Oxidation of Alumina-Forming MAX Phases in Turbine Environments

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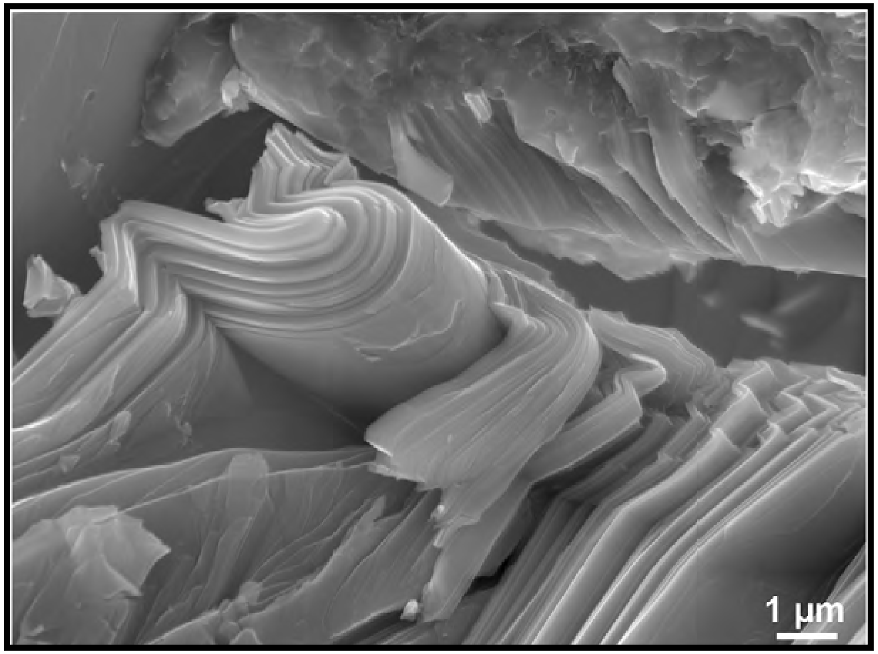
Materials for High Temperature Applications: Next Generation Superalloys and Beyond
TMS Annual Mtg., San Diego, CA, Feb 26 - Mar 2

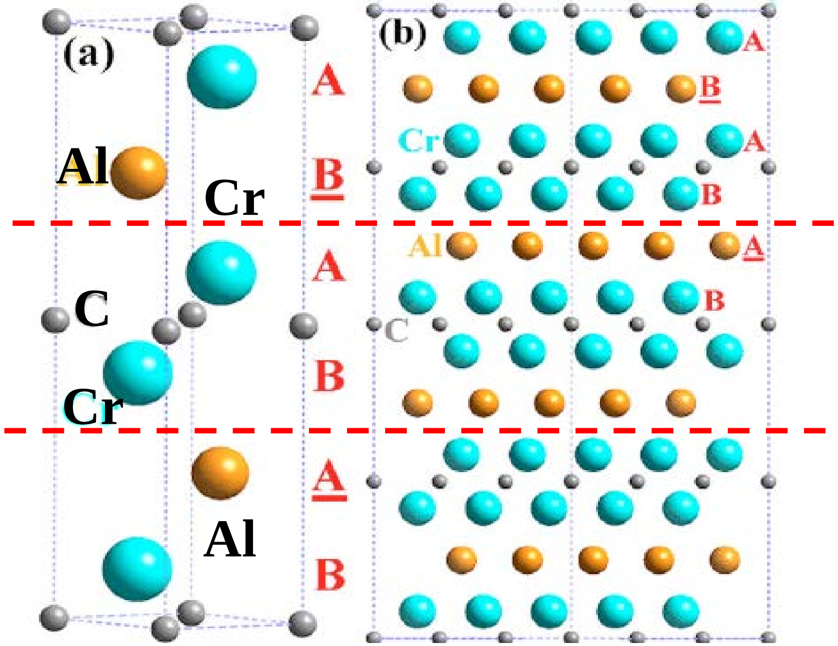
Strain Tolerance:
Kinking and Crack Deflection in $Cr_2Al(Si)C$
Bend test fracture; basal plane nano-laminate

W. Yu, S. Li, W.G. Sloof, 2007



K_{IC} = 6.6 MPa/m$^{1/2}$

Lin et al. 2006



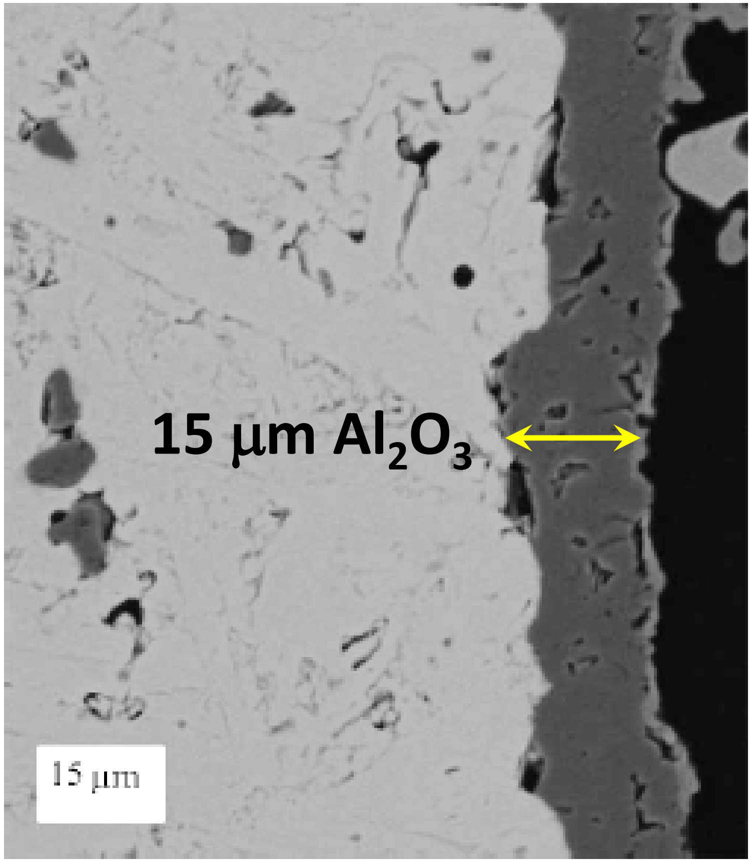
(0001) Sliding

(Cr-Al)/(Cr-C)=0.40 σ_{bond} , 0.43 $\gamma_{cleav.}$

Commercial Ti_2AlC 211 MAXthal (Sandvik/Kanthal)

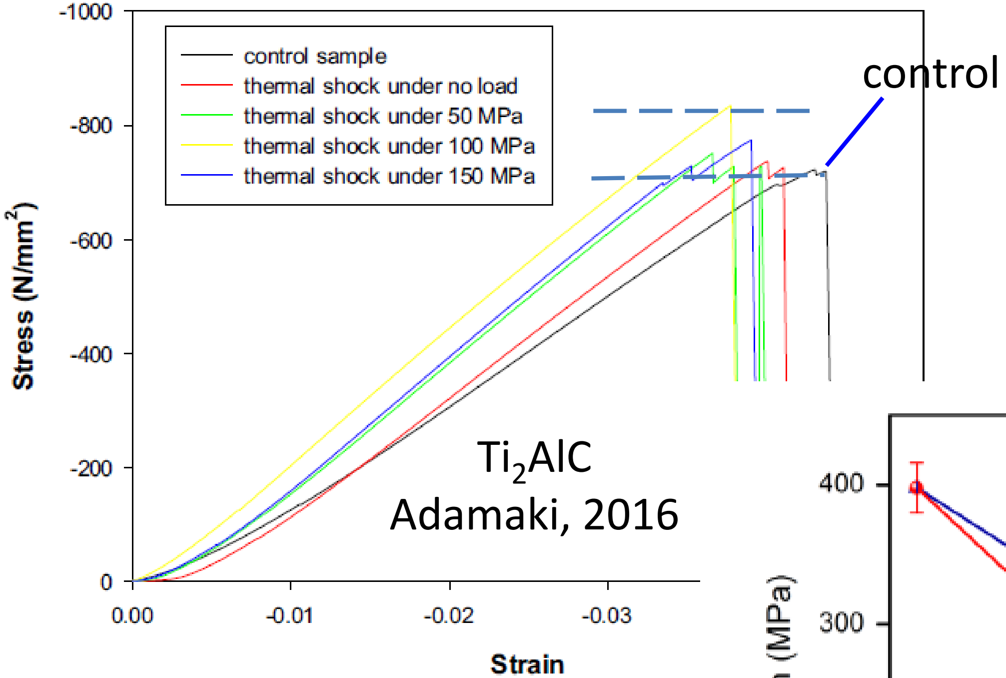
M. Sundberg, G. Malmqvist, A. Magnusson, T. El-Raghy, 2004

8000 cycles to 1350°C!



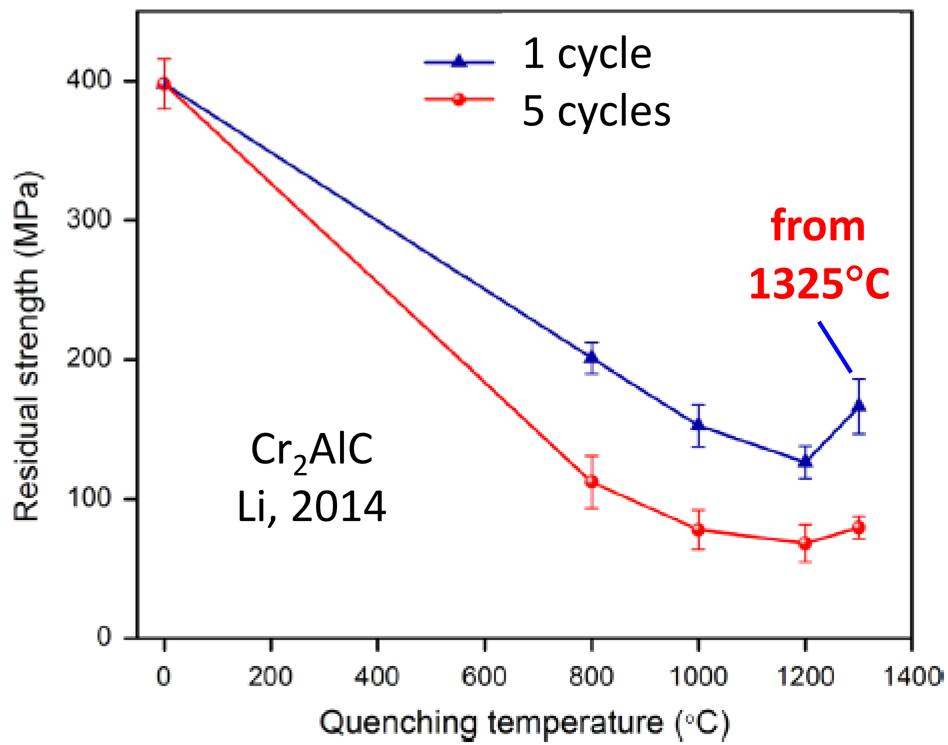
Thermal Shock of M_2AlC

(thermal conductivity x strength) / (CTE x modulus)

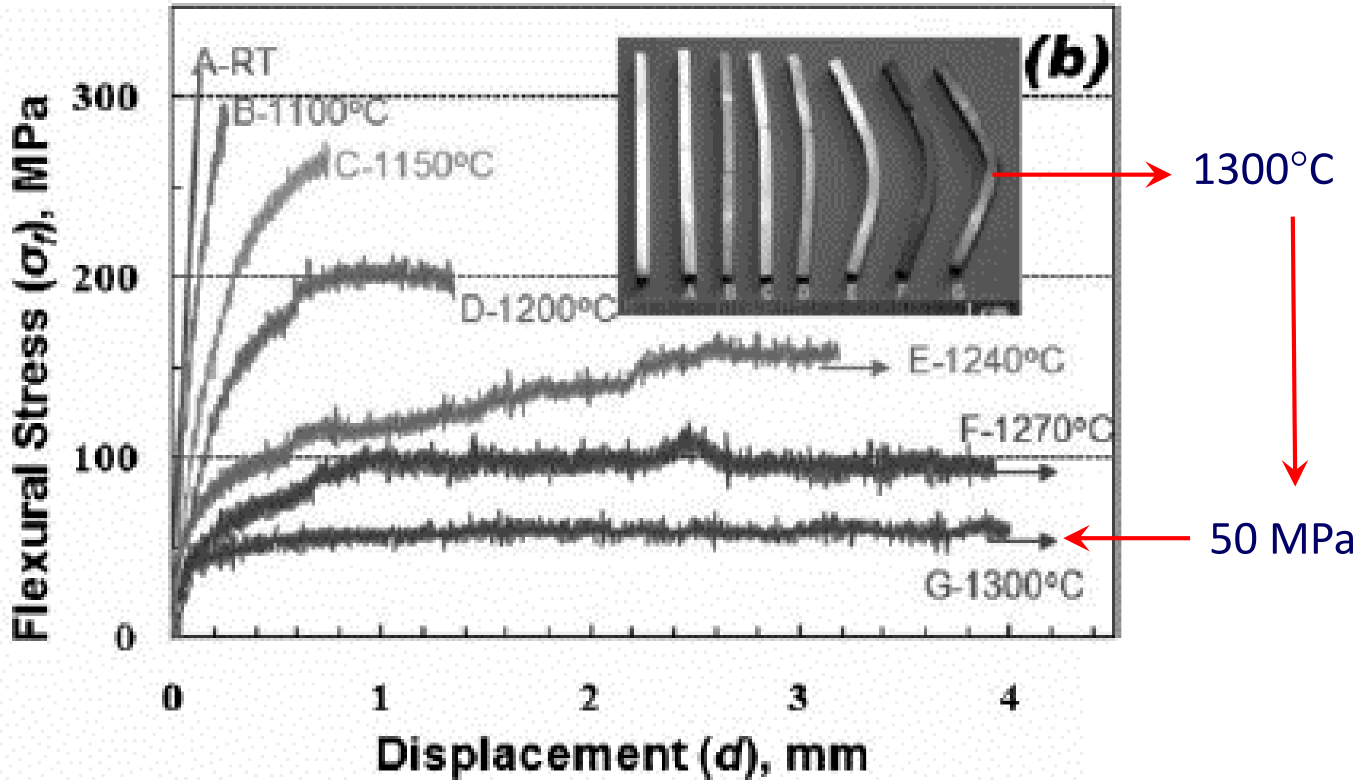


700 MPa Compressive strength retained (Gleeble test) after **-90°C/s quench from 1200°C**

Bend Strength after **Water Quench**



Some ~50 MPa Ti_3SiC_2 High Temperature Bend Strength
(Sun, 2006)



Motivation and Rationale
Ti_3AlC_2, Ti_2AlC, Cr_2AlC

- α-Al_2O_3 formers, (slow, low-volatility)
- Na_2SO_4 corrosion resistance
- CTE close to YSZ, α-Al_2O_3
- Damage (Strain ?) tolerance,

  nano-laminate shear, machinable
- Thermal shock resistance: ~1400°C quench
- $K_{IC} \approx 7$ MPa·$m^{1/2}$

Purpose: Relate Al-MAX phases to Coatings and turbine environments

Kanthal Ti_2AlC, Cr_2AlC

1. High temperature α-Al_2O_3 kinetics
2. High pressure burner rig
3. YSZ Thermal Barrier Coatings
4. Superalloy/MAX Phase Hybrids
5. Hot corrosion/LCF

Al-MAX Phases and Turbine Environments

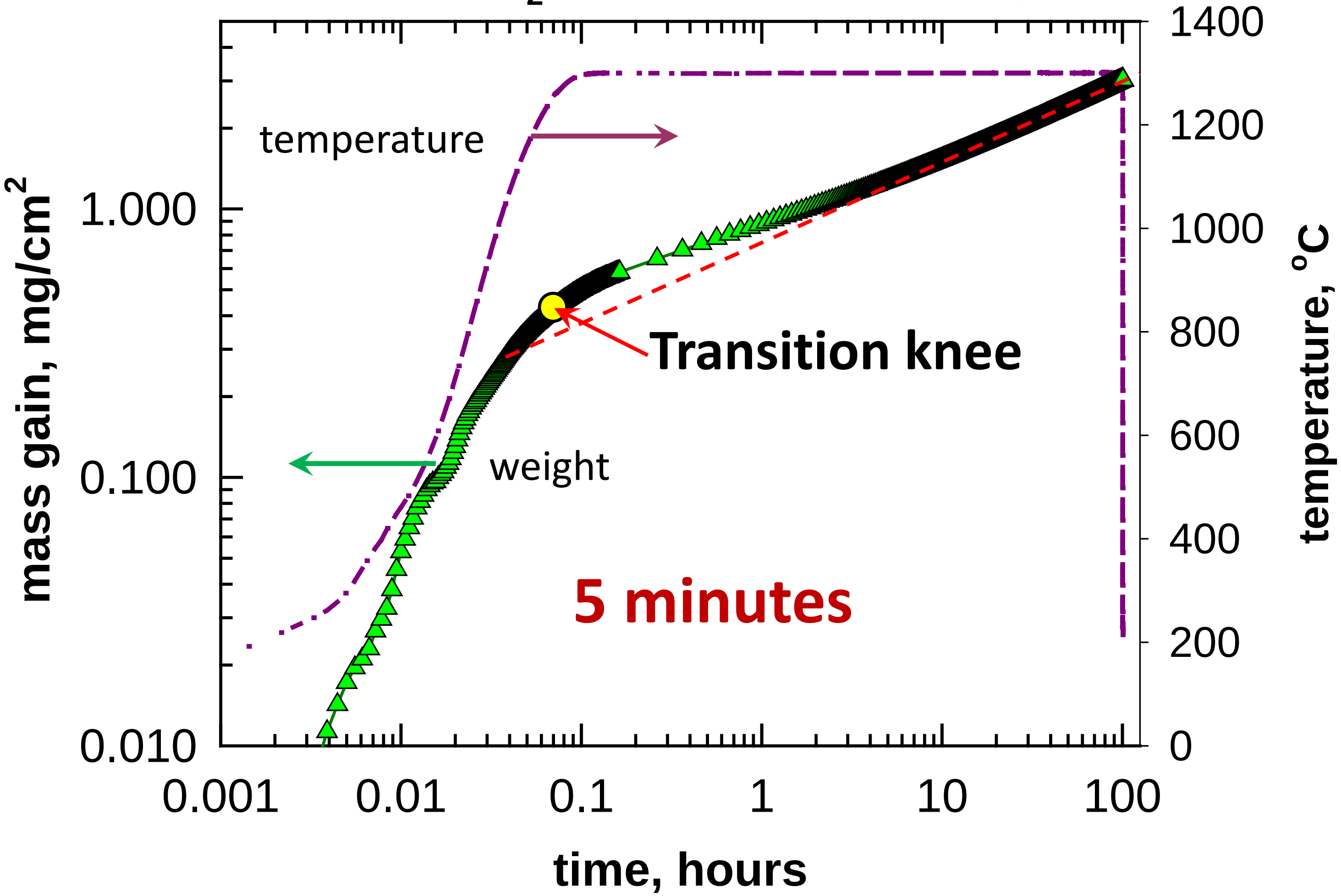
1) High temperature α-Al_2O_3 kinetics

- Al_2O_3 grain boundary diffusivity
- transient TiO_2 growth
- cubic kinetics

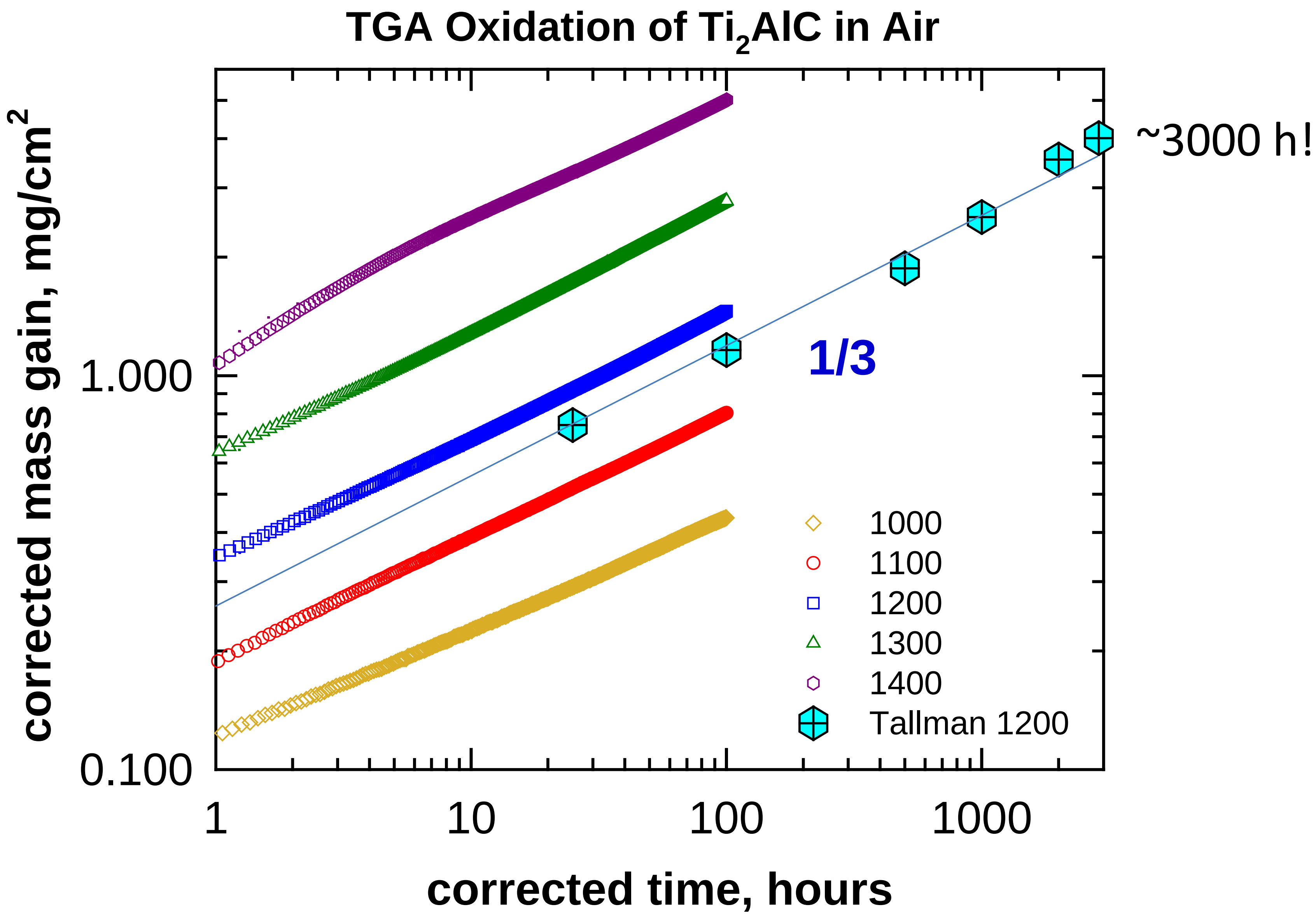
"Oxygen Permeability and Grain-Boundary Diffusion Applied to Alumina Scales," *NASA TM 217855*, pp. 1–14, August 2013.

1300°C Ti_2AlC TGA:

Rapid TiO_2 Transients on heating

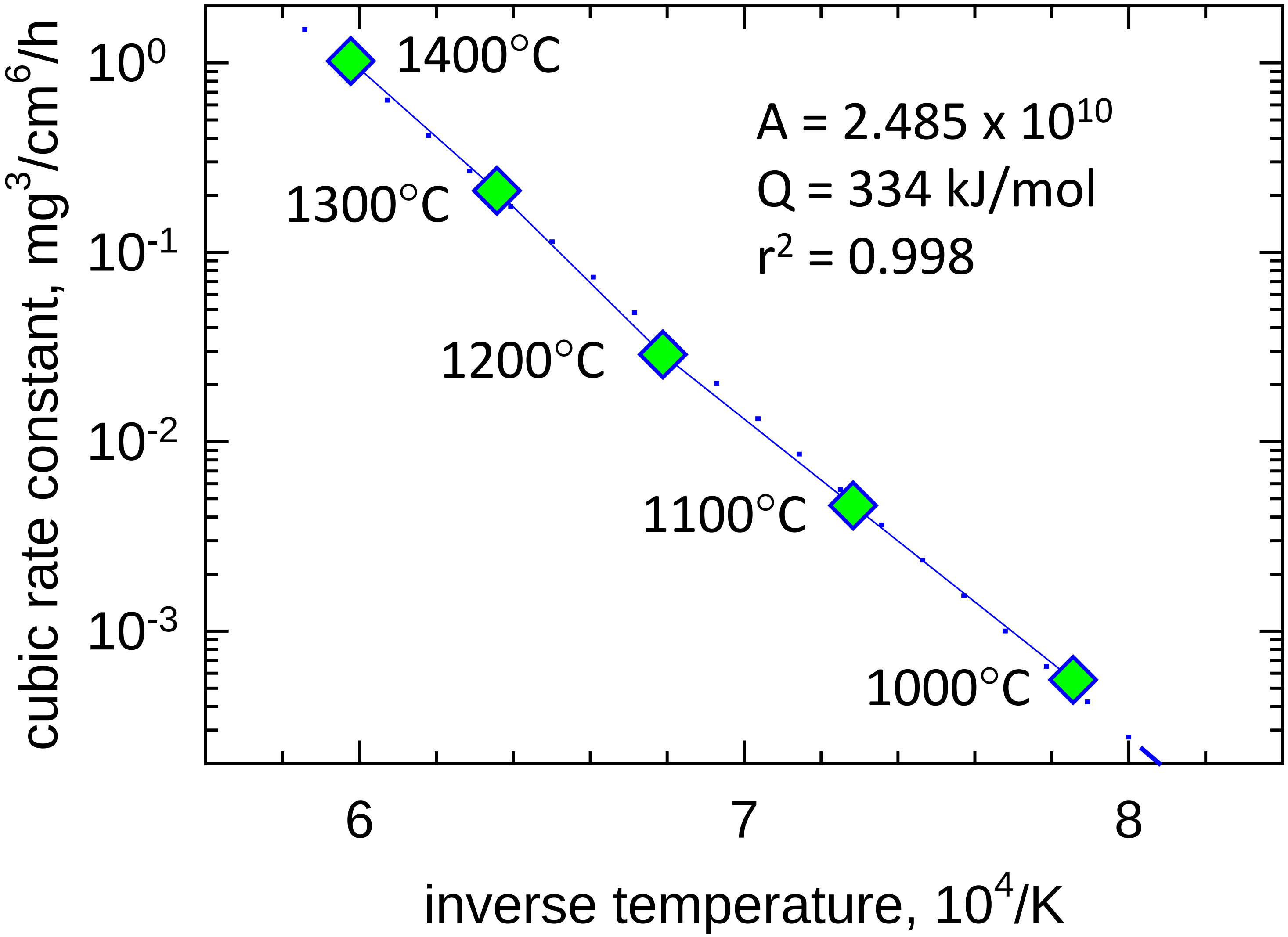


"Kinetic Aspects of Ti_2AlC Oxidation," *Oxidation of Metals*, 83 (2015) 351

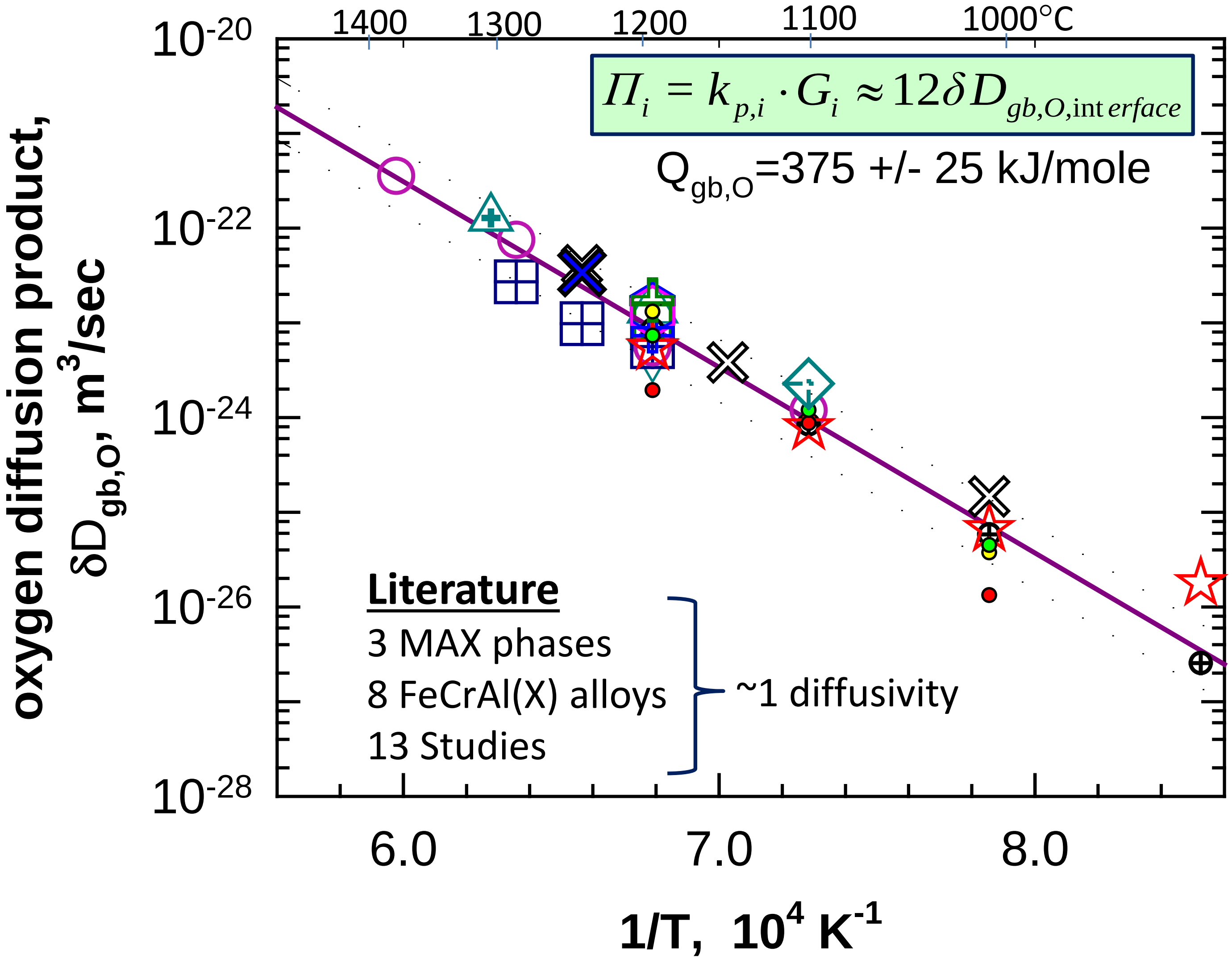


TGA Oxidation of Ti_2AlC in Air
corrected mass gain, mg/cm^2
1.000
0.100
1
10
100
1000
corrected time, hours
1/3
~3000 h!
1000
1100
1200
1300
1400
Tallman 1200

Arrhenius Plot of Cubic Oxidation Rate for Ti_2AlC



Scale Grain Boundary Diffusivity
MAX Compounds and FeCrAl(X) Alloys



"Oxygen diffusivity in alumina scales grown on Al-MAX phases," *Corrosion Science*, vol. 91, pp. 281–286, Feb. 2015.

Al-MAX Phases and Turbine Environments

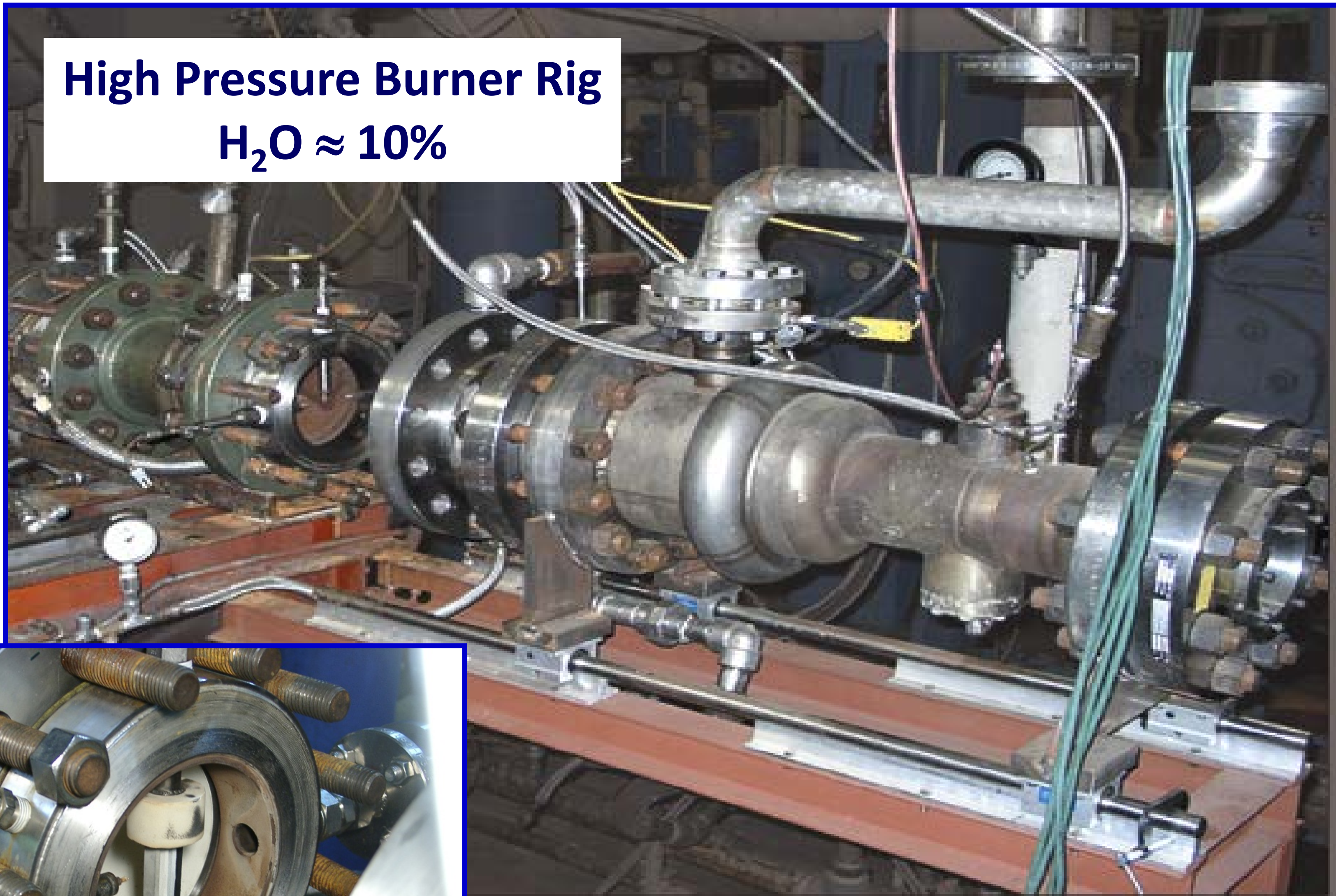
2) First high pressure burner rig test of Ti_2AlC

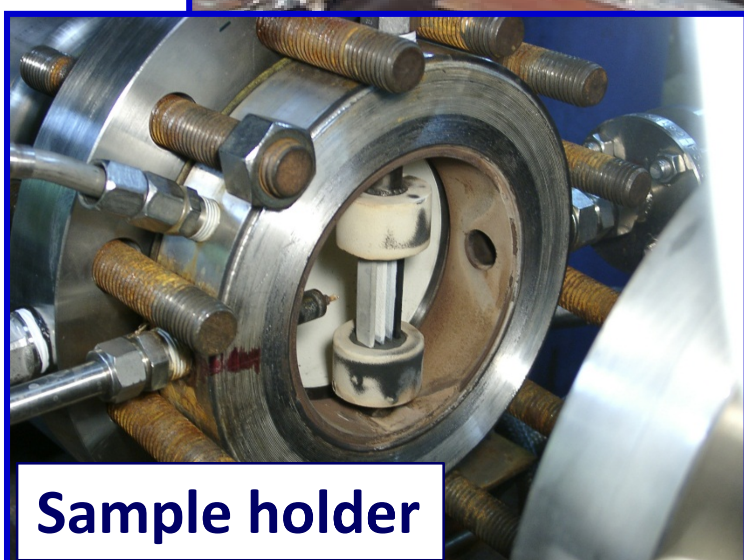
(1100°-1300°C, Jet A fuel, 25 m/s,

6 atm., 10% water vapor)

- transient TiO_2 growth
- cubic kinetics
- **H_2O - scale volatility issues (?)**

"Environmental resistance of a Ti2AlC-type MAX phase in a high pressure burner rig," *J. Eur. Ceram. Soc*. 37 (2017) 23–34.





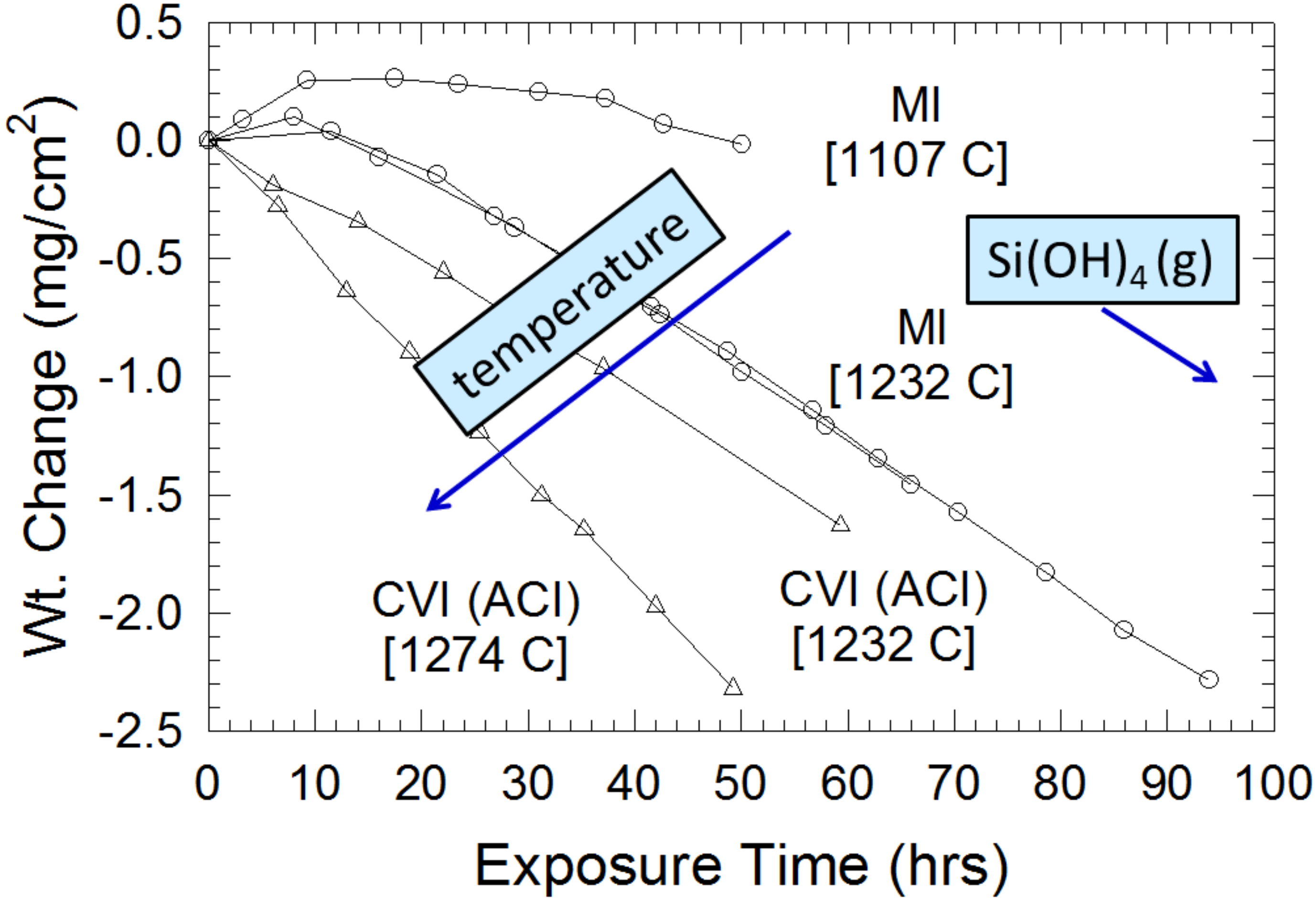
Up to ~1500°C, ~15 atm, ~200 m/s
(decommissioned 2016)

HPBR SiC/SiC CMC *Paralinear* Weight Change

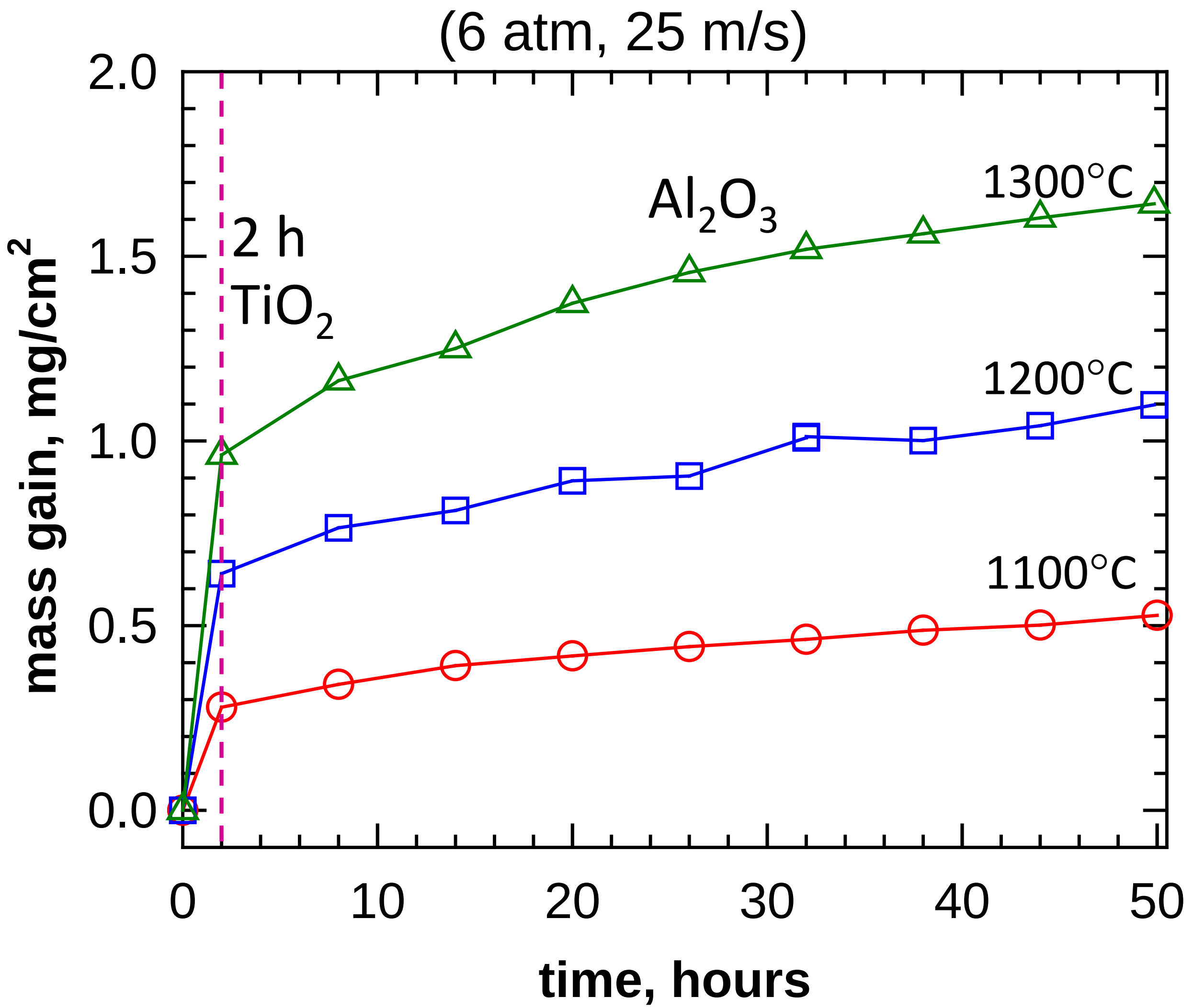
(1100 °-1300°C, 6 atm, 25 m/s; **Robinson**/Smialek 1998)

$$\{SiC + H_2O/O_2\} \rightarrow SiO_2\,(s) \rightarrow Si(OH)_4\,(g)$$

(Opila et al., 1998-2006)

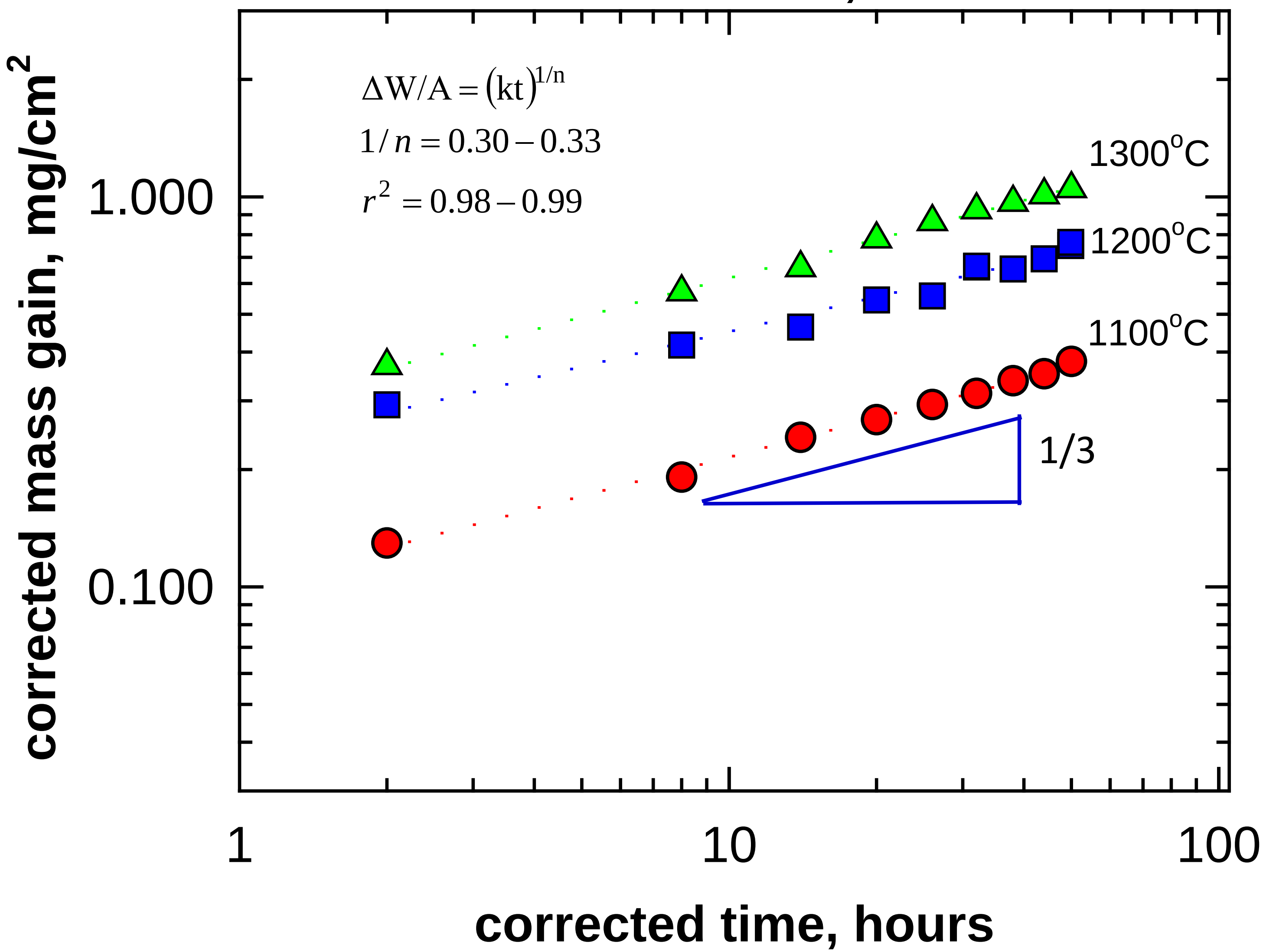


HPBR Oxidation *Gains* for Ti_2AlC

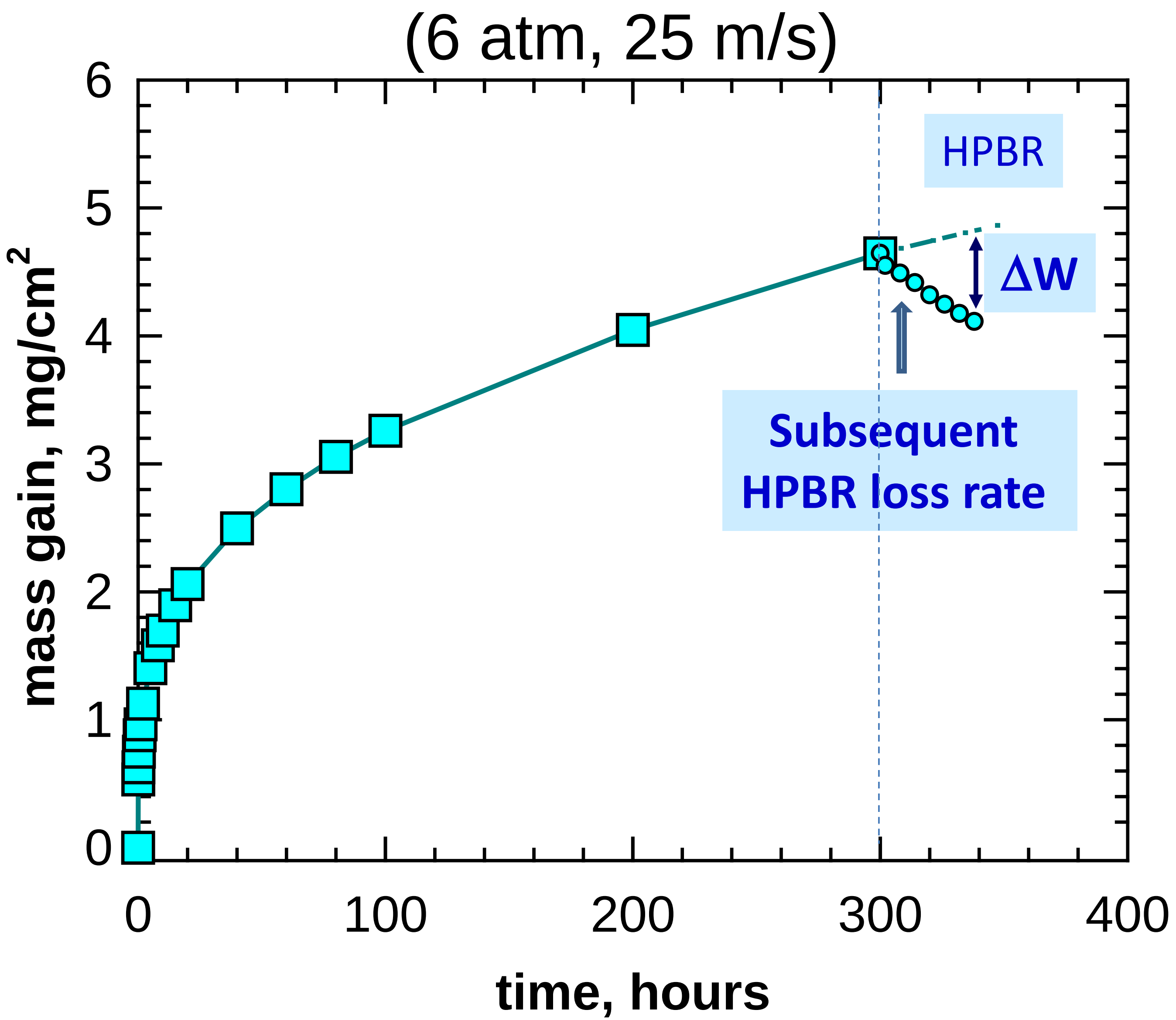


Offset Corrected Ti_2AlC HPBR Oxidation:

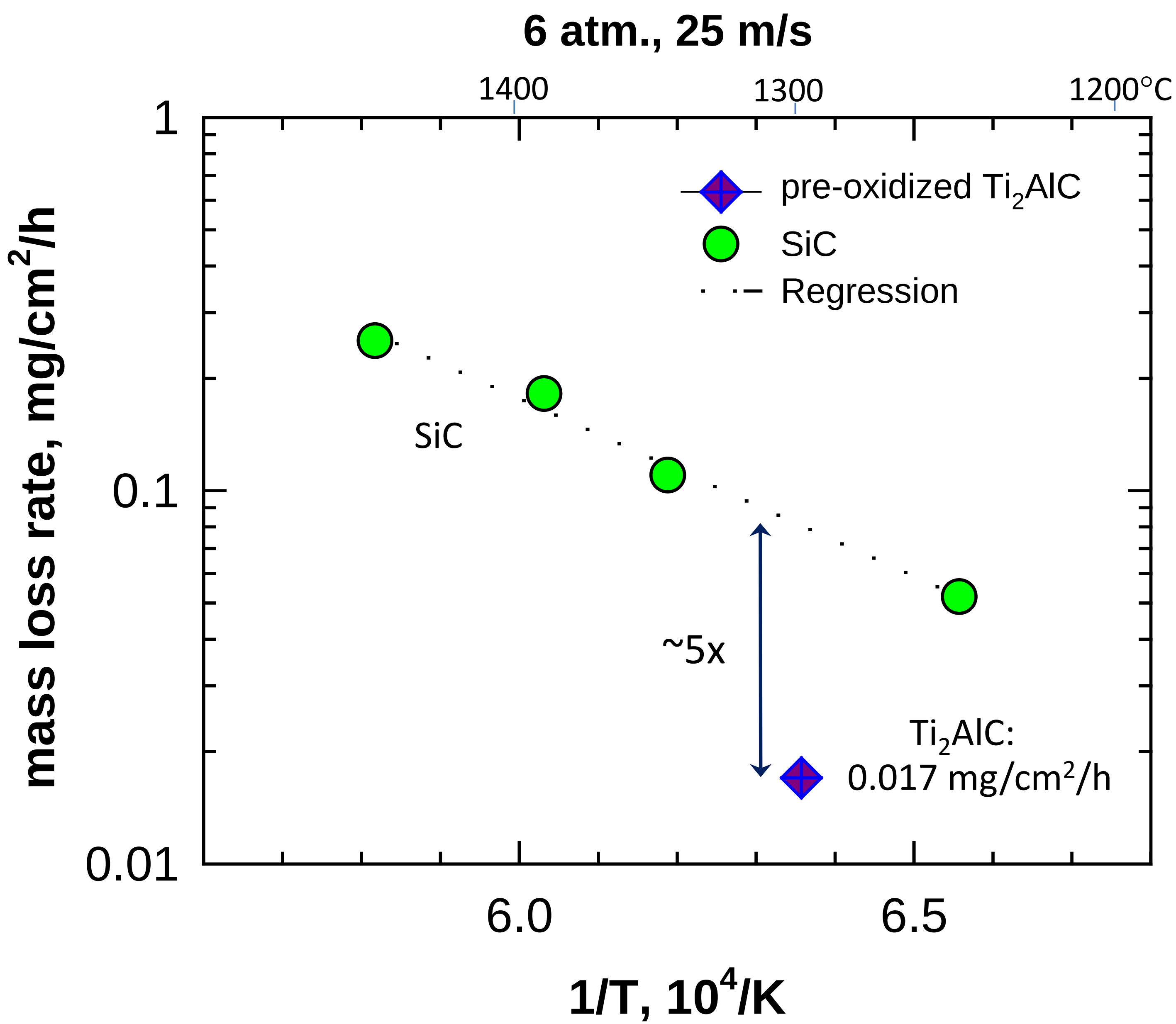
Good cubic behavior, ~1/2 TGA



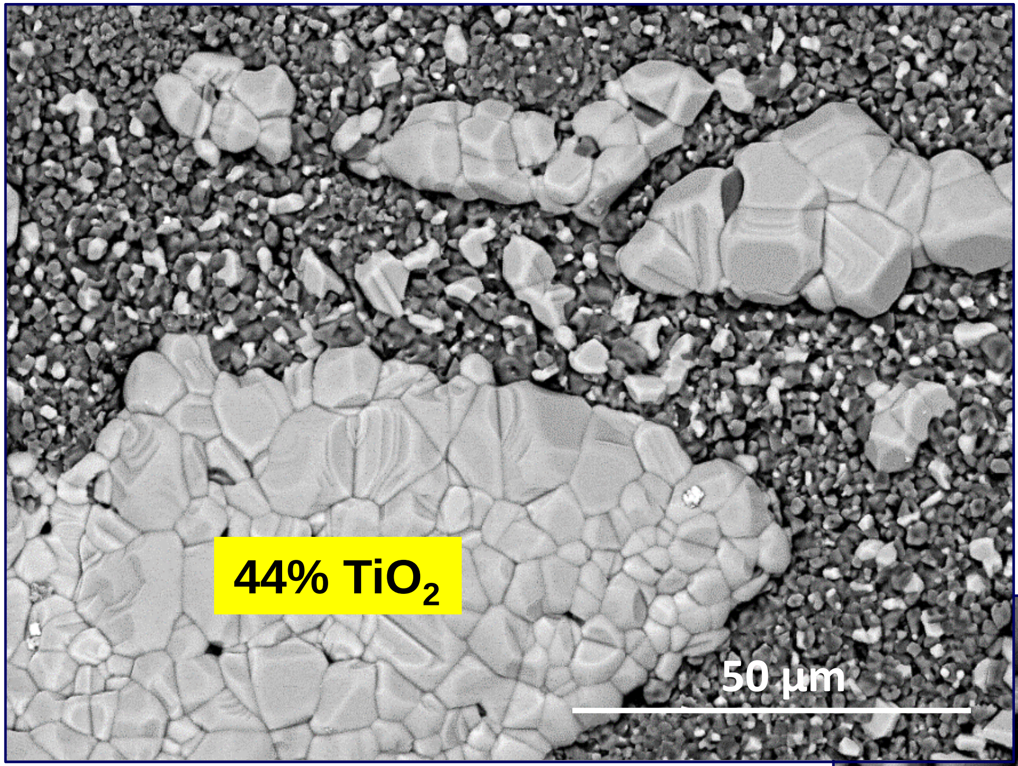
HPBR after 1300°C Pre-oxidation of Ti_2AlC



HPBR Recession Rates for Ti_2AlC and SiC

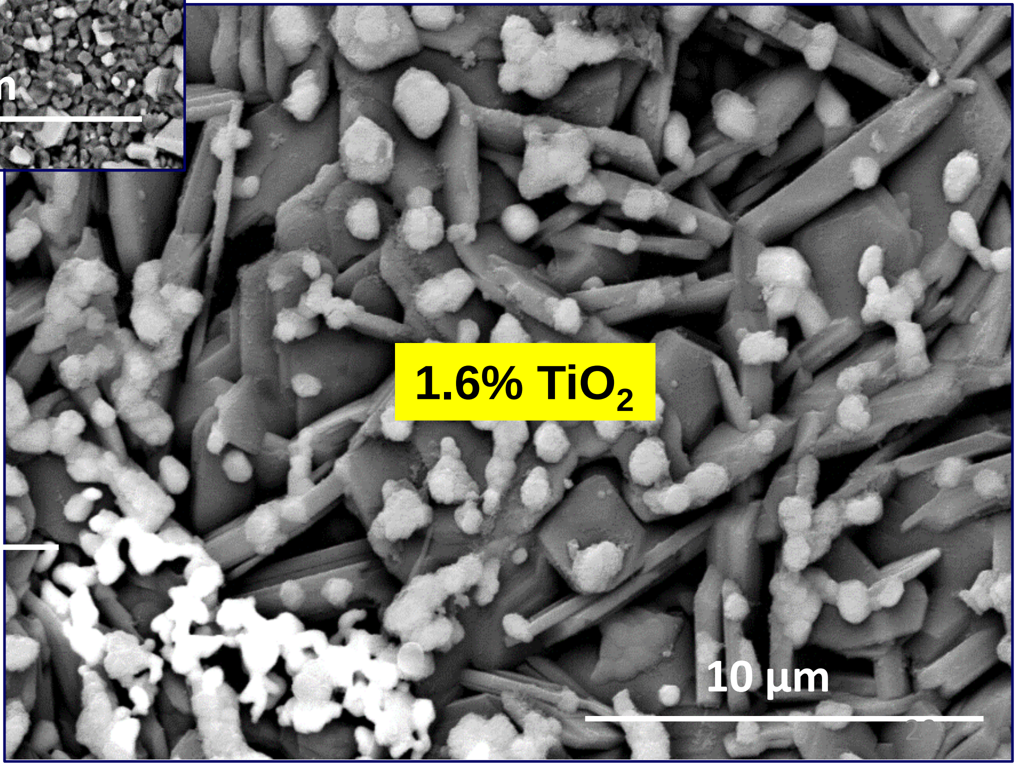


TiO_2 Reduced in 1200°C HPBR Exposures



TGA, 100 h

HPBR, 50 h



Hybrid Concepts (EBC/TBC) Enabled by MAX Phases

Intermediate CTE, Strain Tolerance, YSZ Compatibility

Liner, Seals, Bond Coats (?)

CTE (10^{-6}/°C)

YSZ	**10**	**Top Coat**
Al_2O_3	**9**	**Scale**
Ti_2AlC **Ti_3AlC_2**	**8** **9**	**Bond Coat**
Rene N5 **SiC CMC** Mo, Nb, Ti	**15** **4** 10	**Substrates**

← Critical interface

Attachment ?

Al-MAX Phases and Turbine Environments

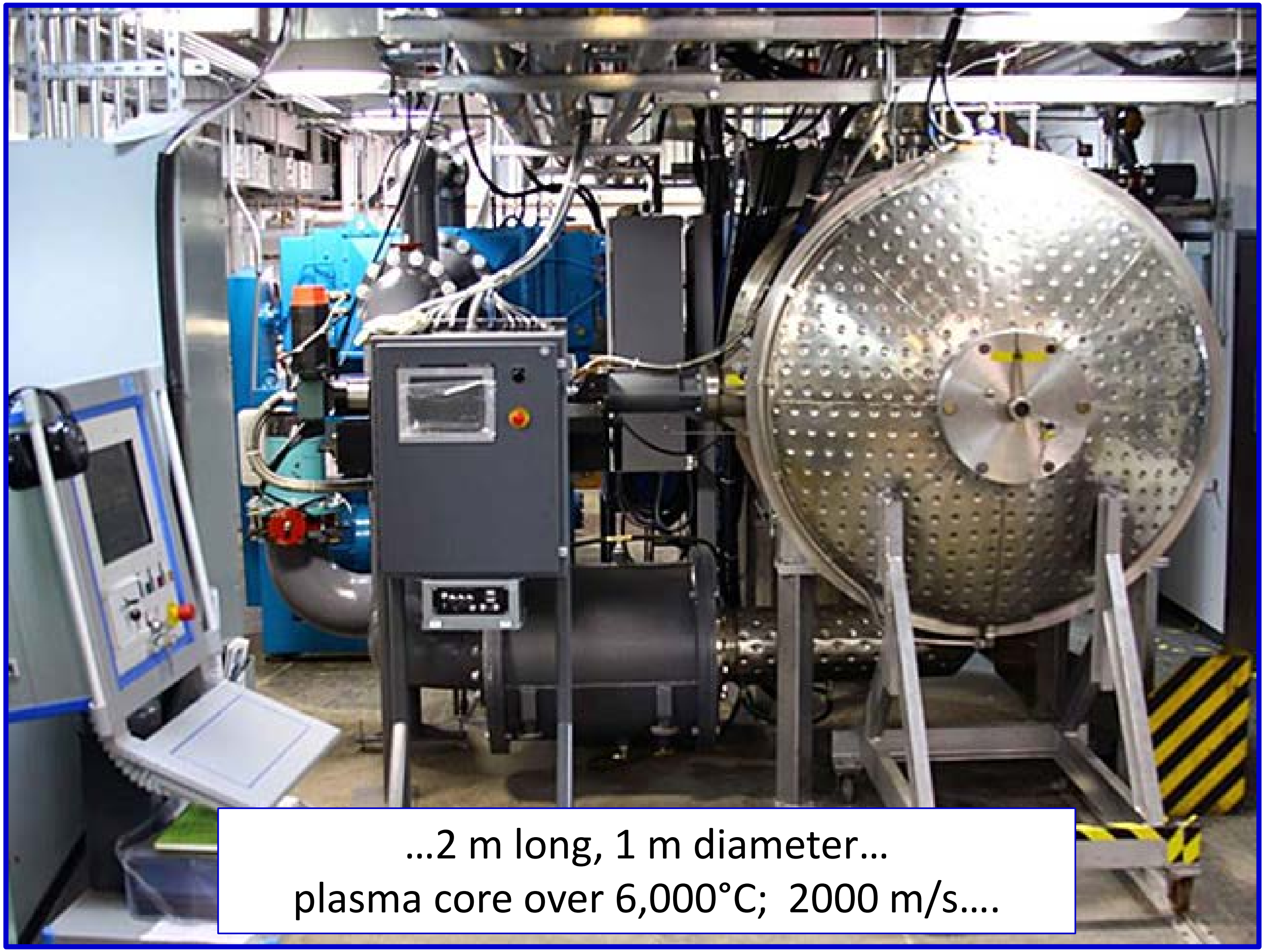
Baseline 1150°C/<1000 h life
(YSZ/Ni(Pt)Al on CMSX-4)

3) YSZ Thermal Barrier Coatings on MAX Phases

- APS and PS-PVD (~100 μm)
- Ti_2AlC (CTE 9); Cr_2AlC (CTE 13)
- Stepped furnace test
  - 1100° - 1300° C
  - 500 h each → 2500 h

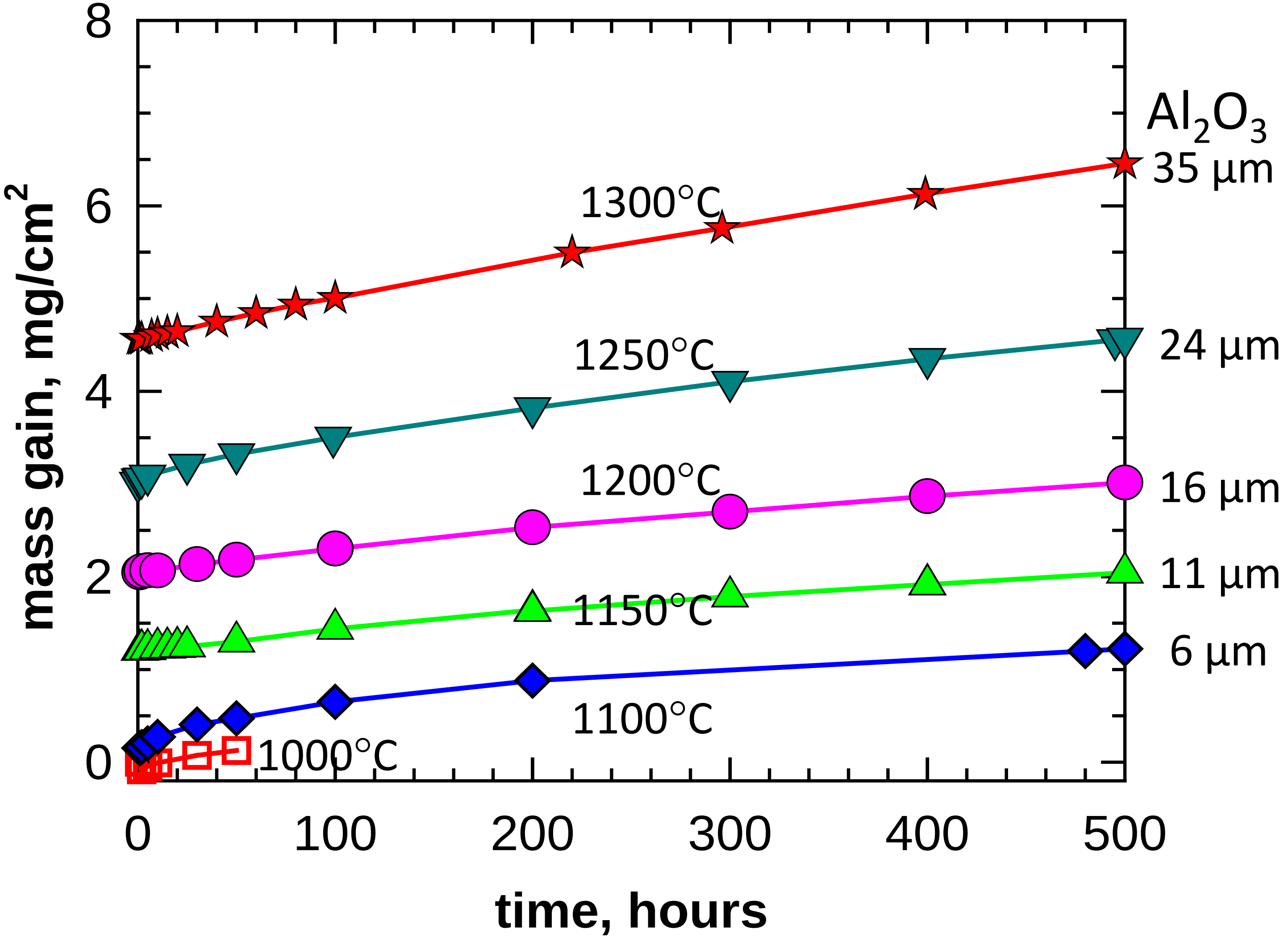
"Oxidative Durability of TBCs on MAX Phase Substrates,"
Surface and Coatings Technology, 285, 15 2016, 77–86.

Plasma Spray-Physical Vapor Deposition
PS-PVD



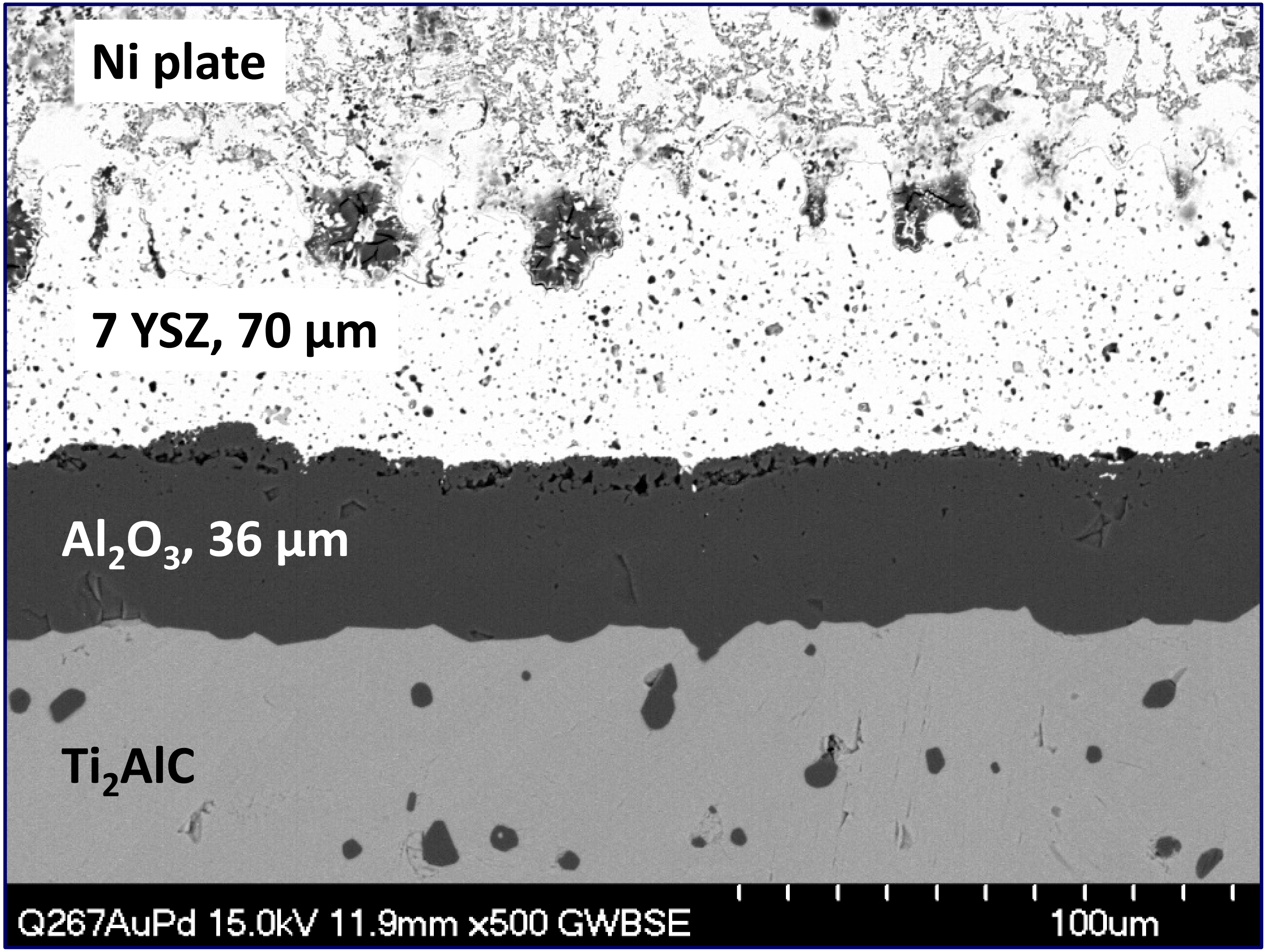
…2 m long, 1 m diameter…
plasma core over 6,000°C; 2000 m/s….

Interrupted Oxidation of PS-PVD YSZ on Ti_2AlC

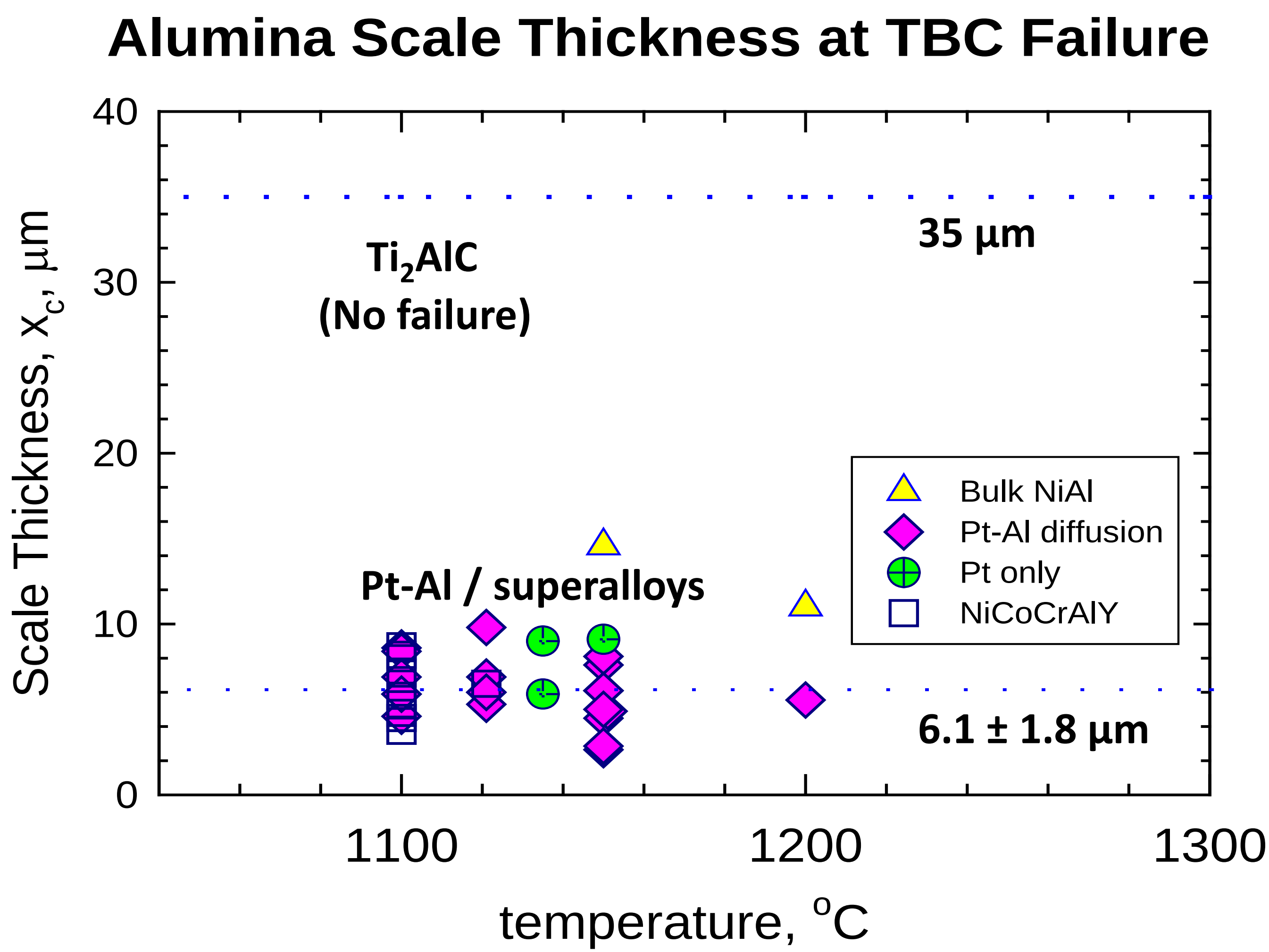


Intact PS-PVD TBC

(Ti_2AlC, **1300°C**, 500 h) SEM/BSE

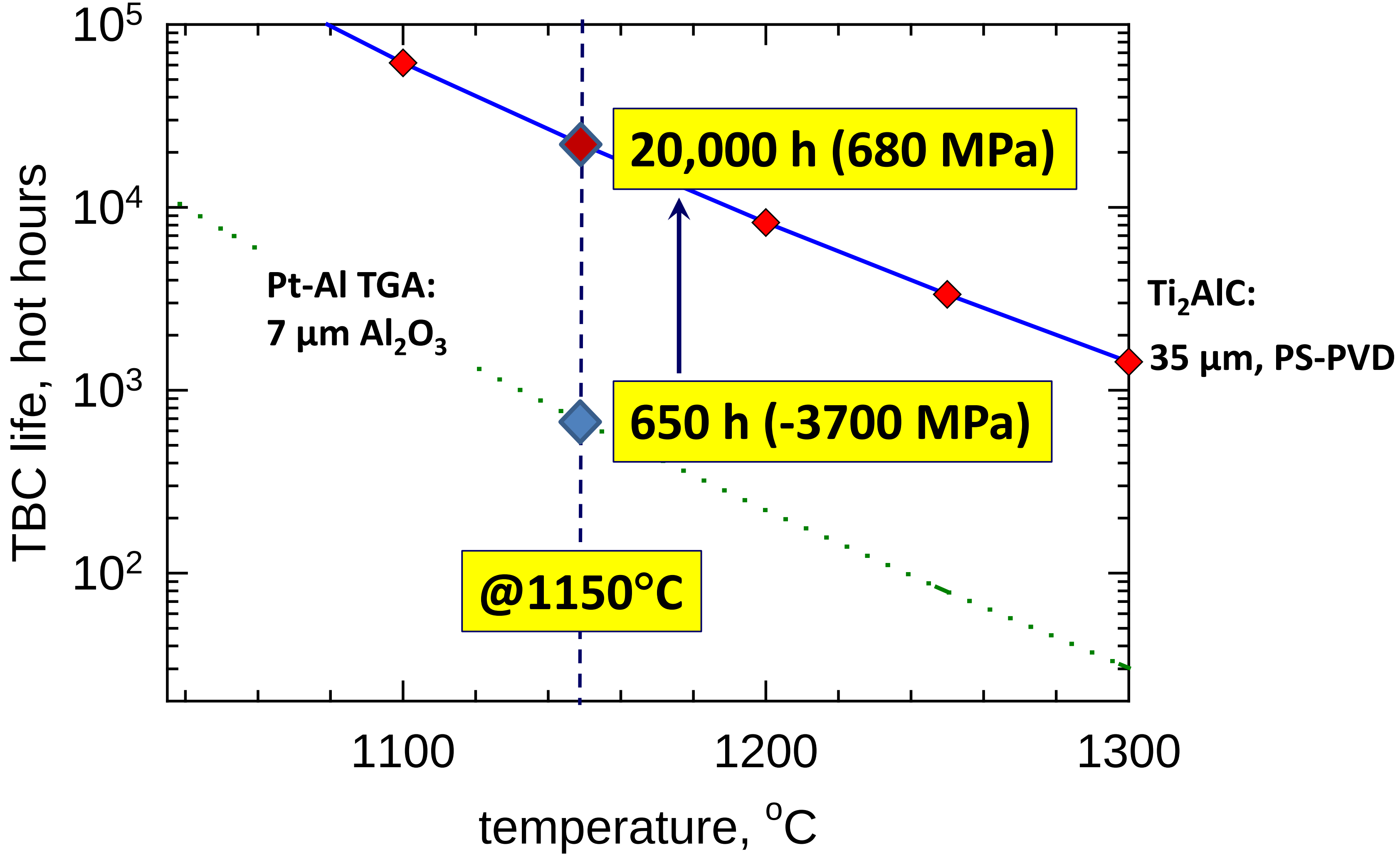


TBC FCT Life Comparison to Literature: "The 7 μm Rule"



"Compiled furnace cyclic lives of EB-PVD thermal barrier coatings," Surface & Coatings Technology 276 (2015) 31–38.

EB-PVD TBC FCT Life on Alumina-Forming Systems



Hybrid Concepts with MAX Phases

Intermediate CTE, Strain Tolerance,

LTHC Corrosion Resistance

CTE, 10^{-6}/°C

Na_2SO_4		Salt
$Al(Cr)_2O_3$	9	Scale
Cr_2AlC	13	Bond Coat
Superalloy	15	Substrates

← Interface stability (between Bond Coat and Substrates)

Al-MAX Phases and Turbine Environments

4) Cr_2AlC / Ni-base Superalloys Interfacial Stability:

LTHC Corrosion resistant coating? (92% LCF deficit)

1100°C hot pressed diffusion couples

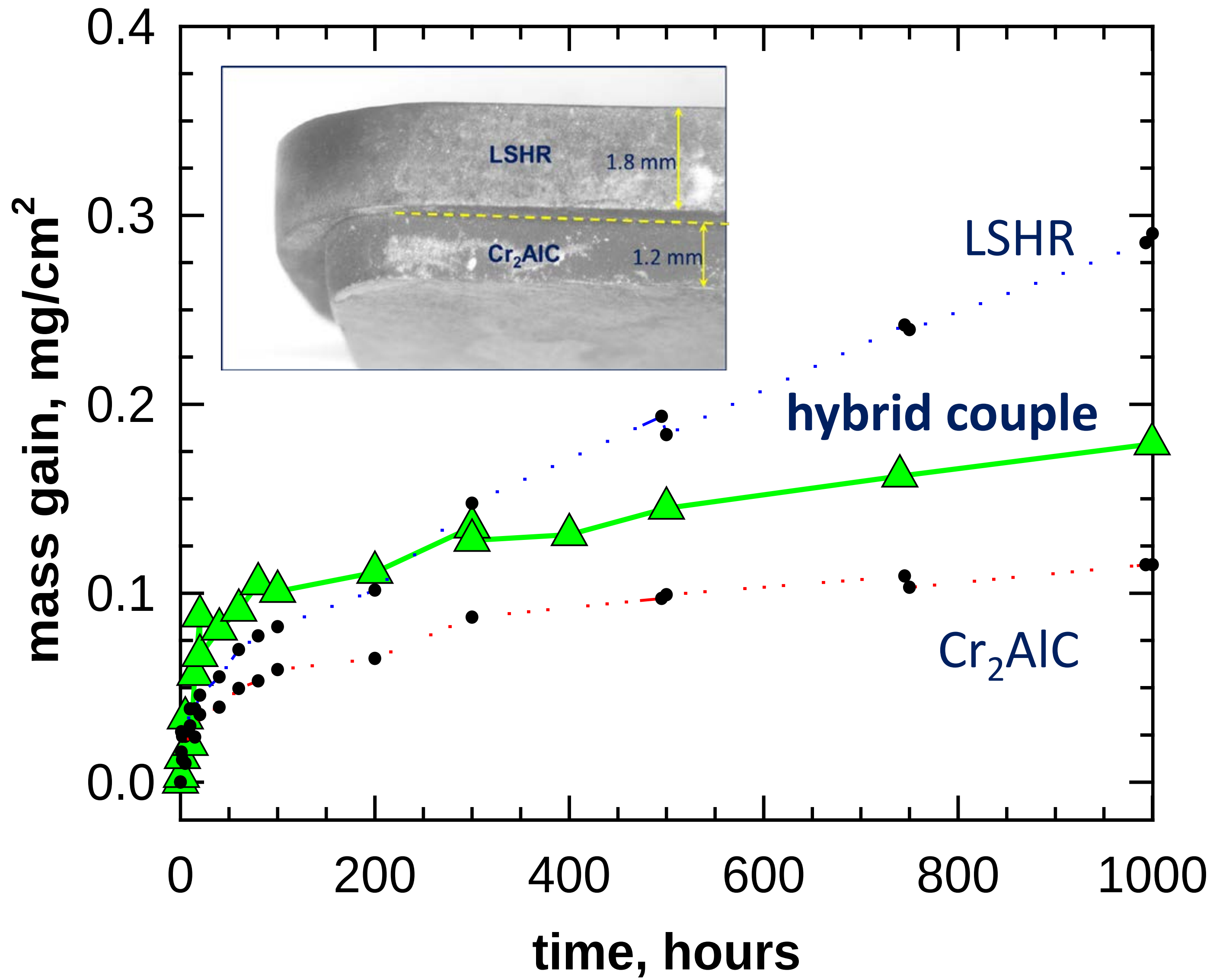
- 0.3 - 3 mm, 2 h @ 10^{-6} torr
- **Cr_2AlC** on **LSHR** disk alloy (or **Rene′N5**)

800°C (or 1150°C) diffusion/oxidation

- 100 h, 1000 h

“Interfacial Reactions of a MAX Phase-Superalloy Hybrid”
Surface and Interface Analysis, 276 (2015) 31

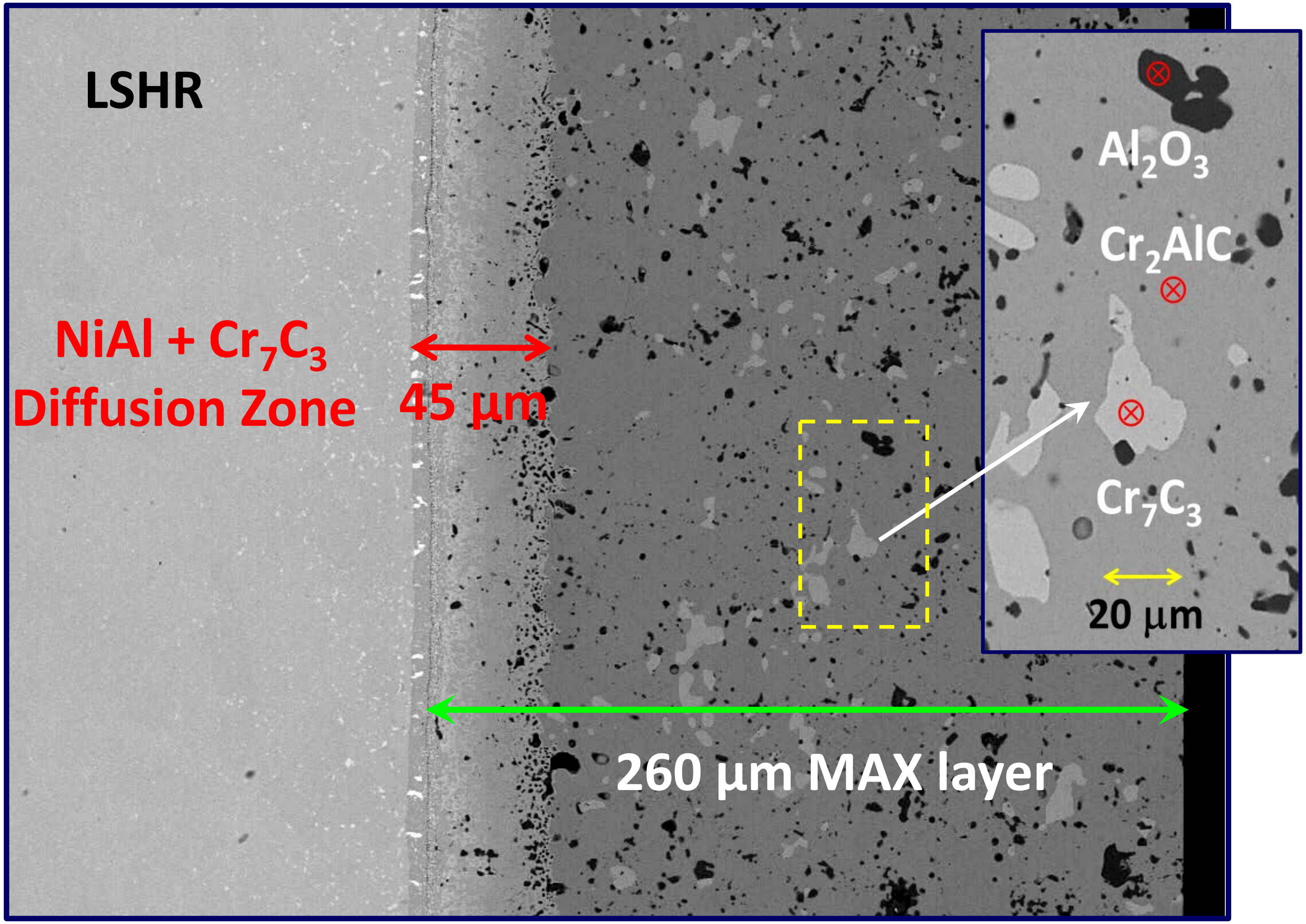
Survives 1000 h of 800°C Furnace Oxidation
LSHR - Cr_2AlC DC3 Hybrid Couple



As-Hot Pressed Cross Section

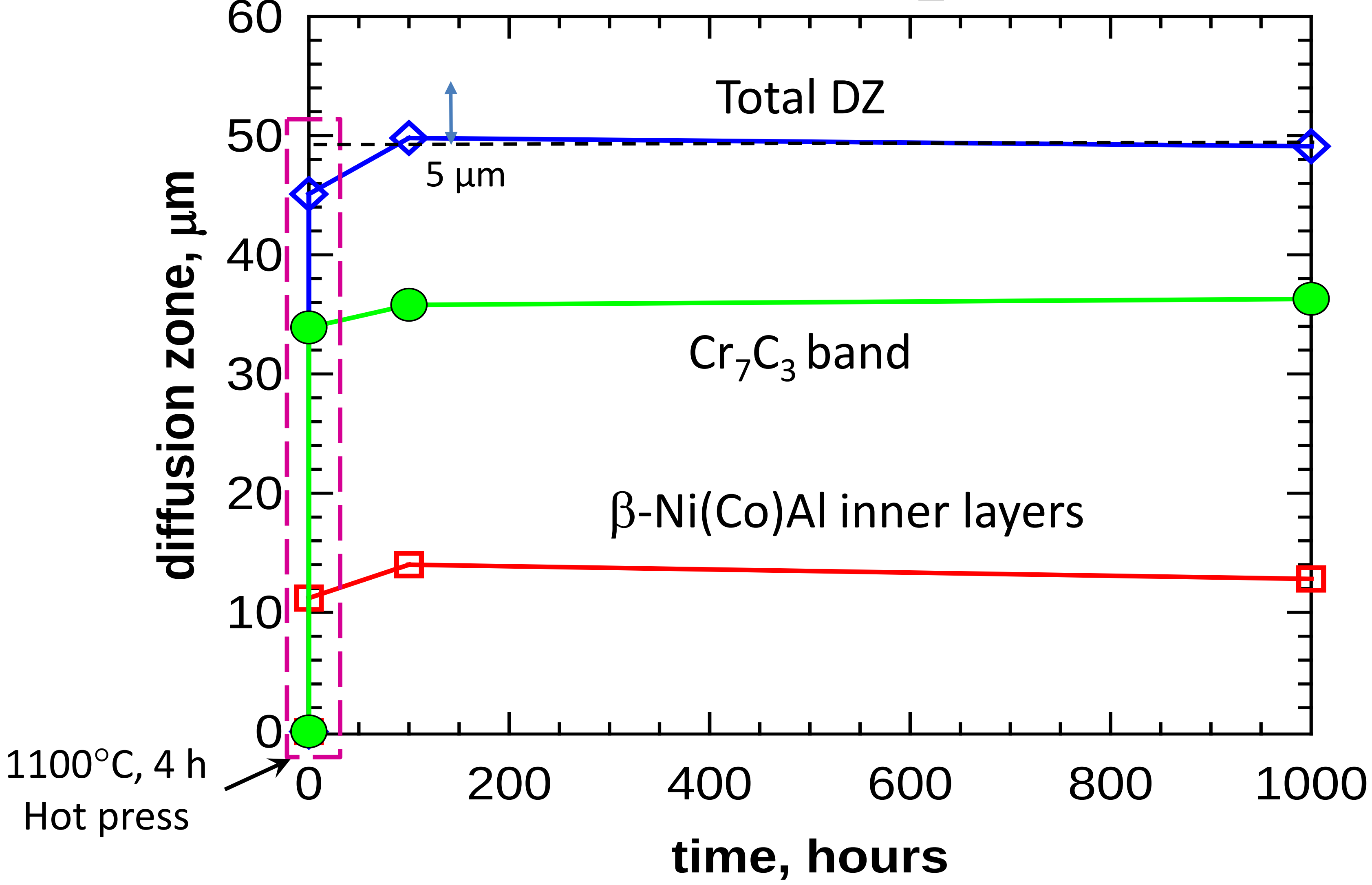
(2h @ 1100°C produced ~ 50 μm layer)

SEM/BSE

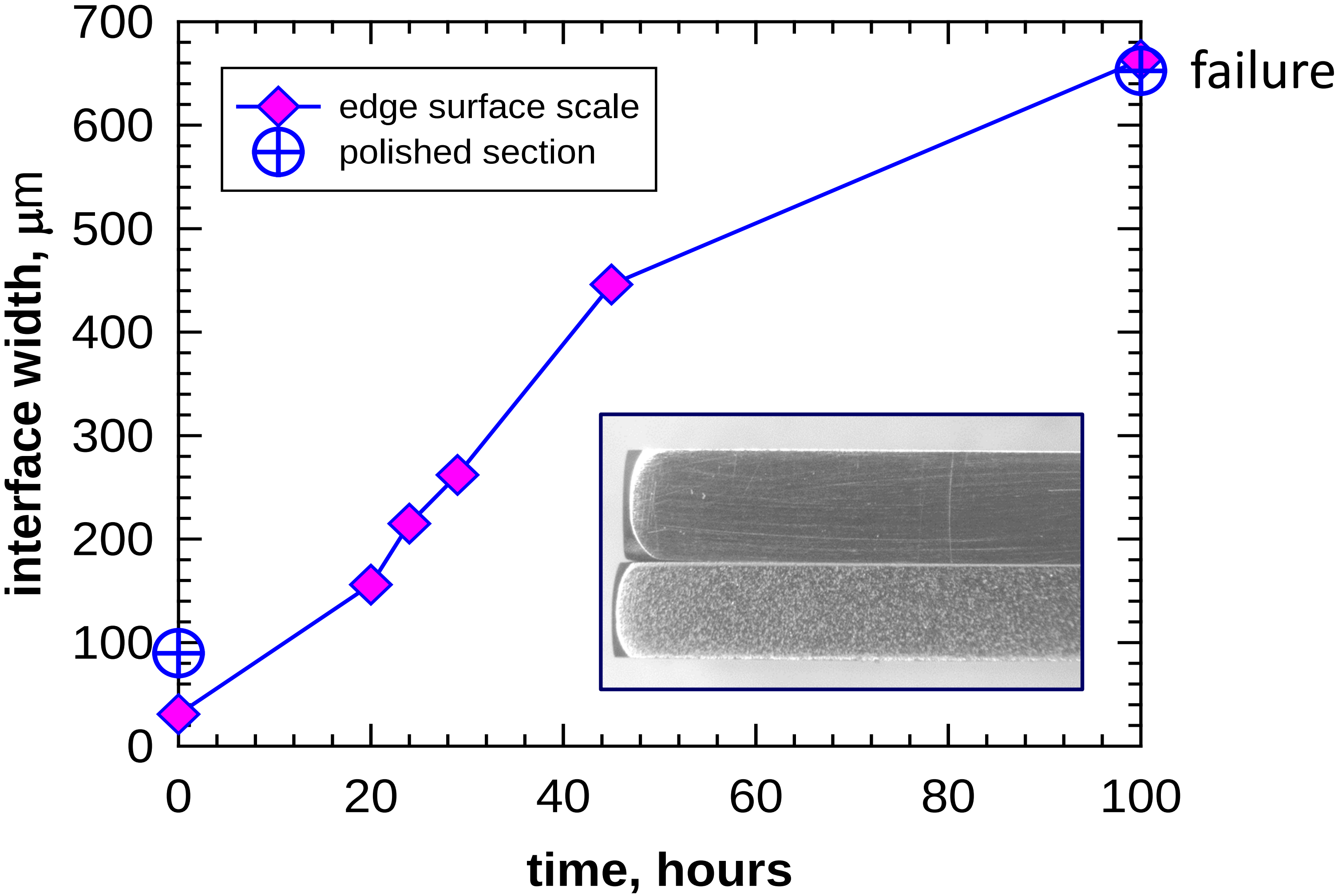


Minor Diffusion Zone Growth at 800 ^{o}C

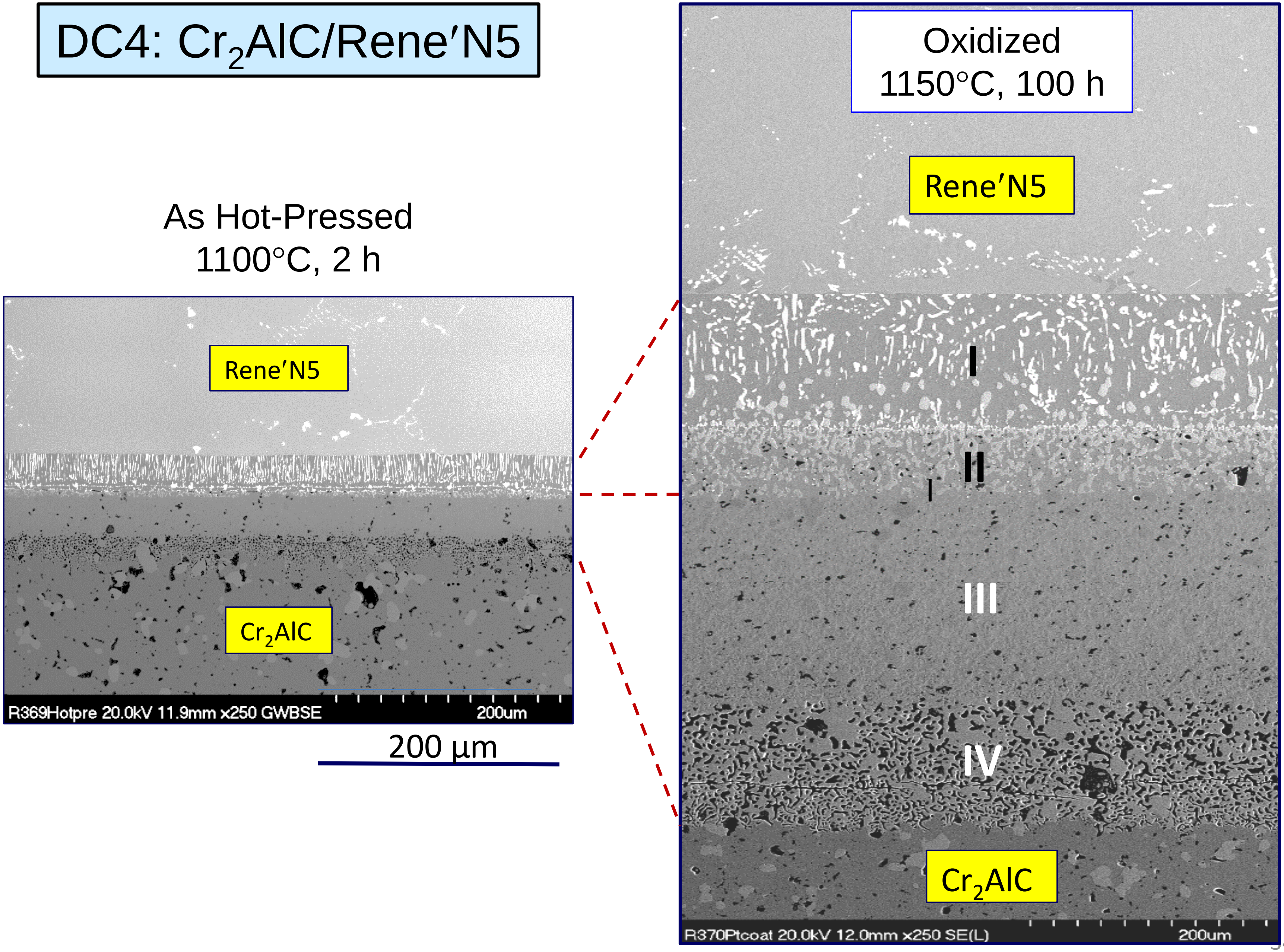
LSHR Alloy/Cr_2AlC



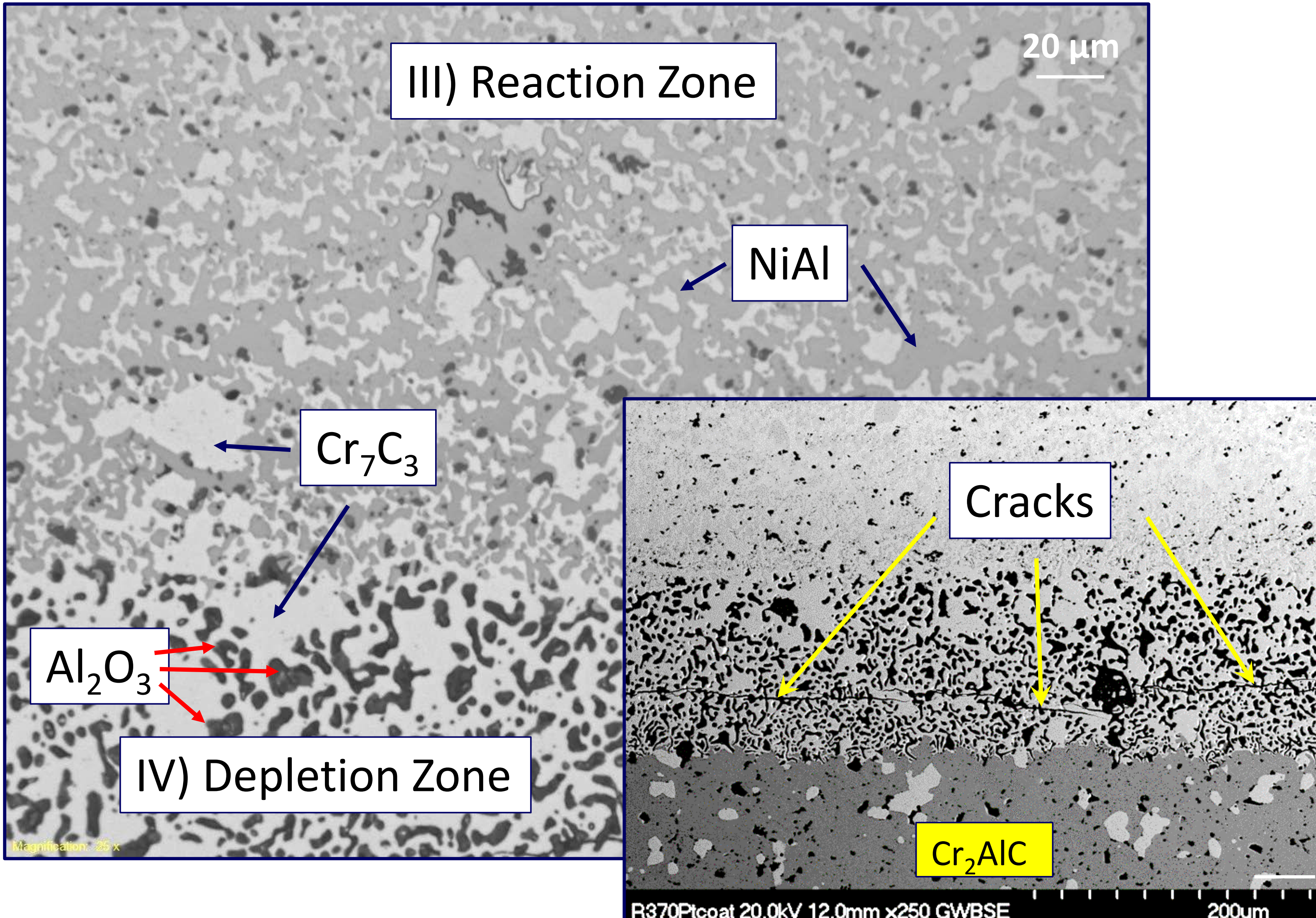
Cr_2AlC-Rene'N5 Hybrid Couple: Interdiffusion at 1150°C



DC4: Cr_2AlC/Rene′N5



DC4: Cr_2AlC/N5 (1150°C, 100 h) 200-250 x



Hybrid Concepts with MAX Phases

Intermediate CTE, Strain Tolerance,

LTHC Corrosion Resistance

CTE, 10^{-6}/°C

Na_2SO_4		Salt
$Al(Cr)_2O_3$	9	Scale
Cr_2AlC	13	Bond Coat
Superalloy	15	Substrates

← Critical chemistry

Al-MAX Phases and Turbine Environments

5) Cr_2AlC / Disk Alloy Hot Corrosion:

700°C ***bulk*** LTHC:

500 h, $(Na,K)_2SO_4$ (T_e= 823°C)

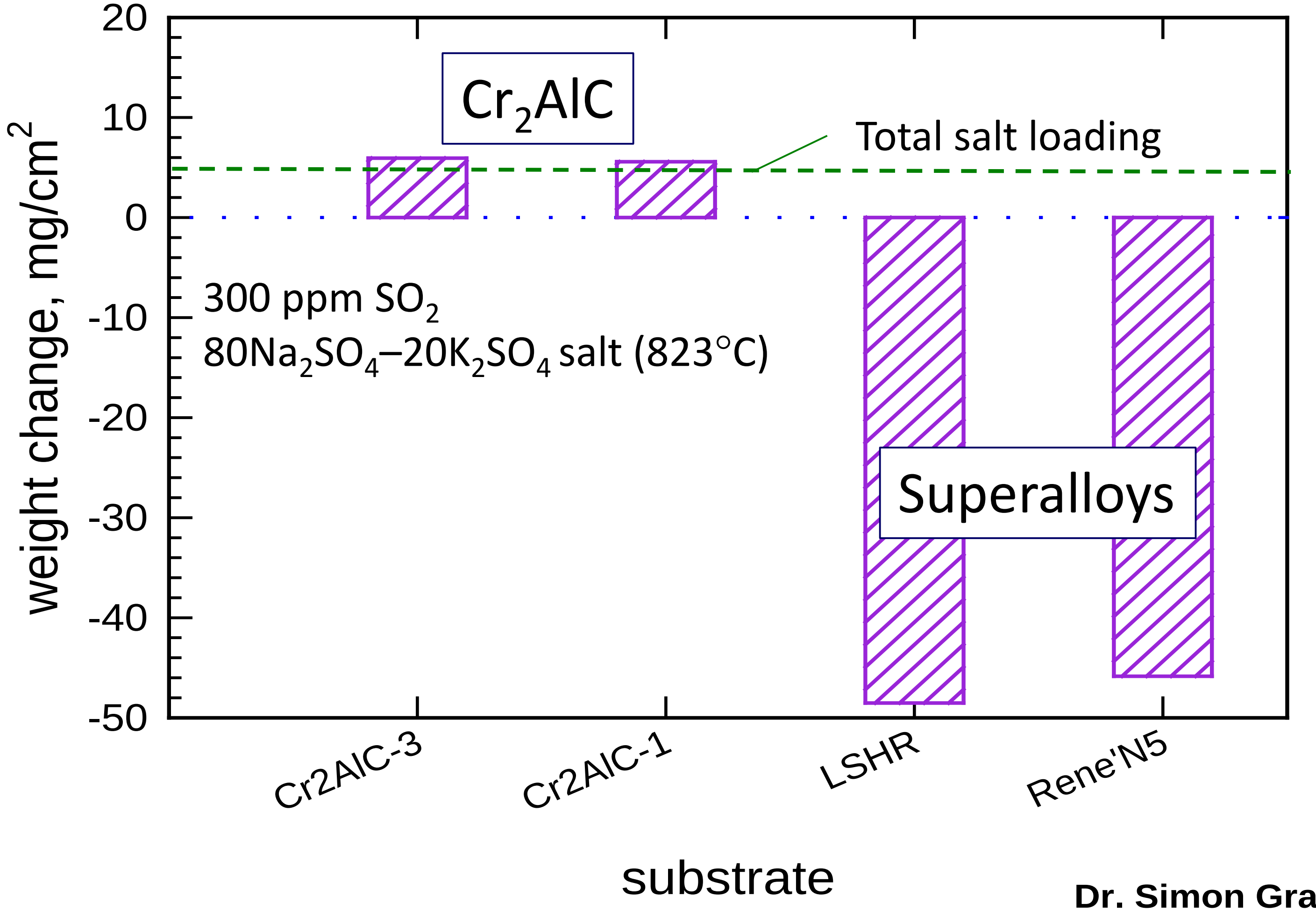
760°C ***Coated*** LSHR LCF:

840 / -430 MPa at 0.33Hz

50 h, $(Na,Mg)_2SO_4$ (T_e= 660°C)

Type II LTHC of Cr_2AlC (3) and Superalloys (7)

700°C, 500 h, 0.5 mg/cm² salt recoat every 50 h



Dr. Simon Gray
Cranfield University

500hrs, surface macros

Cranfield UNIVERSITY

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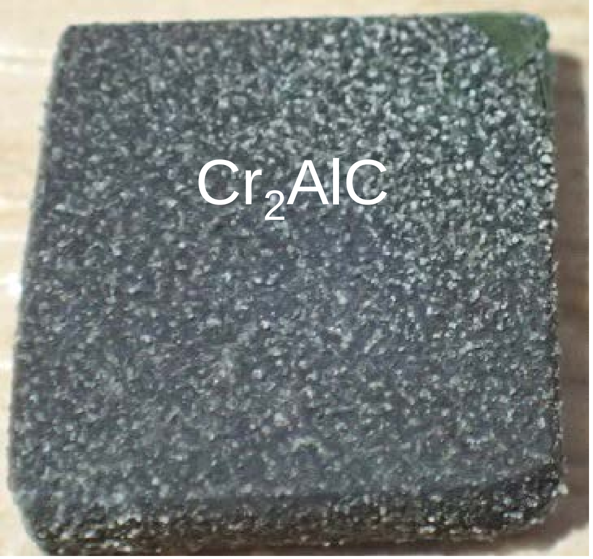

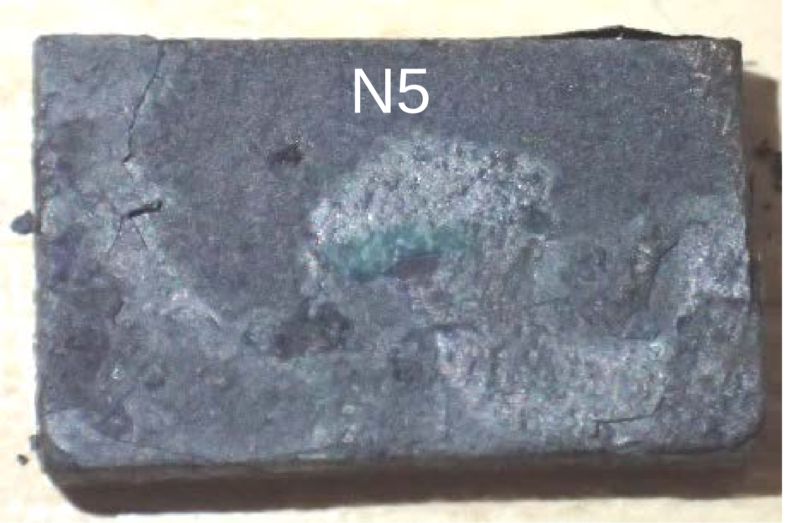

500hrs, section SEM

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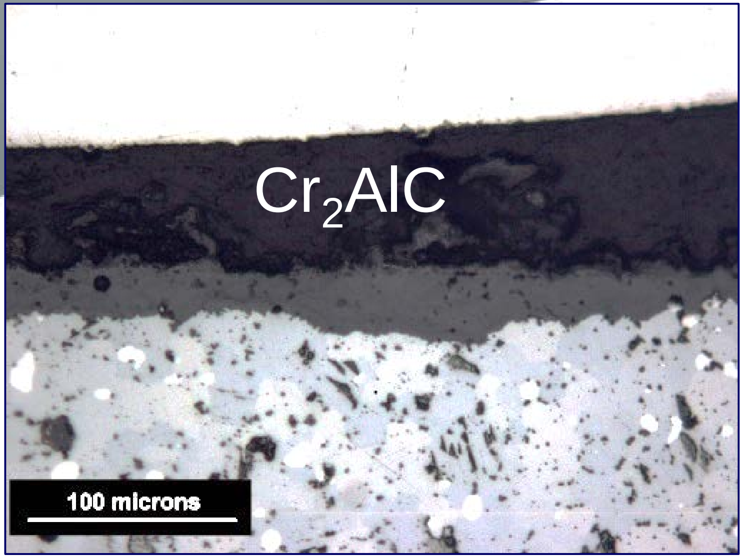

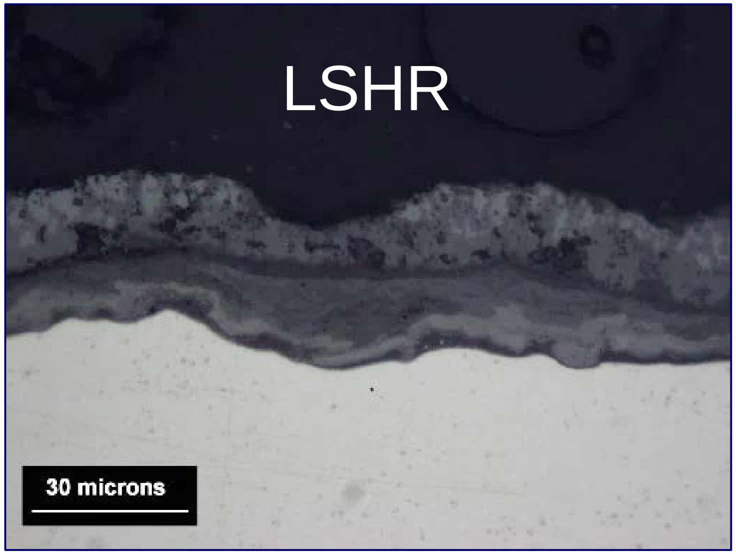

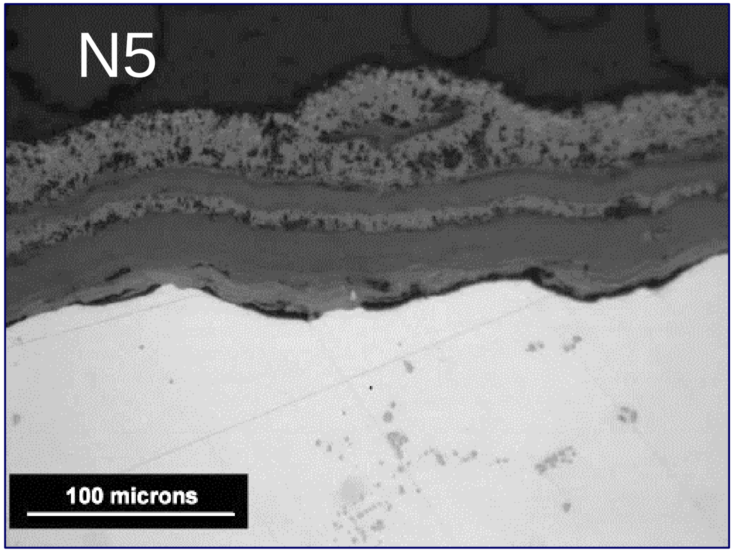

Sulfur maps

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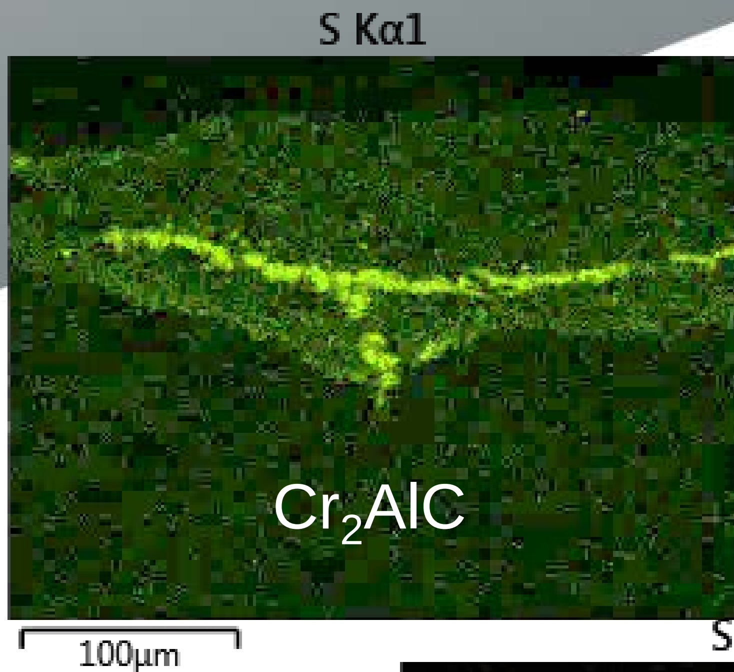
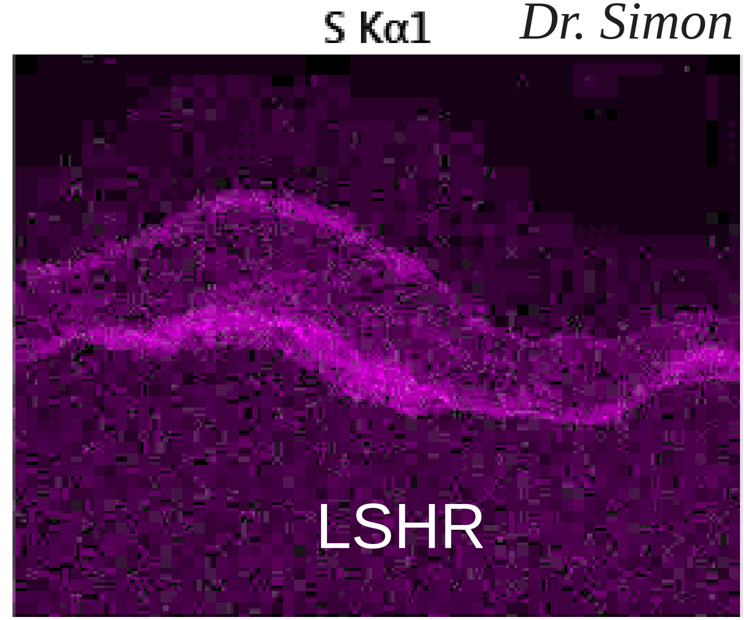
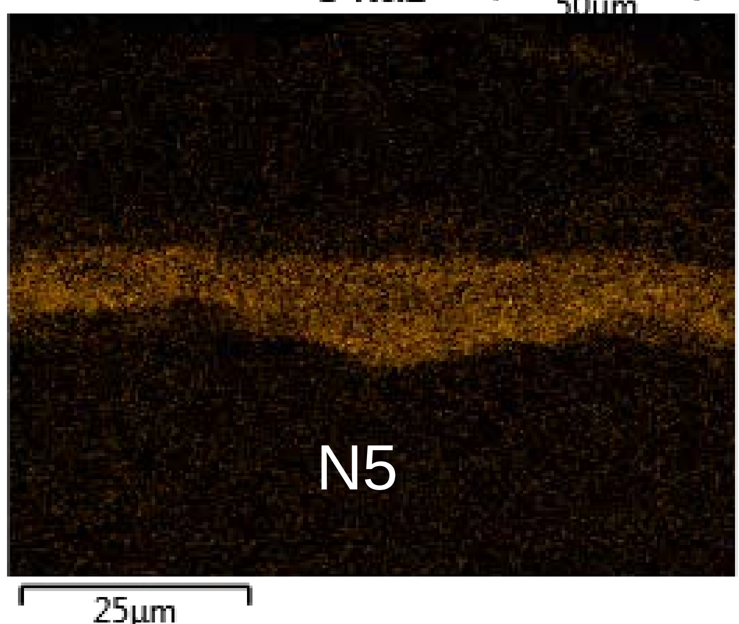
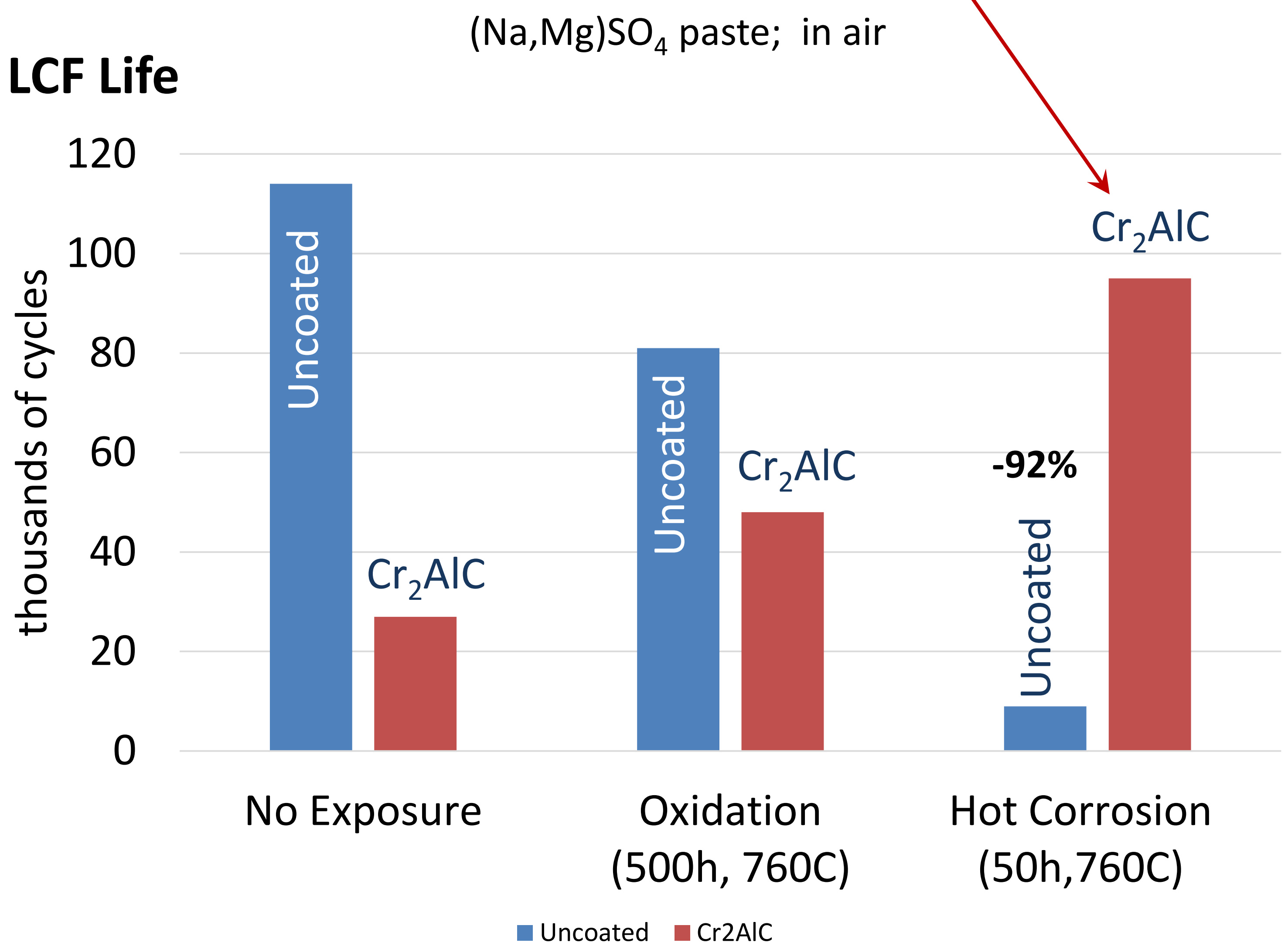




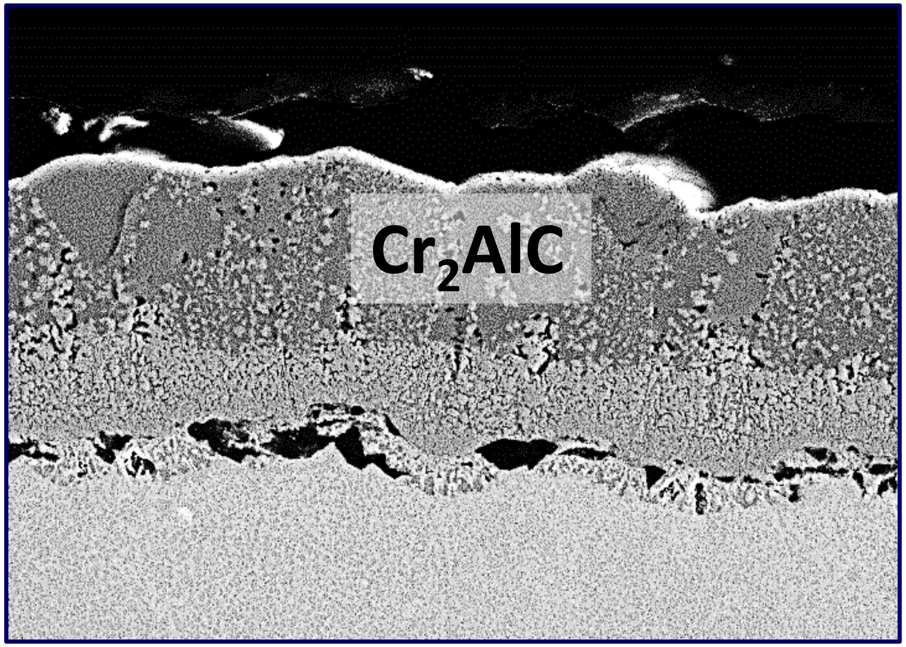


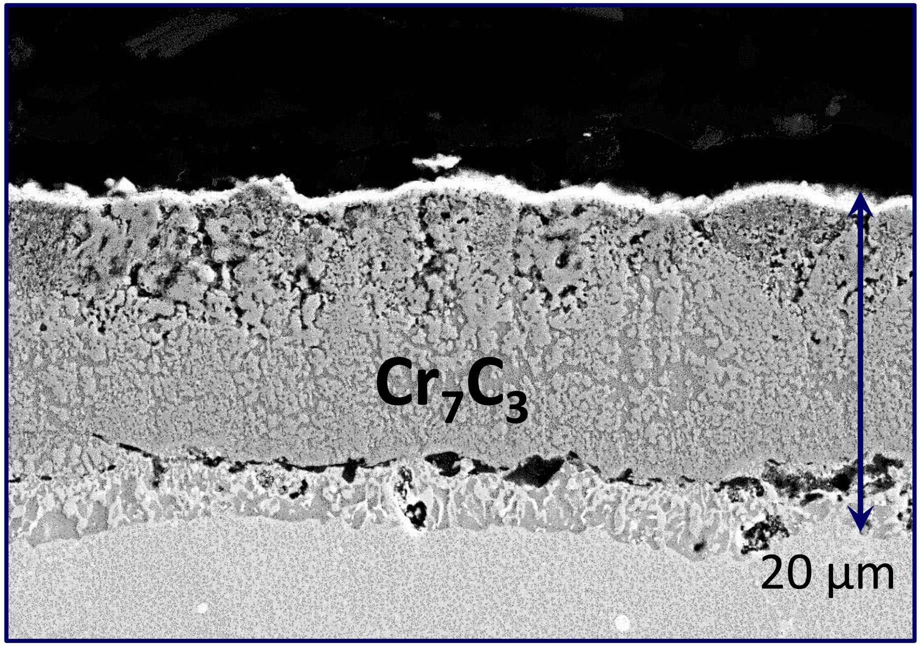
Al, Ni, Co
Na, S, Cr

Cr_2AlC Max Phase Coatings on LSHR
Prevents LTHC Pitting, LCF Debit



Cr_2AlC Corrosion Resistance on LSHR Disk Alloy (LCF Samples)





As- processed
heat treated 760°C, 8 h

+760°C, 500 h oxidation
+ 50 h hot corrosion

Ti_2AlC, Cr_2AlC MAX Phases: **Items of Potential Interest for Turbines**

1. Rate Control by Al_2O_3 grain boundary diffusion;

   cubic rate protective to 1400°C; Q = 334 kJ/mole
2. Ti_2AlC stable in 1300°C combustion (HPBR) gas.
3. Extensive TBC furnace life @ 1300°C for Ti_2AlC.
4. Superalloy / Cr_2AlC hybrids stable:

   800°C, but not 1150°C.
5. Minimal 700° C Type II LTHC of Cr_2AlC

INTRIGUING ALUMINA FORMERS

Ti_3AlC_2, Ti_2AlC, Cr_2AlC MAX Phase **Oxidative Shortcomings**

1. Ti_2AlC breakaway TiO_2 growth:

   < critical Al content; or damaged areas

2. Cr_2AlC isothermal oxidation: CrO_3 losses (Cr_7C_3)
3. Cr_2AlC cyclic oxidation:

   interfacial spallation; Cr_7C_3 depletion zones

4. Superalloy / Cr_2AlC compatibility:

   interdiffusion at, delamination from 1150°C.

Al-MAX Phases and Turbine Environments

Current Engineering Assessment

substrate	MAX phase	top coat	use	advantage	max temp.
none	Ti_2AlC	none	gas path	protective k_c, low volatility, adherent Al_2O_3	~1300°C
none	Ti_2AlC	YSZ	TBC	CTE match, adherent Al_2O_3	~1300°C
superalloy	Cr_2AlC	none	hot corrosion	higher CTE, Cr, Al	~900°C