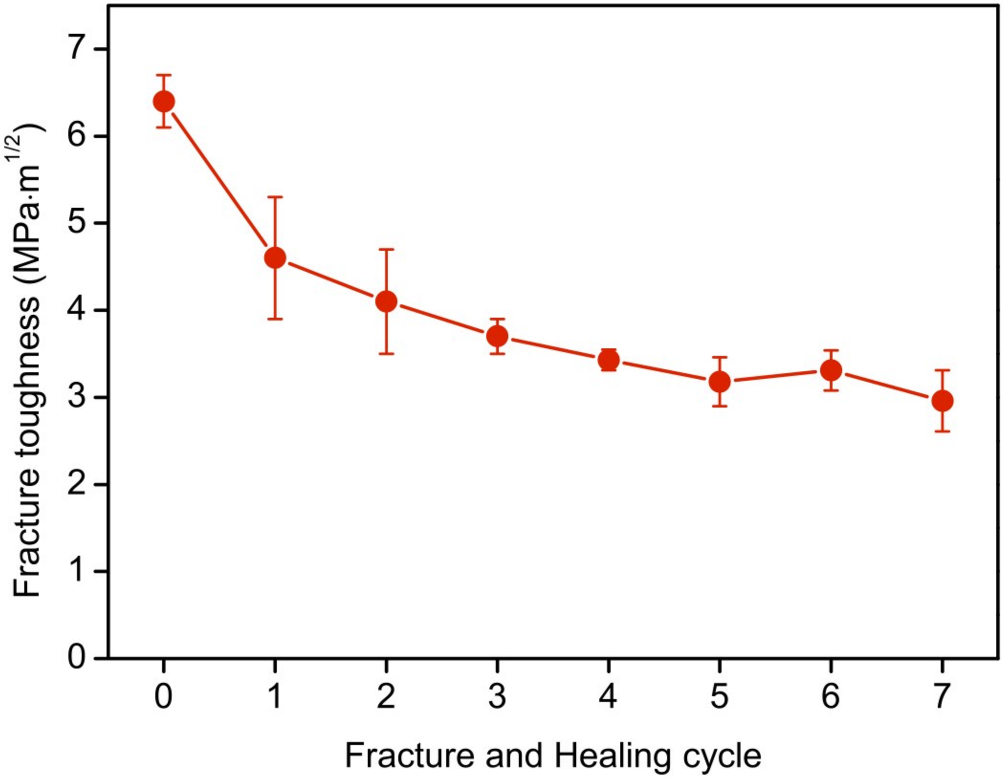
(A) Crack path after four fracture and healing cycles, and subsequent fracture

(B) Subsequent crack healing after the fifth fracture and healing cycle



➢ Crack runs along original healed crack path

Fracture thoughness evolution upon multiple crack healing



Fracture toughness at n cycles:

$$K_{Ic}(n) = \sigma Y \sqrt{\pi a_c(n)}$$

'Remnant' crack length:

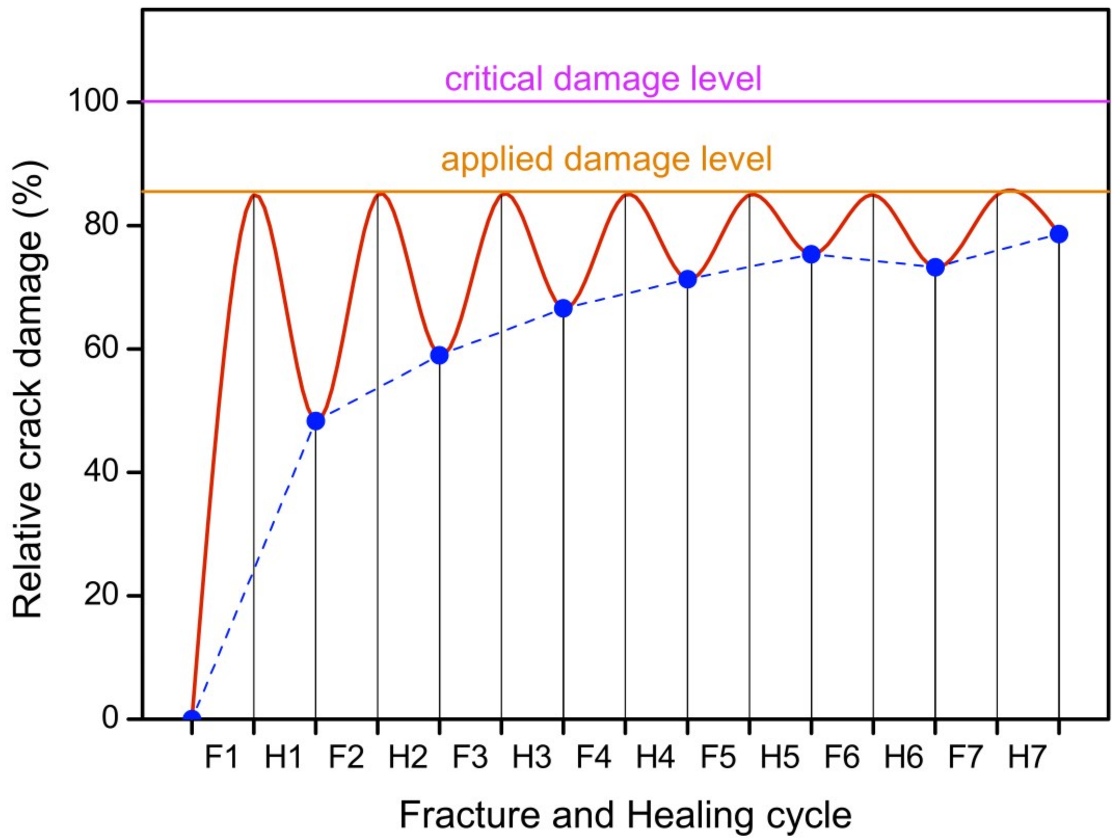
$$a_r(n) = a_c(0) - a_c(n)$$

$$a_r(n) \propto K_{Ic}^2(0) - K_{Ic}^2(n)$$

- Fracture toughness decreases due to scars and remnant cracks

S.B. Li, J. European Cer. Soc., 32 (2012) 1813-1820

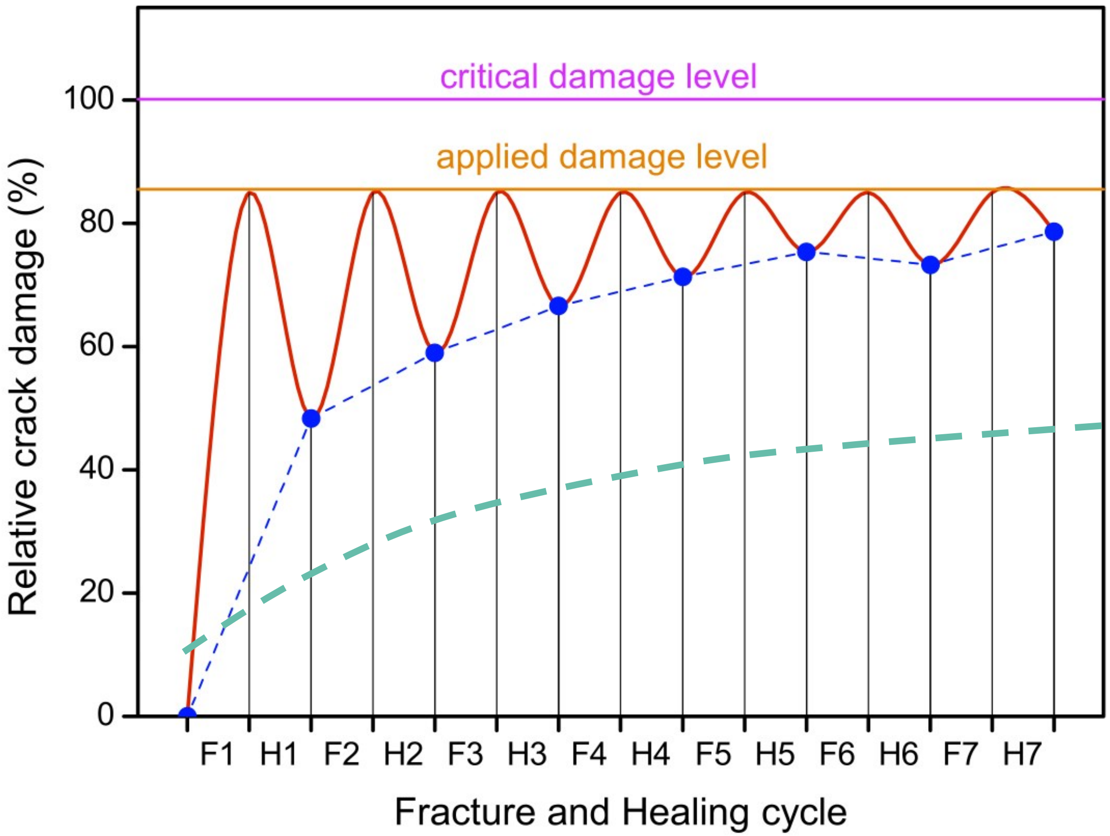
Multiple crack healing



- 'remnant' crack length

'Remnant' crack length: $a_r(n) = a_c(0) - a_c(n) \quad a_r(n) \propto K_{Ic}^2(0) - K_{Ic}^2(n)$

Multiple crack healing



- ‘remnant’ crack length

‘remnant’ crack length
at lower damage level

‘Remnant’ crack length: $a_r(n) = a_c(0) - a_c(n) \square \quad a_r(n) \propto K_{Ic}^2(0) - K_{Ic}^2(n)$

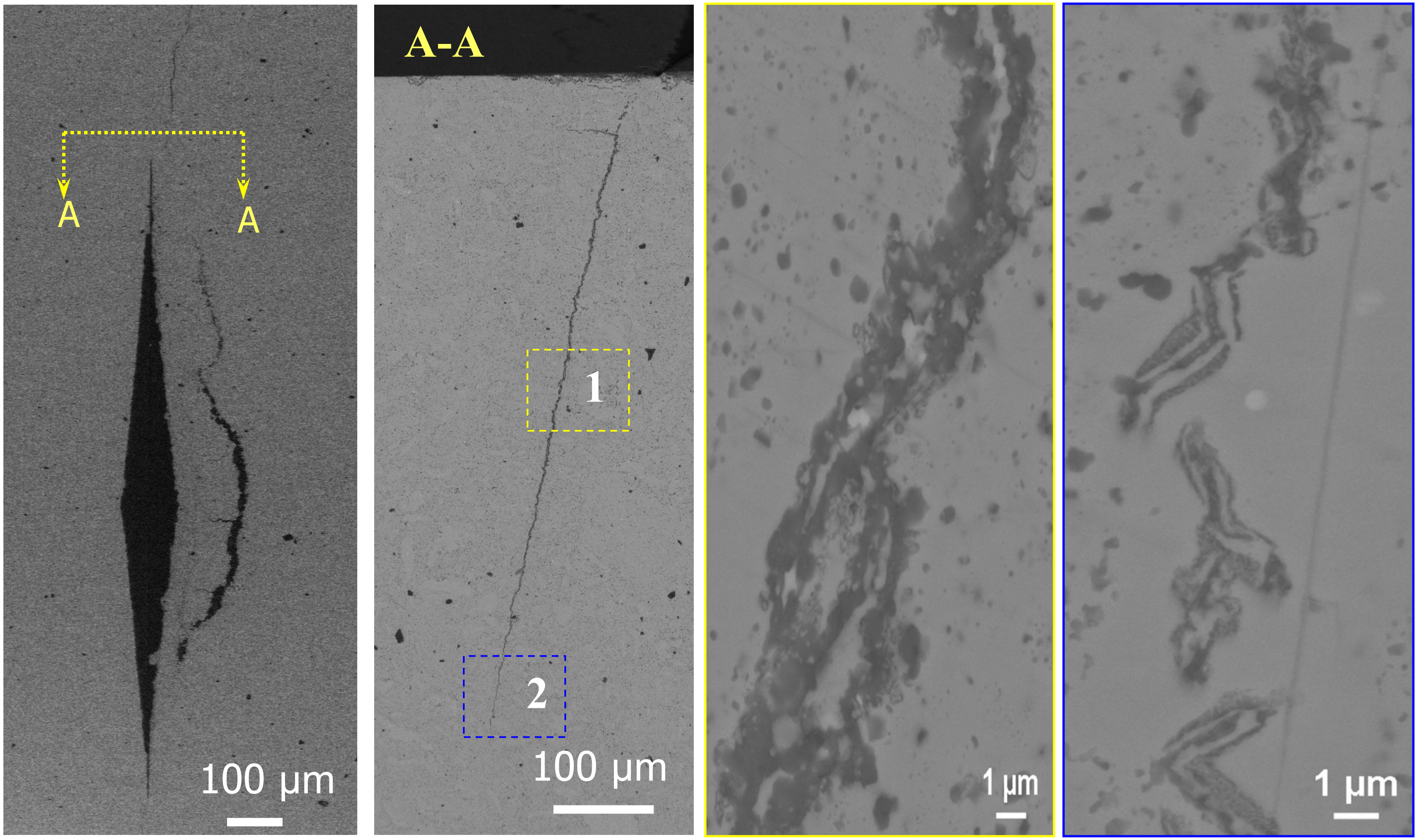
➢ Depends on sample dimensions and applied damage level

Other Self-Healing MAX-Phases?

Other Self-Healing MAX Phases?

M\A	Al	Si	Ge	Ga	As	P	S	In	Sn	Tl	Pb	Cd	
Ti	Ti_2AlC Ti_2AlN Ti_3AlC_2 Ti_4AlN_3 Ti_3AlN_2*	Ti_3SiC_2 Ti_4SiC_3 Ti_2SiC* Ti_5SiC_4 Ti_2SiN*	Ti_2GeC Ti_3GeC_2 Ti_4GeC_3	Ti_2GaC Ti_2GaN Ti_4GaC_3	Ti_2AsC	Ti_2PC	Ti_2SC	Ti_2InC Ti_2InN	Ti_2SnC Ti_3SnC_2 Ti_7SnC_6	Ti_2TlC	Ti_2PbC	Ti_2CdC	25
Cr	Cr_2AlC	Cr_2SiC Cr_3SiC_2	Cr_2GeC	Cr_2GaC Cr_2GaN		Cr_2PC	Cr_2SC						8
V	V_2AlC V_3AlC_2 V_4AlC_3	V_2SiC V_3SiC_2*	V_2GeC	V_2GaC V_2GaN	V_2AsC	V_2PC	V_2SC						11
Sc	Sc_2AlC			Sc_2GaC Sc_2GaN				Sc_2InC		Sc_2TlC			5
Nb	Nb_2AlC Nb_4AlC_3	Nb_3SiC_2	Nb_2GeC	Nb_2GaC	Nb_2AsC	Nb_2PC	Nb_2SC	Nb_2InC	Nb_2SnC				9
Mo		Mo_3SiC_2		Mo_2GaC									2
Zr	Zr_2AlC Zr_2AlN	Zr_3SiC_2					Zr_2SC	Zr_2InC Zr_2InN	Zr_2SnC	Zr_2TlC Zr_2TlN	Zr_2PbC		9
Hf	Hf_2AlC Hf_2AlN	Hf_3SiC_2					Hf_2SC	Hf_2InC	Hf_2SnC Hf_2SnN	Hf_2TlC	Hf_2PbC		9
Ta	Ta_2AlC Ta_3AlC_2 Ta_4AlC_3 Ta_6AlC_5	Ta_3SiC_2		Ta_2GaC									6
	19	13	6	12	3	4	6	7	7	5	3	1	86

Crack healing in Cr_2AlC

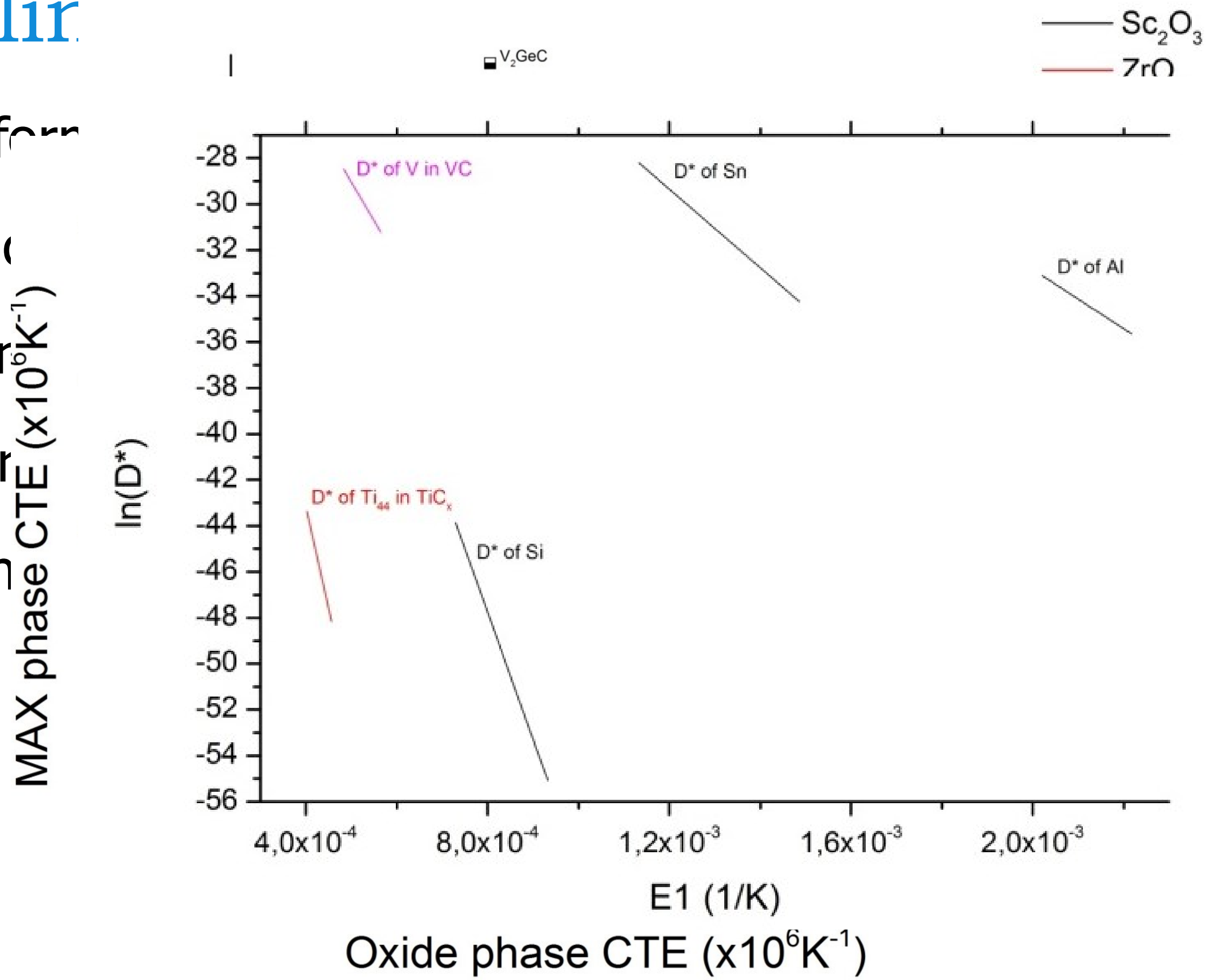


Cr_2AlC crack damage by Knoop indent exposed at @ 1100 ° C for 4 h in air

S.B. Li et al. J Am Cer Soc. (2013)

Selection of MAX Phases for Self-Healir

- ΔG of Oxide forr
- Diffusivity of (
- Volume expar
- Mechanical pr
- Adhesion of h



Selection of MAX Phases for Self-Healing

- Al containing ceramics due to an excellent CTE match, high oxide melting temperature and strong affinity to react with oxygen.

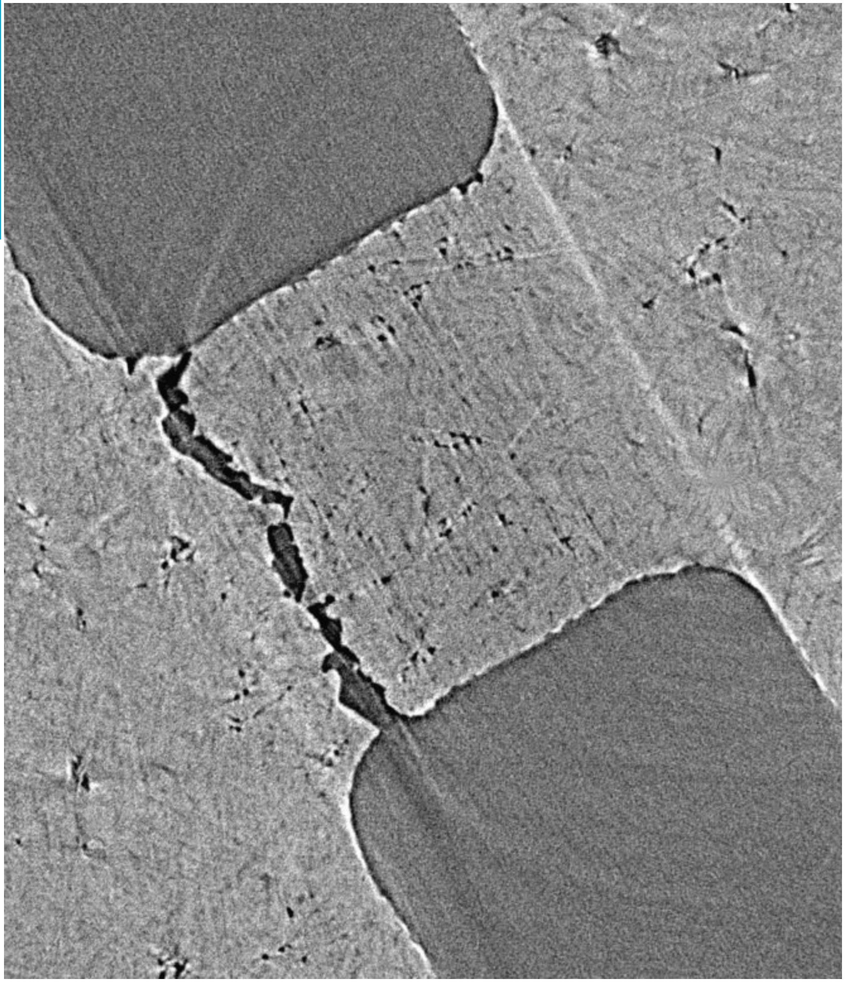
- SiO_2 would be a viable healing agent, though to date only Ti_3SiC_2 of the Si containing MAX-phase compounds has been successfully synthesized.

- Of the M-Oxides ZrO_2 shows beneficial crack filling properties

Summary

- Crack healing by selective oxidation demonstrated for Ti_3AlC_2; healing products: Al_2O_3 and TiO_2
- Initial fast and subsequent slow formation of healing product; beneficial for crack healing
- Multiple crack healing demonstrated; evolution of 'remnant' crack length depends on size of damage with respect to component dimensions
- Crack healing and strength recovery of Cr_2AlC is possible; healing product: pure Al_2O_3
- Identification of potentially self-healing MAX phases underway

Crack Healing in Ti_2AlC



SHeMat

PEOPLE

MARIE CURIE ACTIONS

Avecom

Fraunhofer UMSICHT

ceratec® Technical Ceramics BV

EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

ARKEMA The world is our inspiration

UNI FREIBURG

BIOKON international The Biomimetics Association

University of BRISTOL

KLM

ESPCI ParisTech

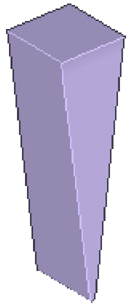
GKT GmbH

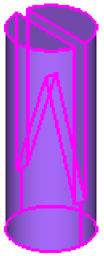
UNIVERSITEIT GENT

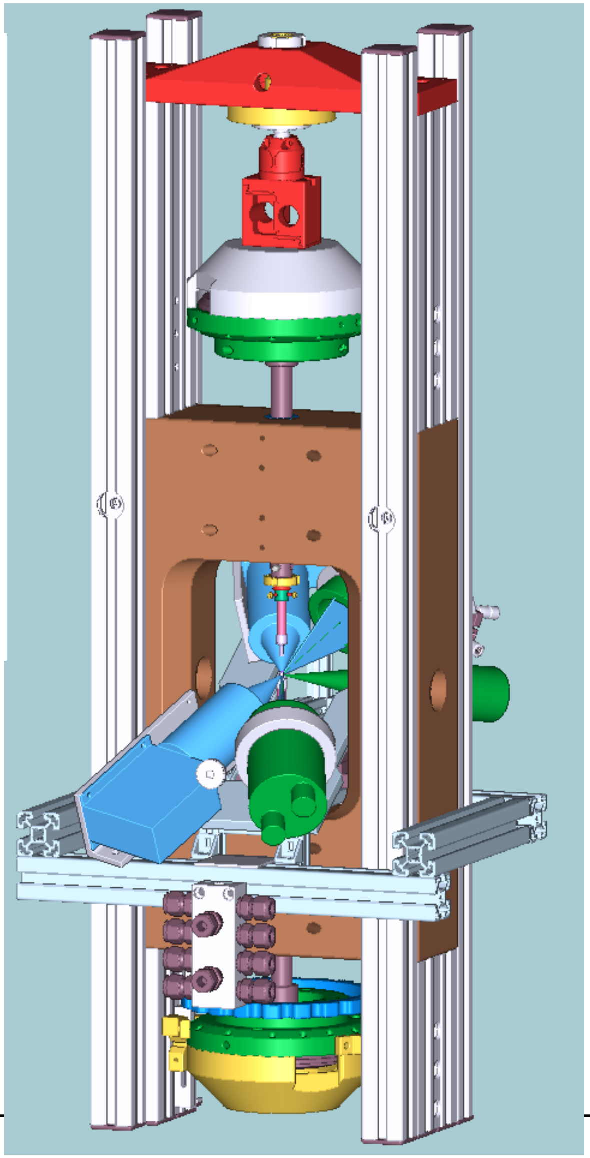
Second Synchrotron experiment

@ PSI Switzerland

- SLS in situ healing
  - Laser furnace
  - Chevron notch samples
- ESRF strain analysis
  - Comparative study between different MAX phase
  - Diffraction experiments done right
- Tomography
  - 3D non destructive characterisation
  - Limits in resolution and sample size
  - Potential to help understanding self healing behaviour



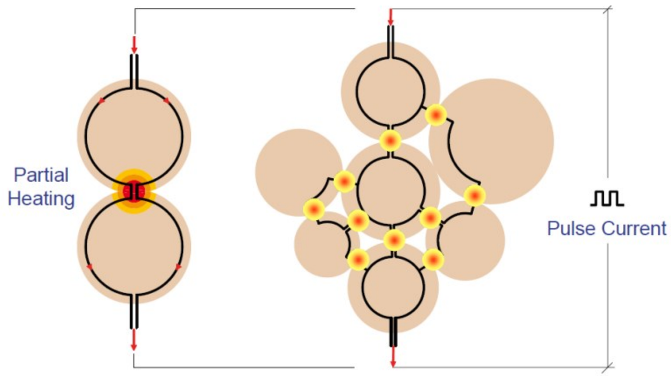




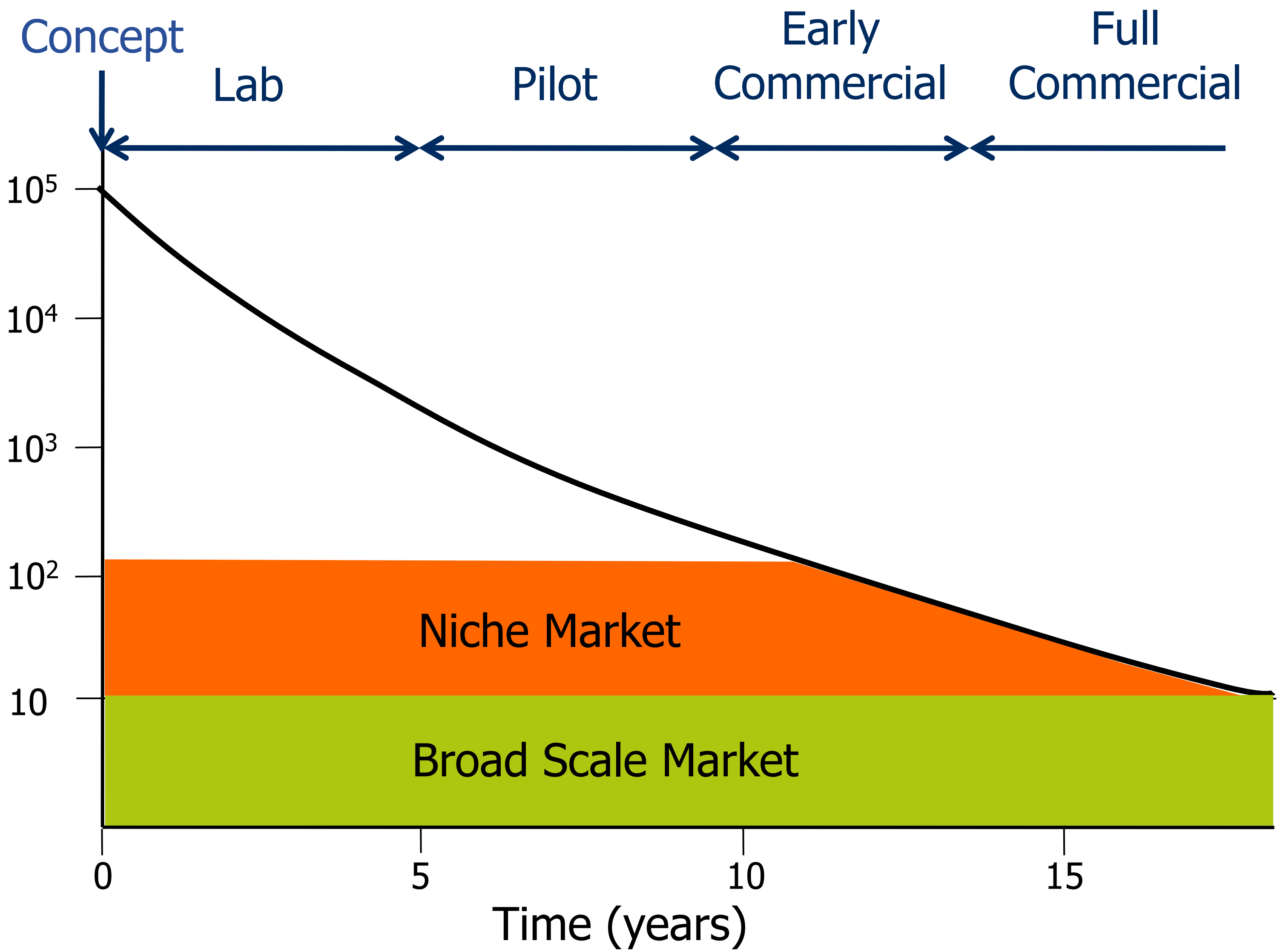
Synthesis of MAX Phase Ceramics

Spark Plasma Sintering

- Pulsed DC current
- ✓ Short processing time
- ✓ Fast consolidation
- ✓ Even heat distribution
- ✓ High level of control



Learning curve for new materials



Source: Ceramic Bulletin 69 (1990) p. 1903