Alumina-Forming MAX Phases in Turbine Material Systems

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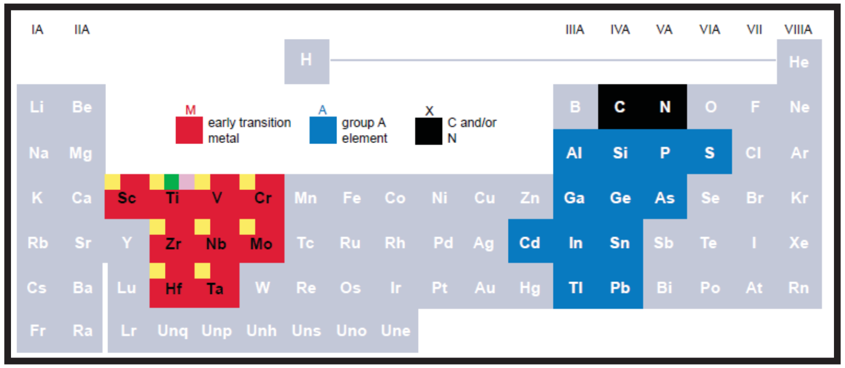
MAX Phases, M_nAX_{n-1}

(Barsoum, 2001,
about 60 phases; >300 papers)



Oxidation Resistant:

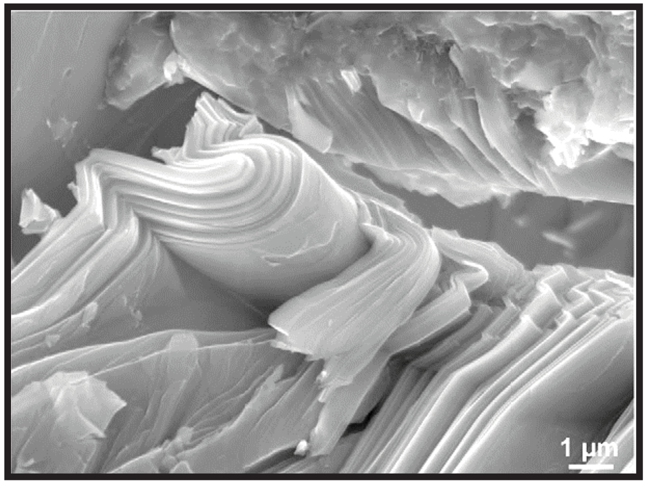
M = Ti, Cr Ti_3AlC_2

A = Al, (Si) Ti_2AlC

X = C, (N) Cr_2AlC

Strain Tolerant Kinking

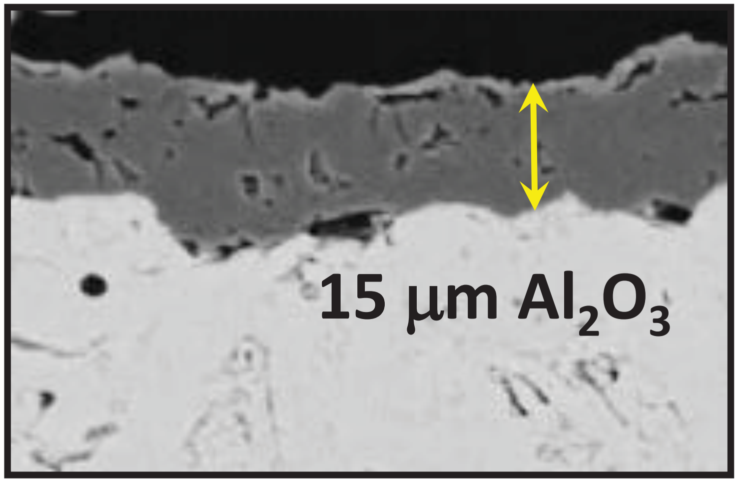
$Cr_2Al(Si)C$ W. Yu, S. Li, W.G. Sloof, 2007



Ti_2AlC "MAXthal 211" (Kanthal)

M. Sundberg, et al., 2004

8000 cycles to 1350°C!



Purpose: Relate Al-MAX phases to coatings applications/turbine environment

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

Coating Motivation and Rationale

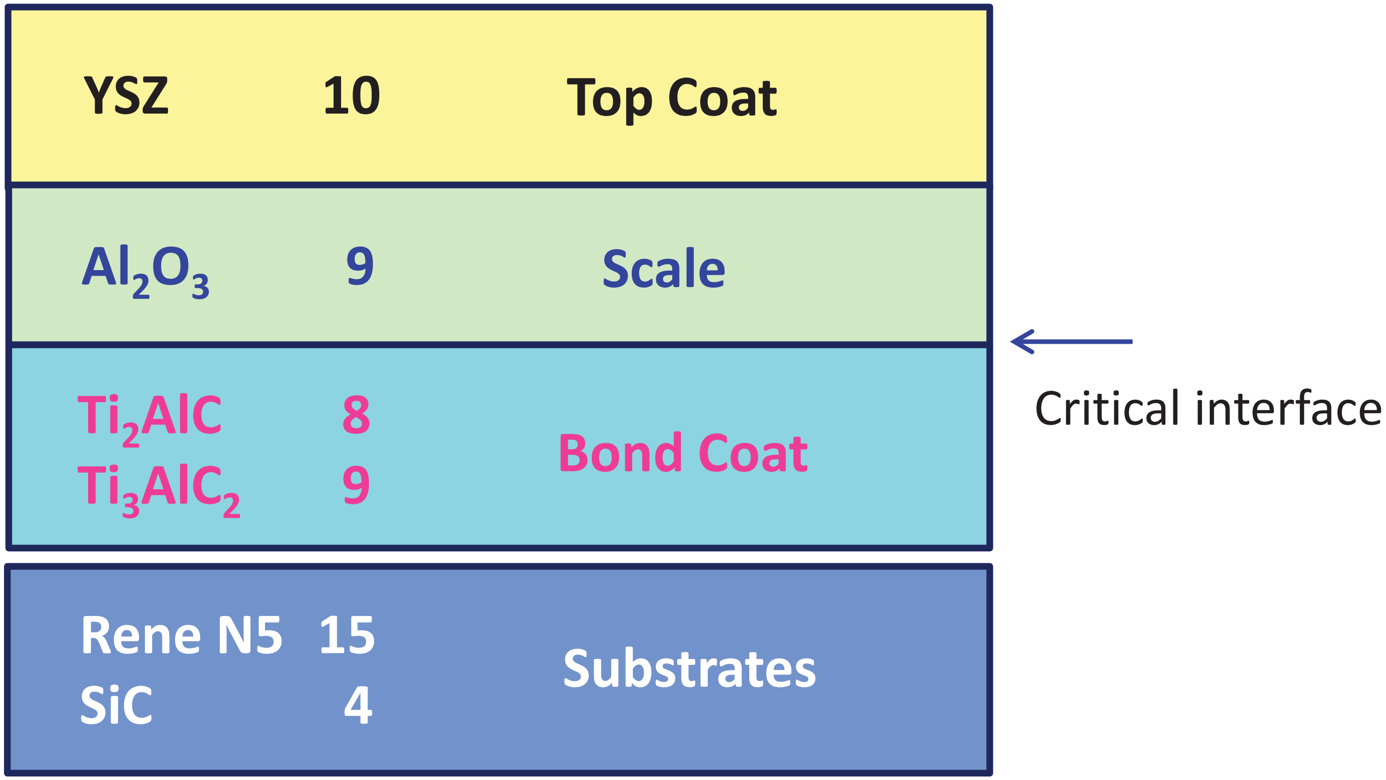
Ti_3AlC_2, Ti_2AlC, Cr_2AlC

- α-Al_2O_3 formers
- CTE close to YSZ, α-Al_2O_3
- Strain tolerance, nano-laminate shear
- Thermal shock resistance: ~1400°C quench
- $K_{IC} \approx 7$ MPa/m$^{1/2}$

Hybrid Concepts (EBC/TBC) Enabled by MAX Phases

Intermediate CTE, Strain Tolerance, YSZ Compatibility

1300°C Bond Coats (?)



YSZ	10	Top Coat
Al_2O_3	9	Scale
Ti_2AlC Ti_3AlC_2	8 9	Bond Coat
Rene N5 SiC	15 4	Substrates

Critical interface

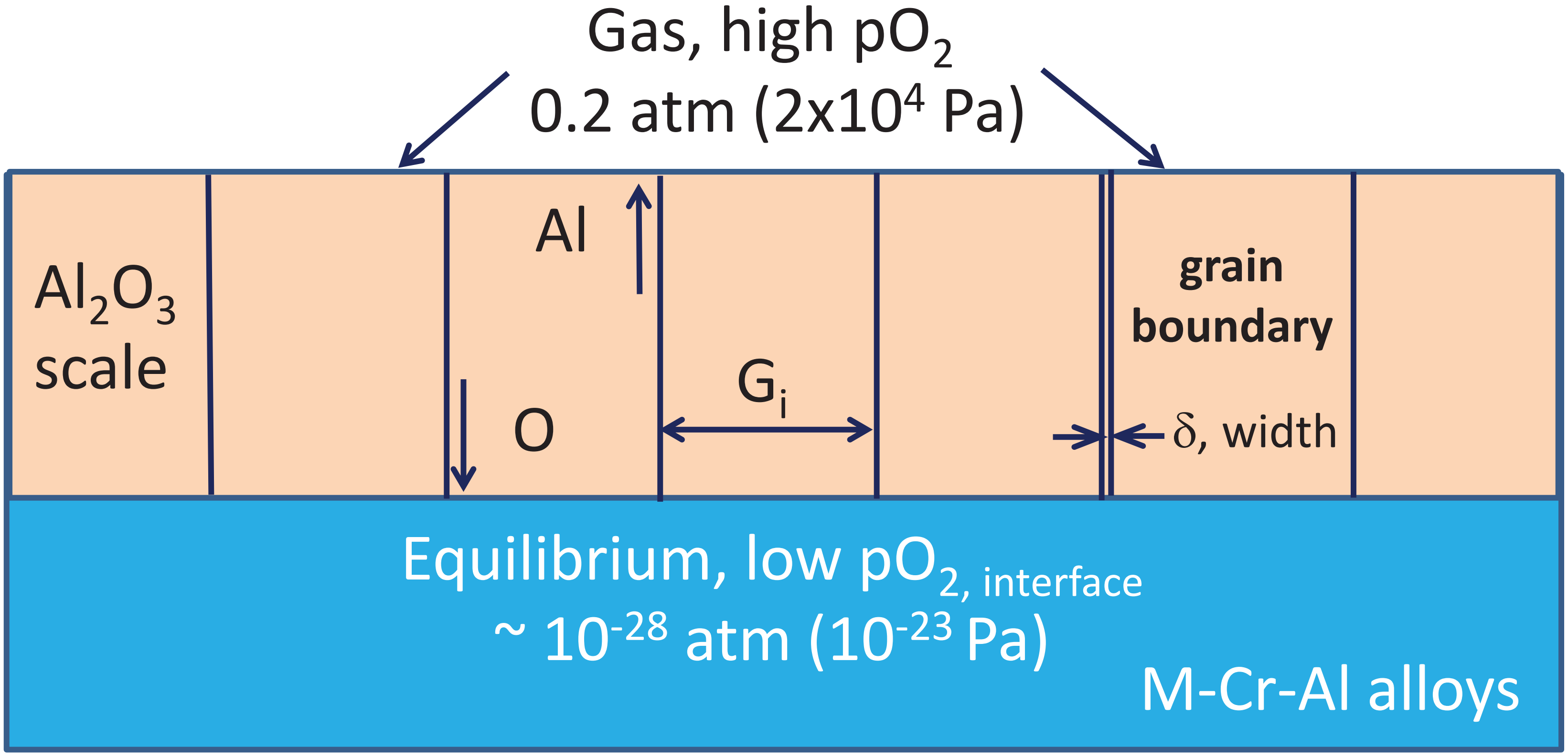
CTE, 10^{-6}/°C

Purpose: Relate Al-MAX phases to coatings applications/turbine environment

1) High temperature α-Al_2O_3 kinetics

- grain boundary diffusivity
- transient TiO_2 growth
- cubic kinetics

Schematic of Alumina Scale Transport



$$\boxed{D_{eff} \approx fD_{gb} = \frac{2\delta}{G_i} D_{gb}\ (\textit{short circuit diffusion}) >> D_{lattice}}$$

Modified Wagner: Derived k_p vs $\delta D_{gb,O}$ Relation: **(oxidation product $\Pi \approx$ constant)**

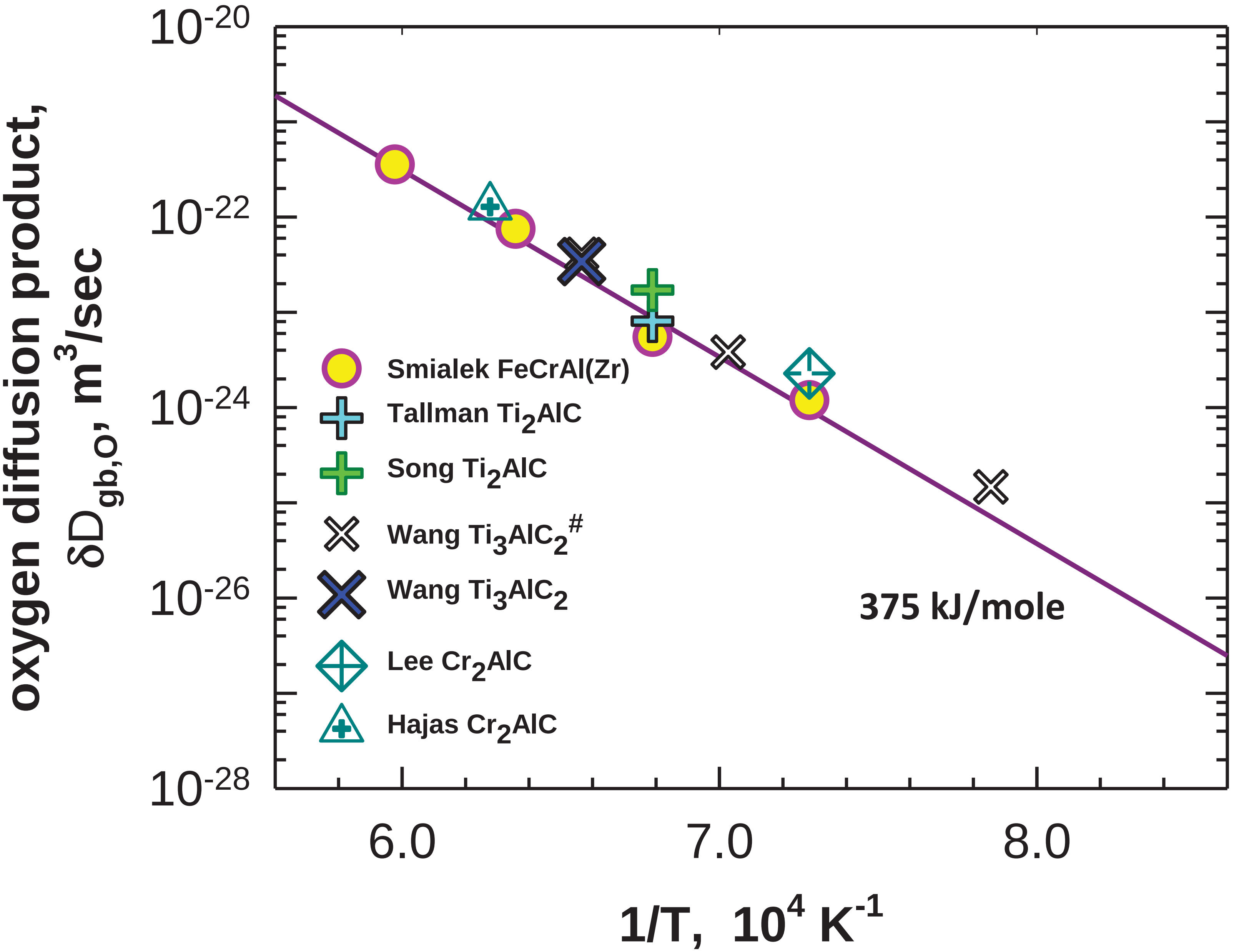
$$k_{p,\text{instant}} = 2x\frac{dx}{dt} \approx \int_{P_{O_2},\text{interface}}^{P_{O_2},gas} D_{eff,O}\, d\ln P_{O_2} \qquad (Wagner\, eqn.)$$

$$\Pi_\text{i} = \text{k}_{\text{p,instant}} \cdot \text{G}_{\text{instant}} \approx 12\delta \text{D}_{\text{gb,O,interface}}$$

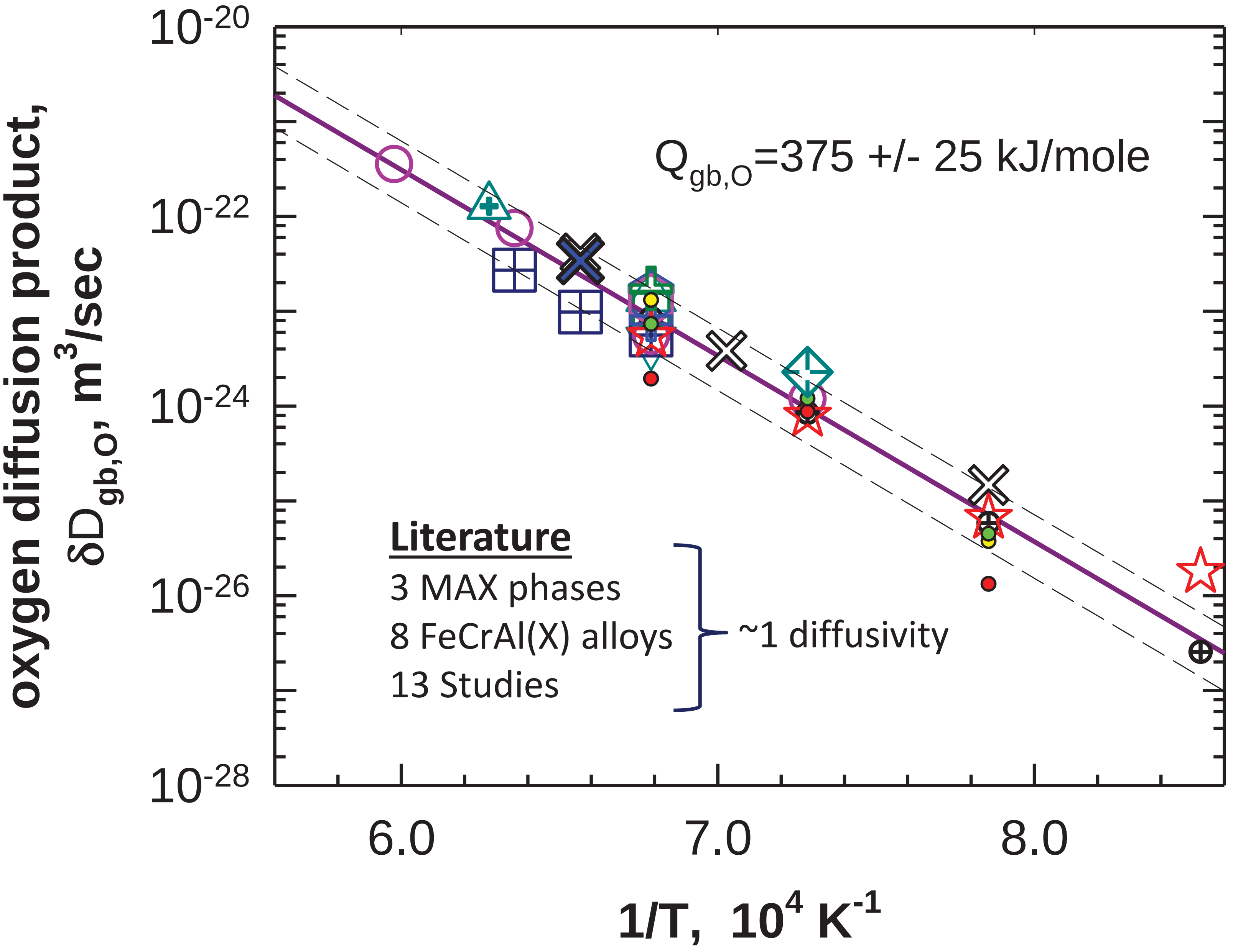
$\therefore$ If scale grain size available,
a nearly invariant diffusivity can be estimated.

Scale Grain Boundary Diffusivity

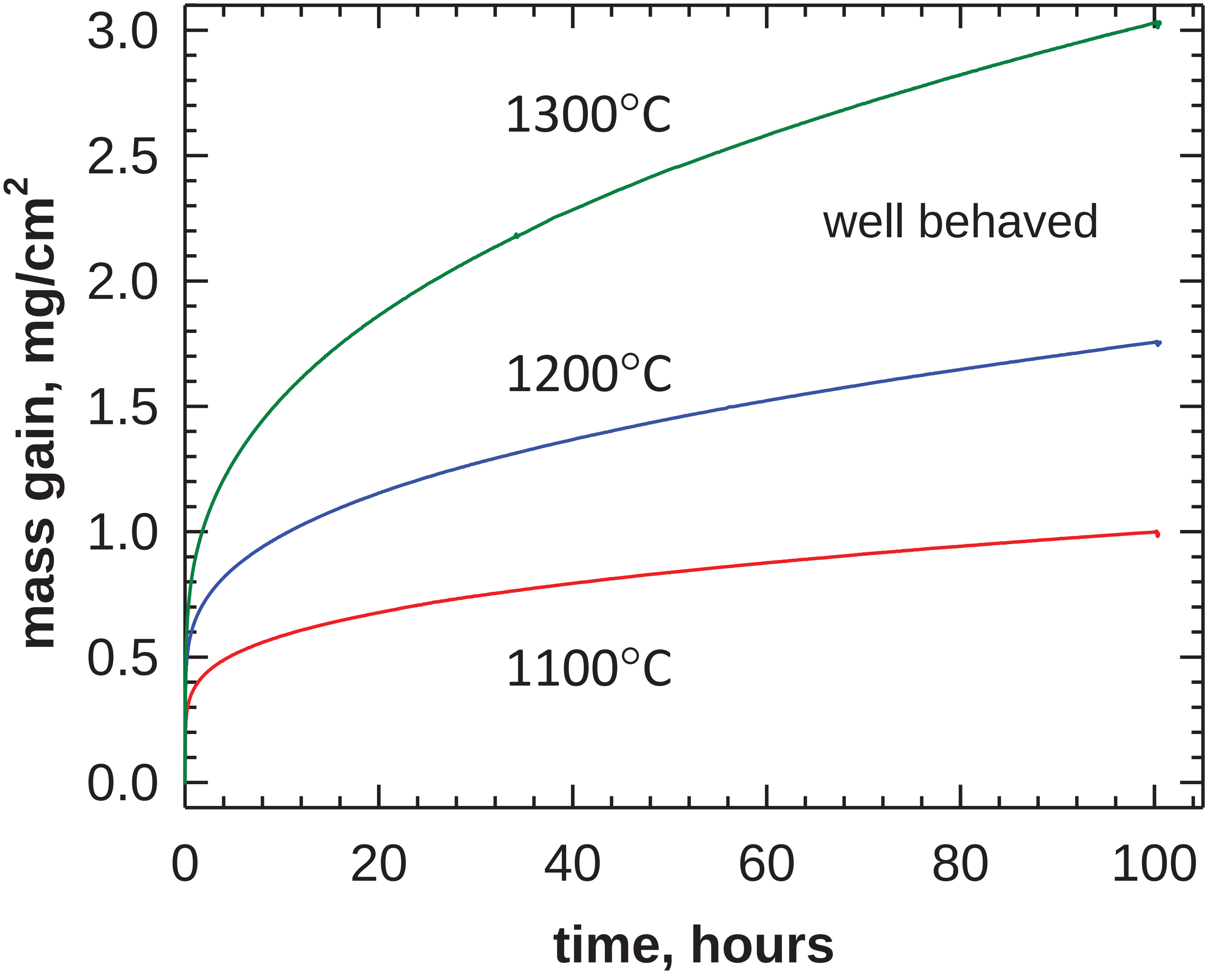
MAX Compounds and FeCrAl(Zr) Alloy



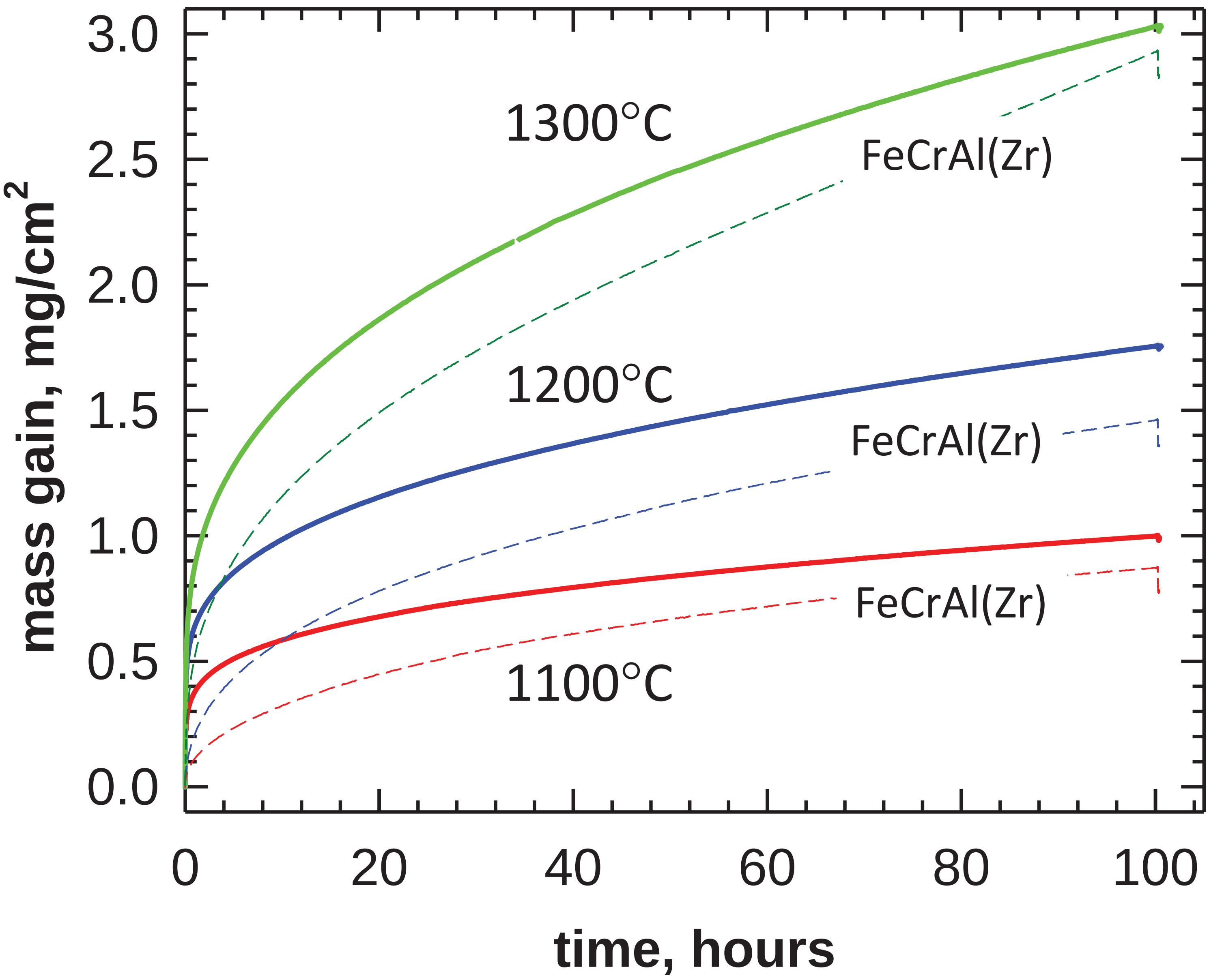
Scale Grain Boundary Diffusivity
MAX Compounds and FeCrAl(X) Alloys



TGA Oxidation of Ti_2AlC in Dry Air

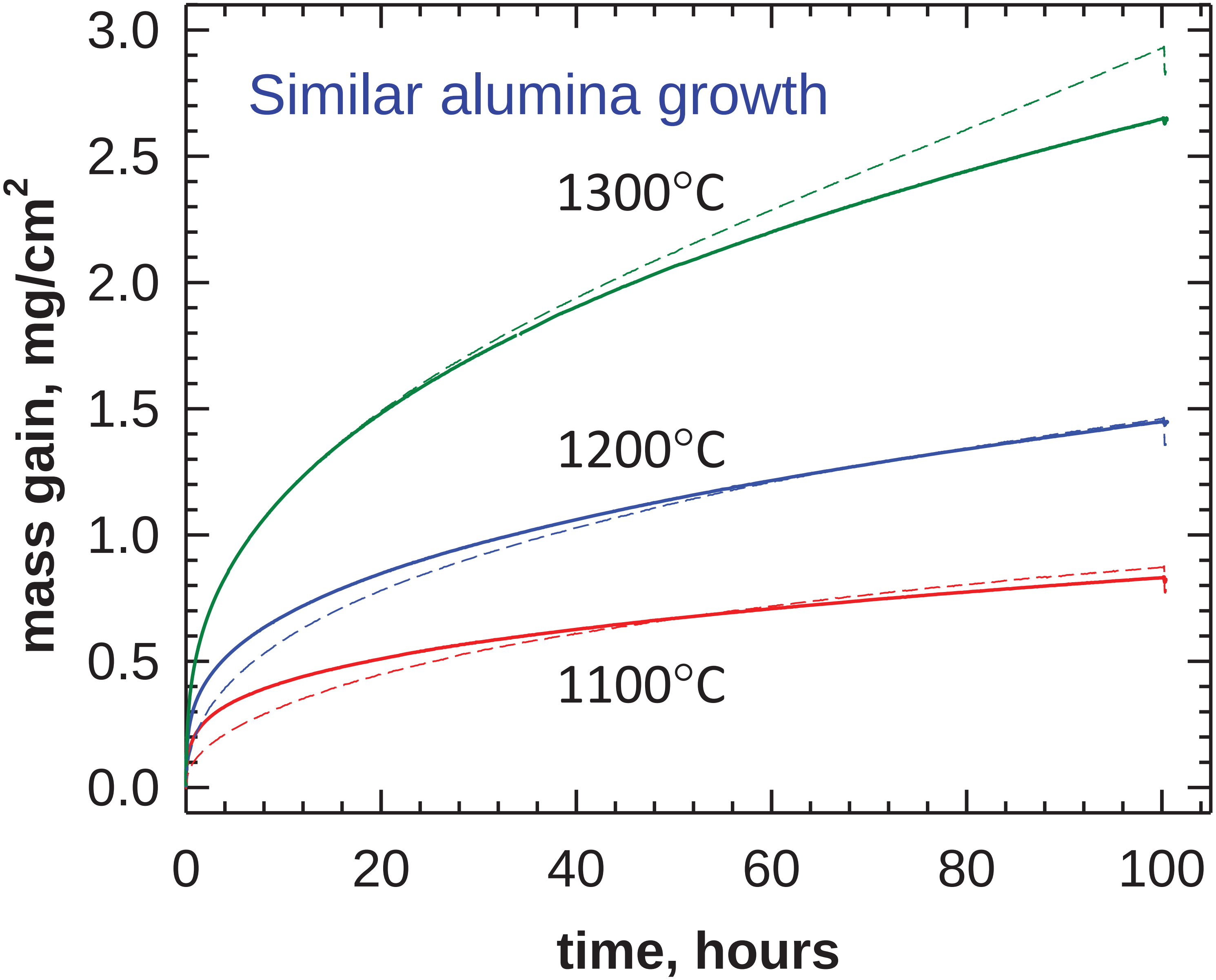


Ti_2AlC Offset from FeCrAl(Zr)



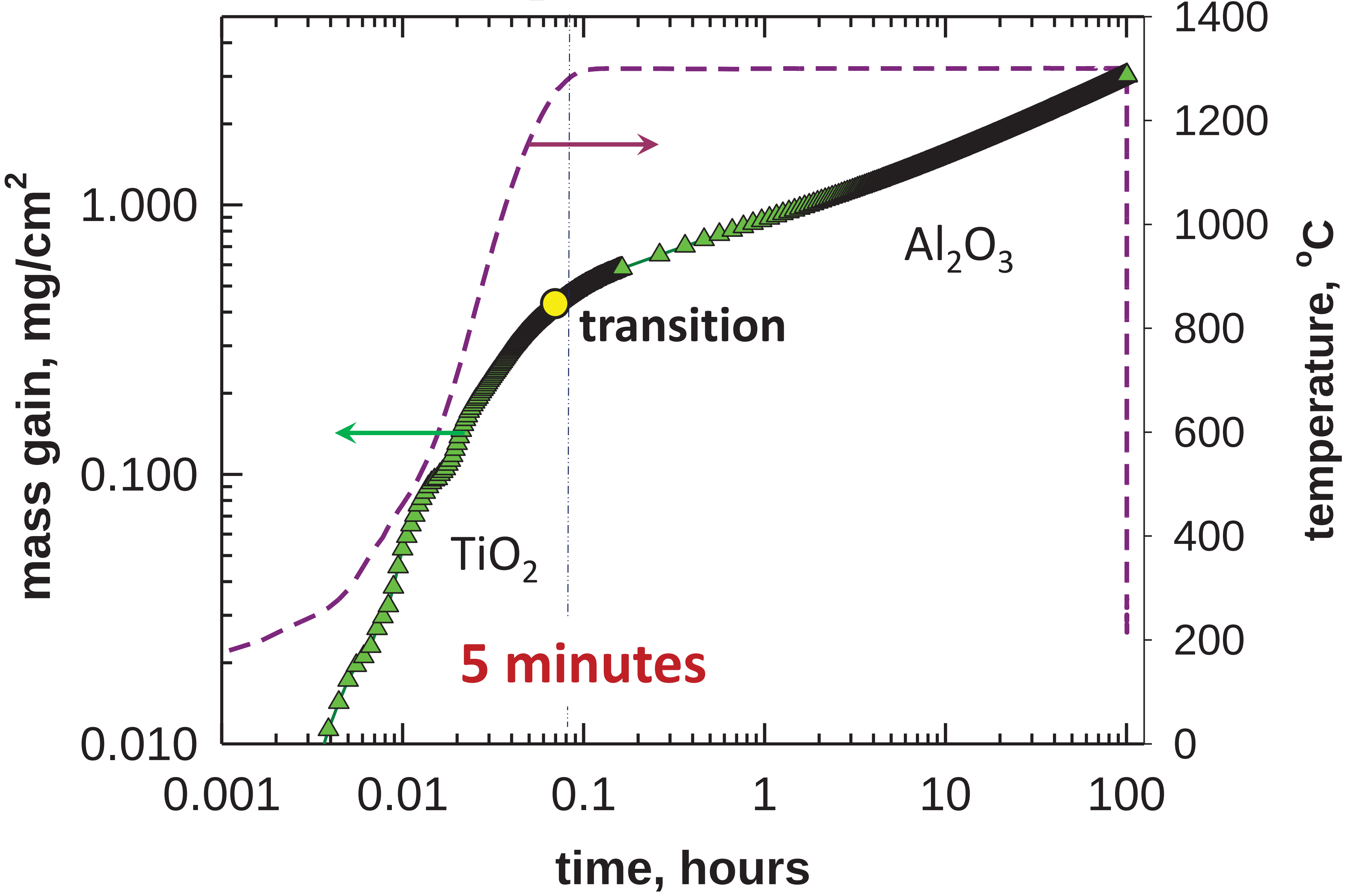
$(\Delta W - \Delta W_0)$ *vs* $(t - t_0)$

Offset Corrected Ti_2AlC ~ FeCrAlZr



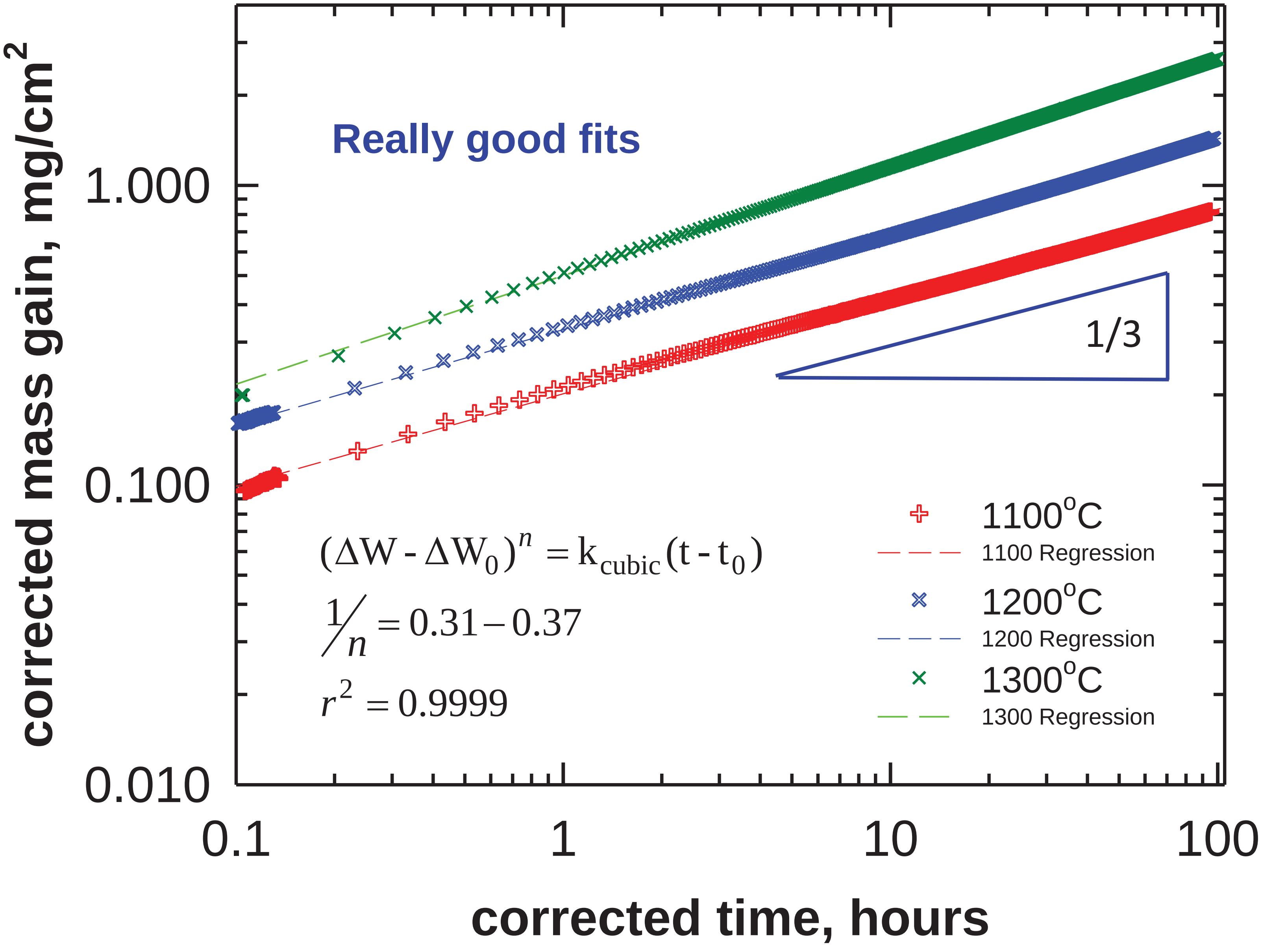
1300°C Ti_2AlC TGA:

Rapid TiO_2 Transients on heating



Cubic Kinetics (Tallman, Anasori, Barsoum, 2013)

Offset Corrected Ti_2AlC TGA



Really good fits

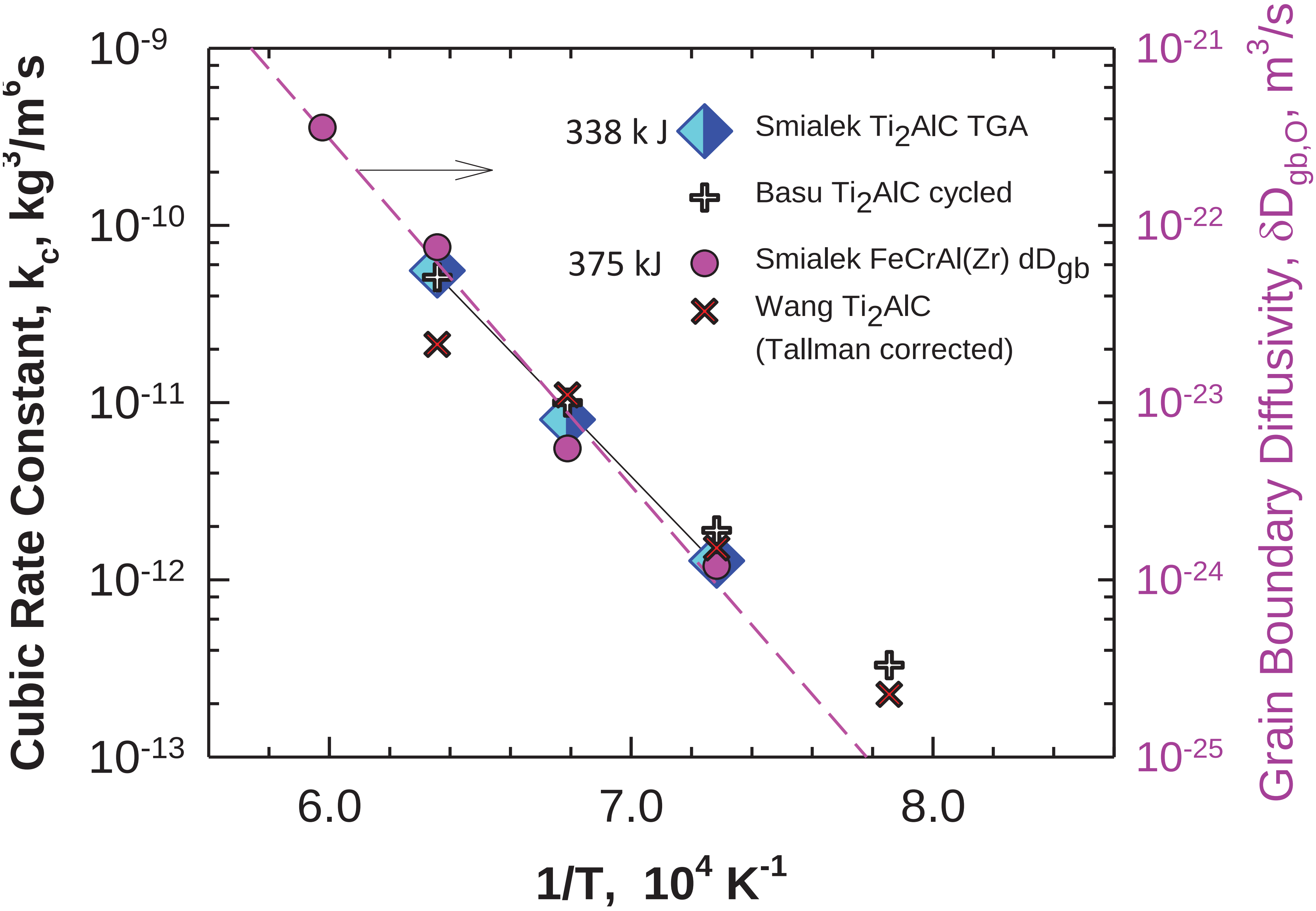
$$(\Delta W - \Delta W_0)^n = k_{cubic}(t - t_0)$$

$$\frac{1}{n} = 0.31 - 0.37$$

$$r^2 = 0.9999$$

MAXthal 211 Ti$_2$AlC: TGA and HPBR Cubic Constant

(vs δD_{gb} FeCrAl(Zr) Alloy)



Purpose: Relate Al-MAX phases to coatings applications/turbine environment

2) First High pressure burner rig test of Ti_2AlC

(Jet A fuel, 6 atm., 25 m/s, 10% water vapor)

- transient TiO_2 growth
- cubic kinetics
- scale volatility issues (?)
- CO/CO_2 (?)

Scale Volatility in Water Vapor Limits Use
(Opila, Jacobson, Myers, Copland, 2006)

p_{max}(volatiles) = 10^{-6} atm
(~1 mil/1000 h) loss

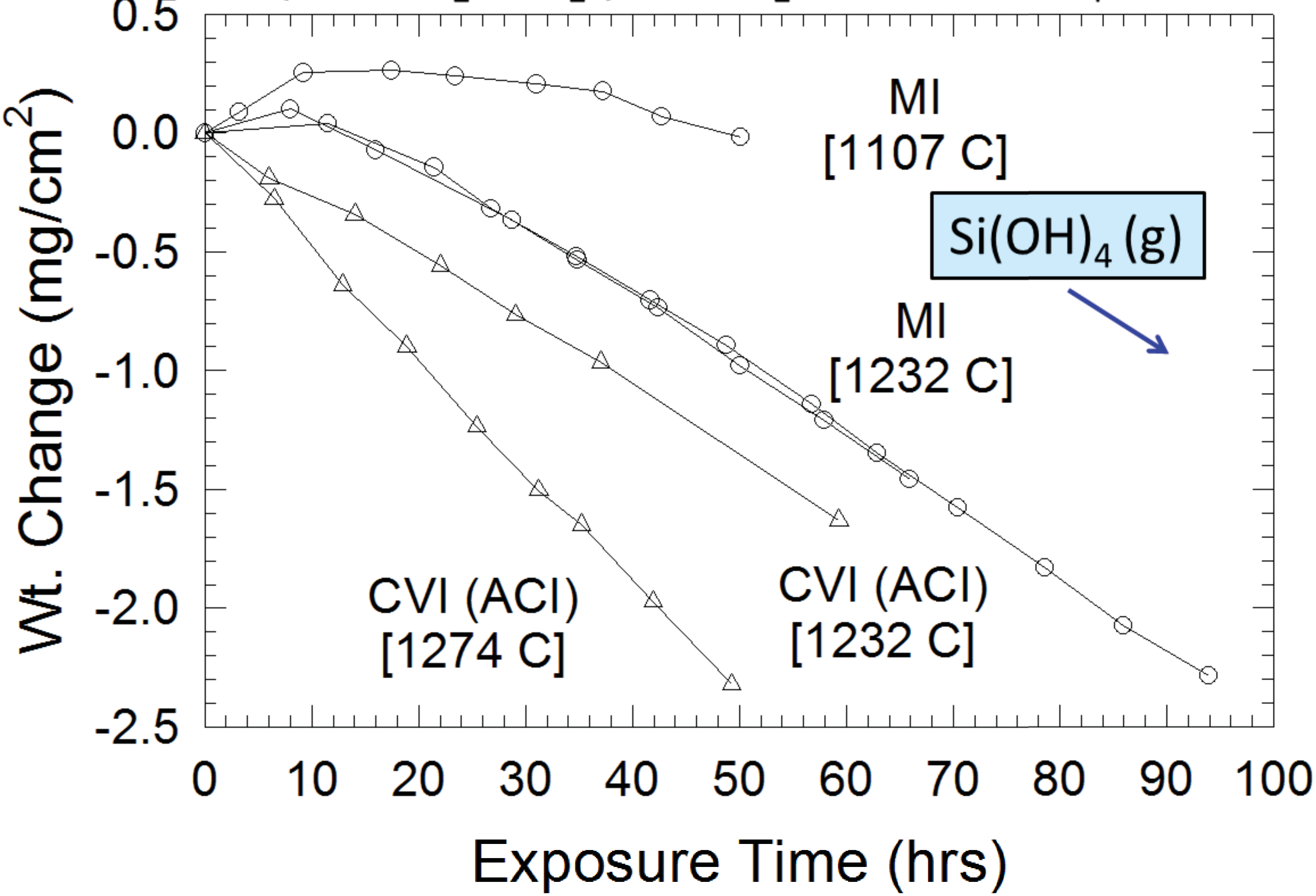
Scale	Volatiles	Upper Temp.
Cr_2O_3	$CrO_2(OH)_2$, CrO_3	500°C
SiO_2	$Si(OH)_4$	970°C
Al_2O_3	$Al(OH)_3$	1350°C
TiO_2	$TiO(OH)_2$	(1100°C)

SiC/SiC CMC HPBR Paralinear Weight Change

(1100 °-1300°C, 6 atm; Robinson/Smialek 1998)

$Si(OH)_4$ volatility (Opila et al., 1998-2006)

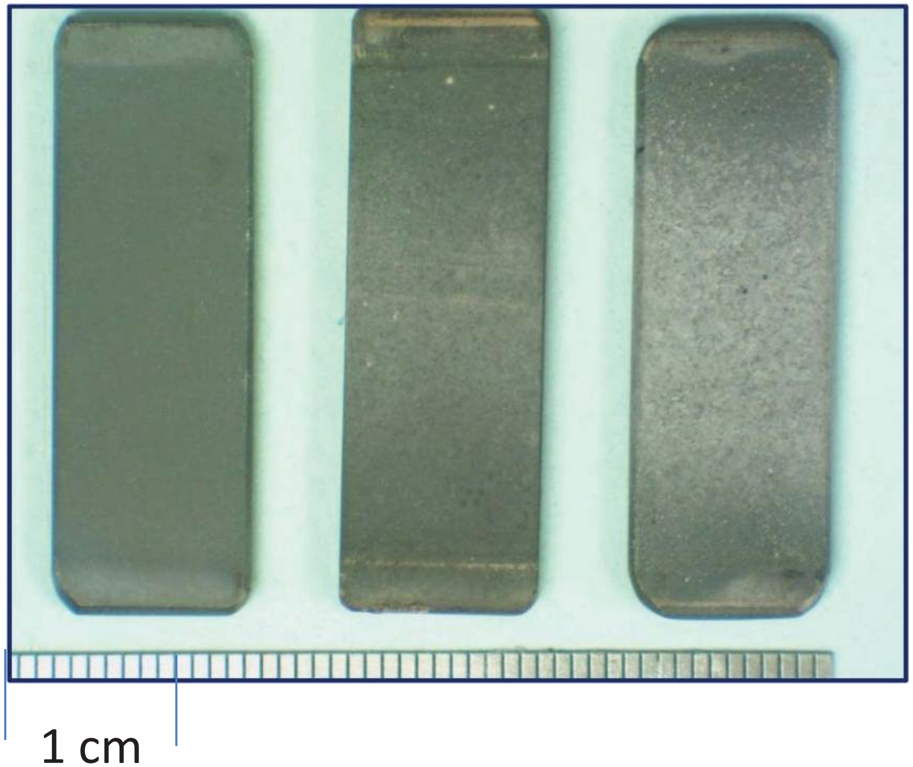
$\{ SiC + H_2O/O_2 \} \rightarrow SiO_2\,(s) \rightarrow Si(OH)_4\,(g)$



Ti_2AlC MAX Phase Oxidation

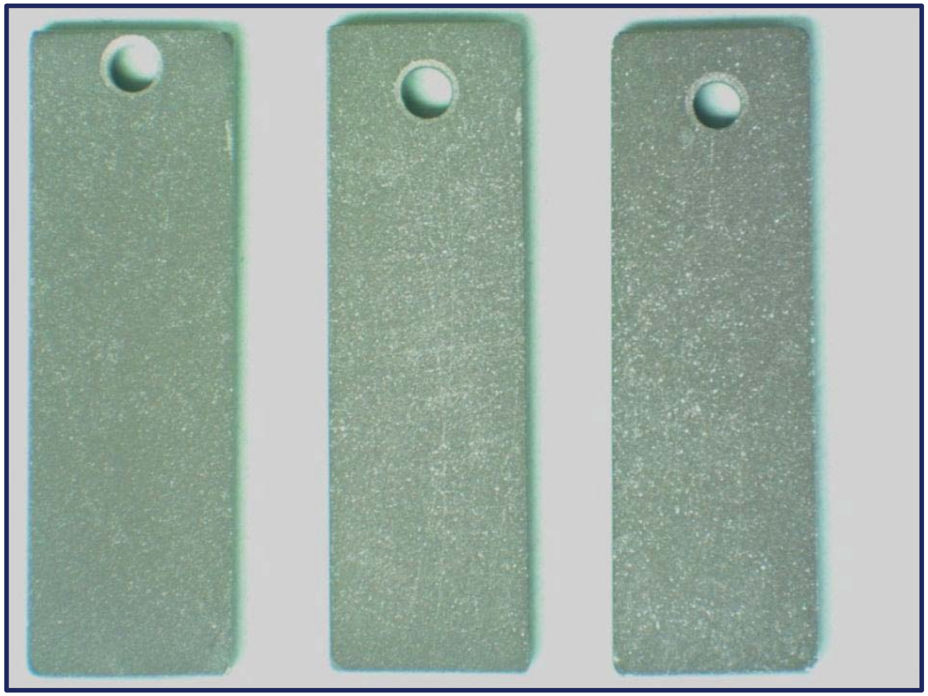
50 h HPBR

1100, 1200, 1300°C

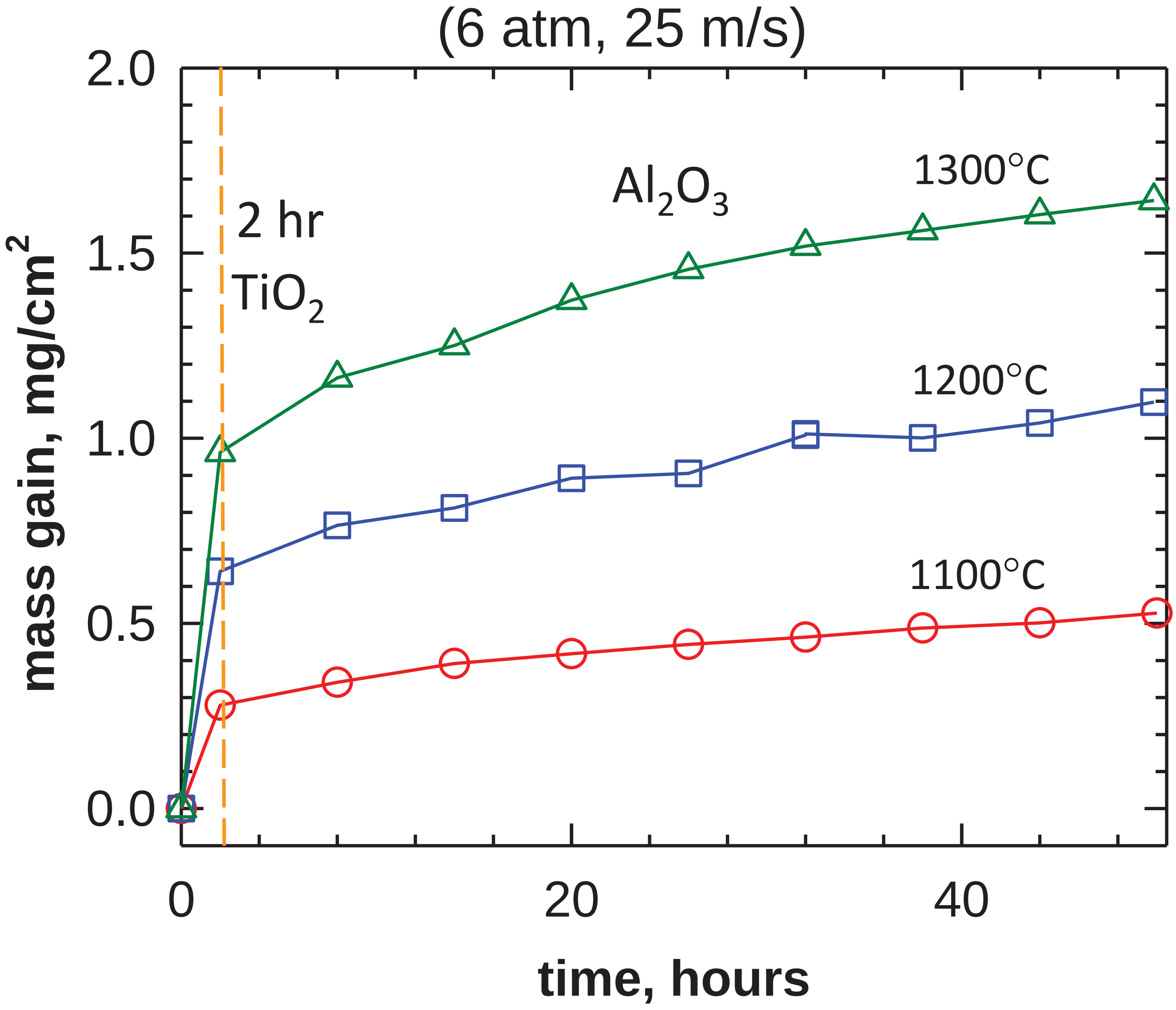


100 h TGA

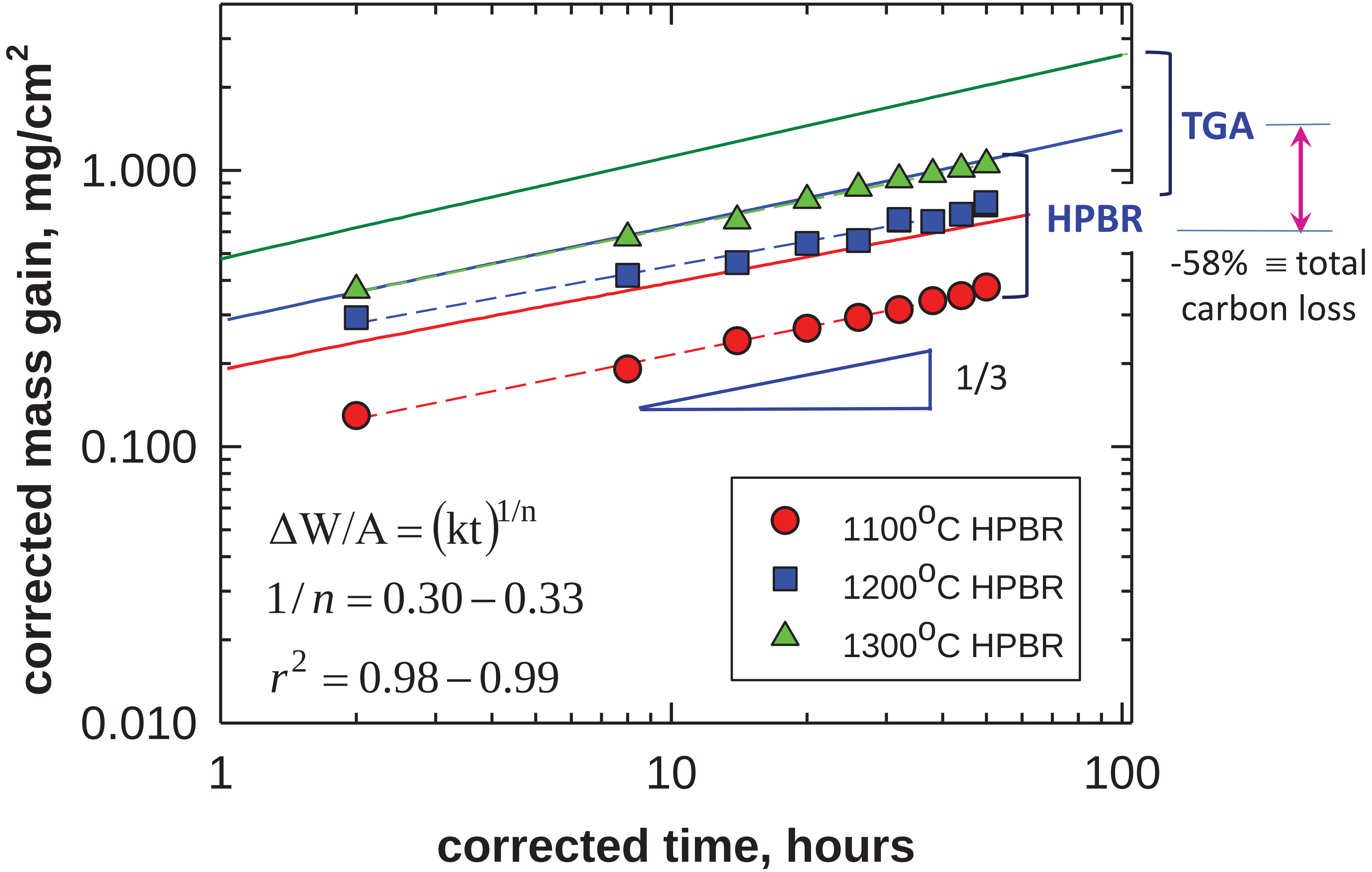
1100, 1200, 1300°C



HPBR Oxidation *Gains* for Ti_2AlC

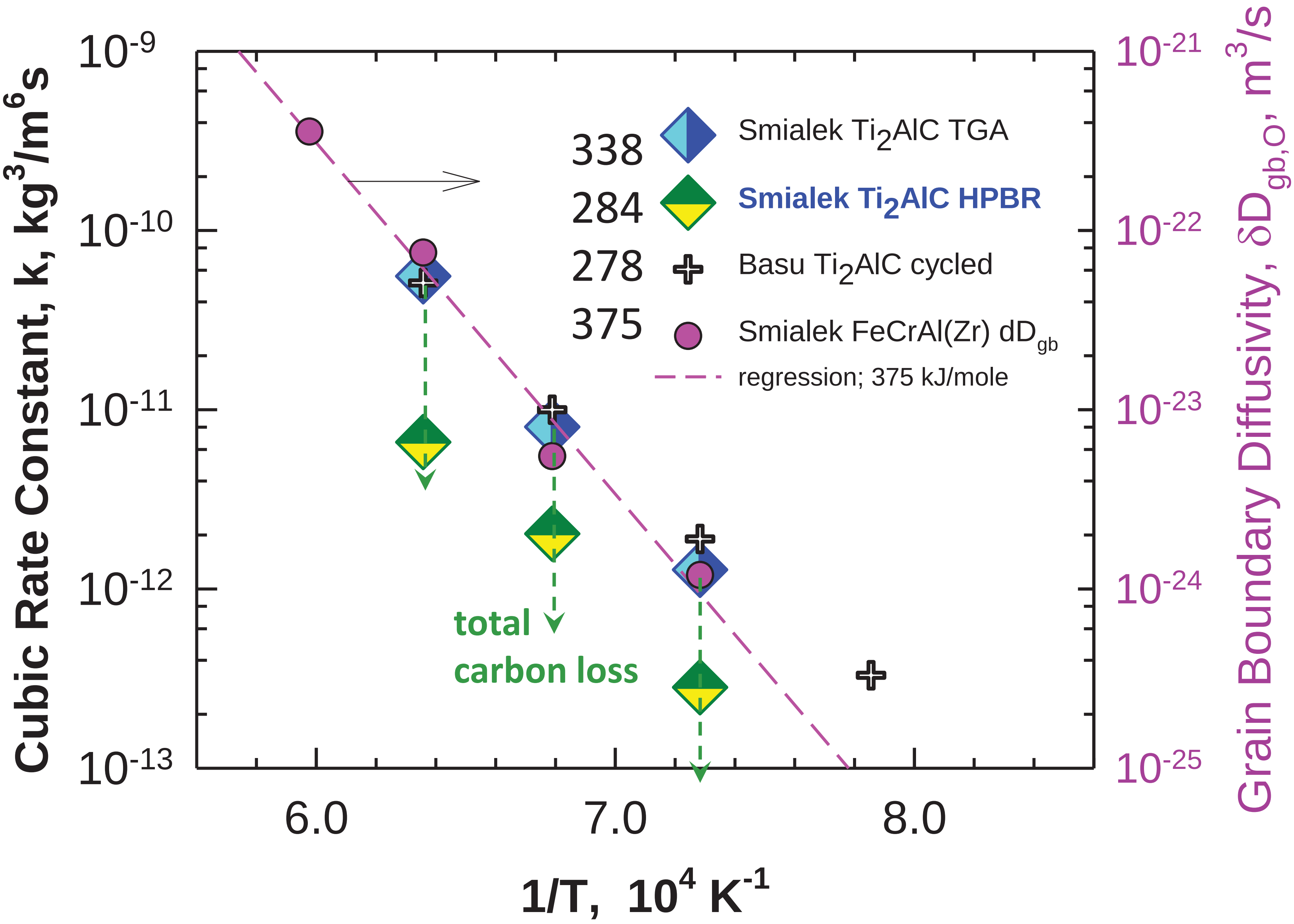


Offset Corrected Ti$_2$AlC HPBR: Good cubic behavior, but below TGA



MAXthal 211 Ti_2AlC: TGA and HPBR Cubic Constant

(vs δD_{gb} FeCrAl(Zr) Alloy)

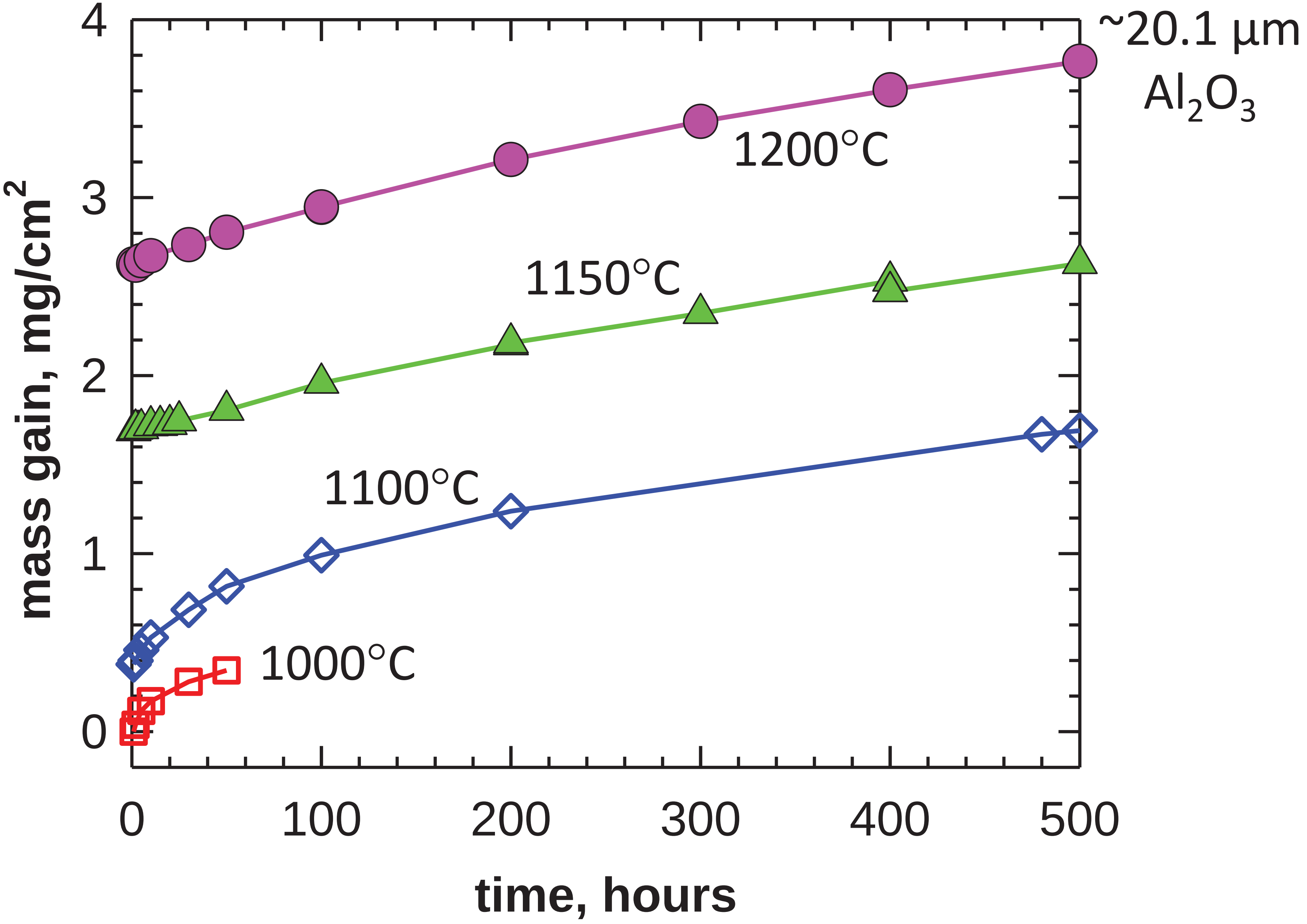


Purpose: Relate Al-MAX phases to coatings applications/turbine environment

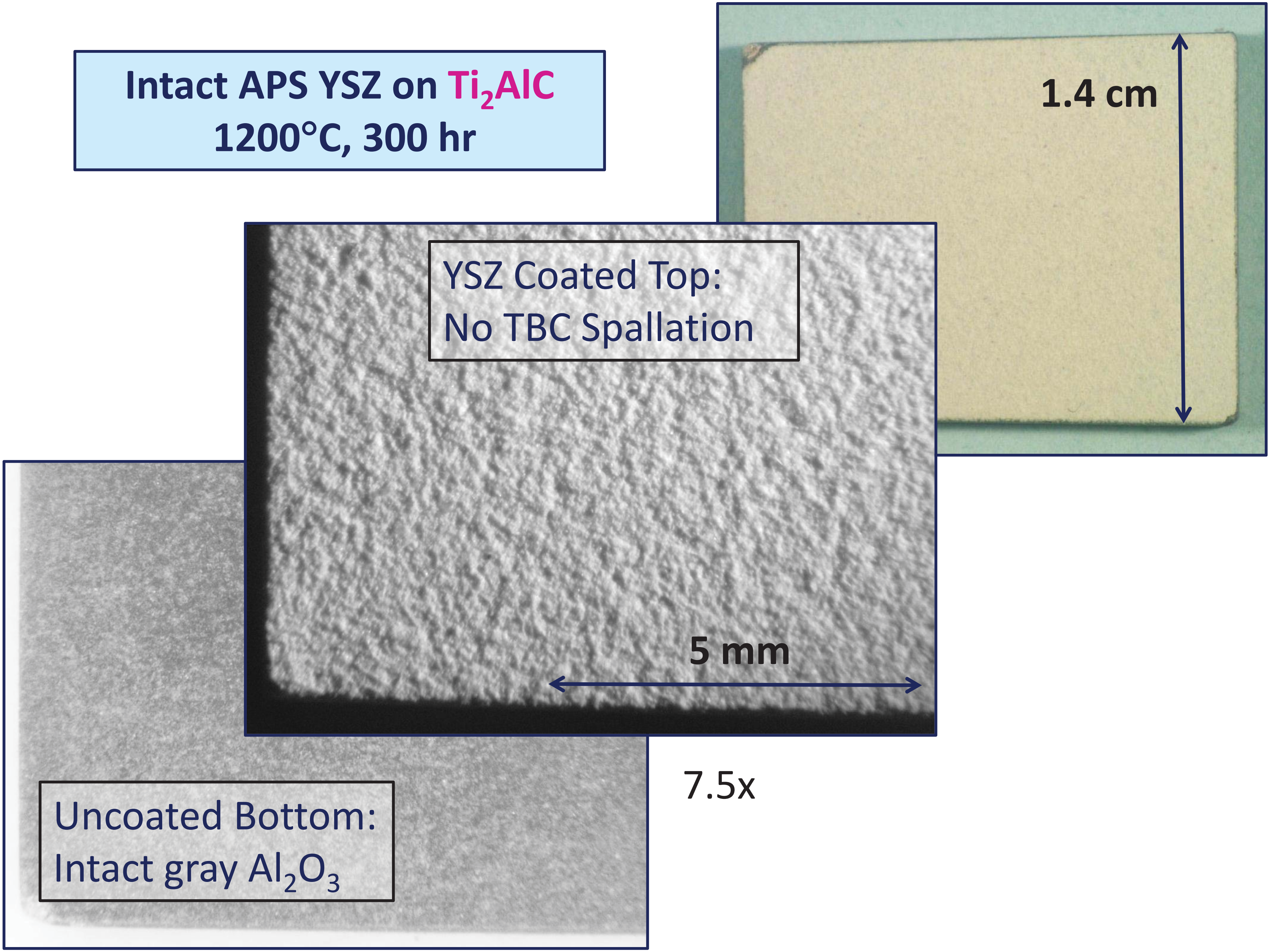
3) First YSZ Thermal Barrier Coatings on MAX Phases

- APS-Ti_2AlC (250 μm) **AND** PS-PVD (125 μm)
- Ti_2AlC; Cr_2AlC grit blast coupons
- 1000°-1200°C furnace test

Interrupted Oxidation of APS YSZ on Ti$_2$AlC



Intact APS YSZ on Ti_2AlC
1200°C, 300 hr



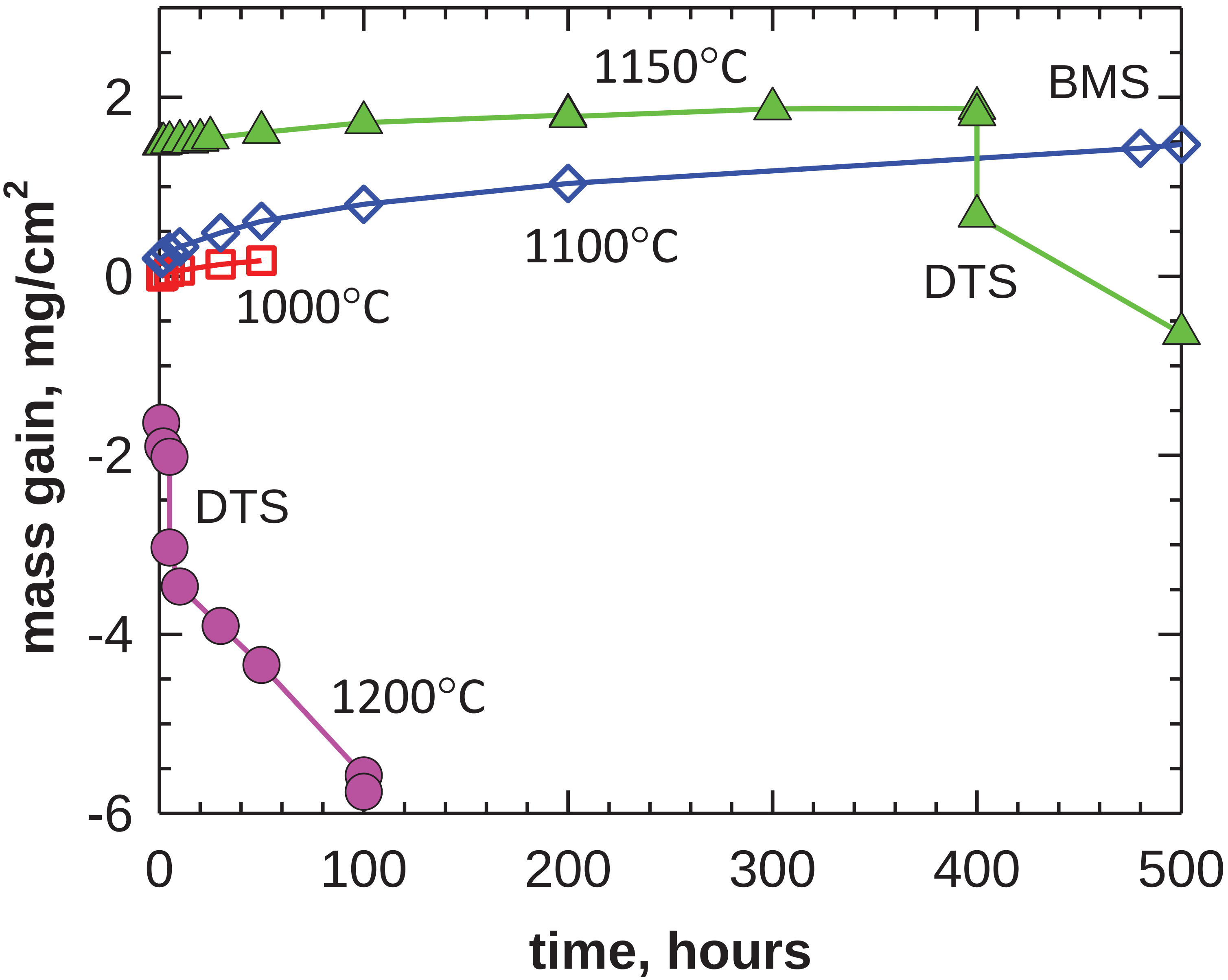
YSZ Coated Top:
No TBC Spallation

Uncoated Bottom:
Intact gray Al_2O_3

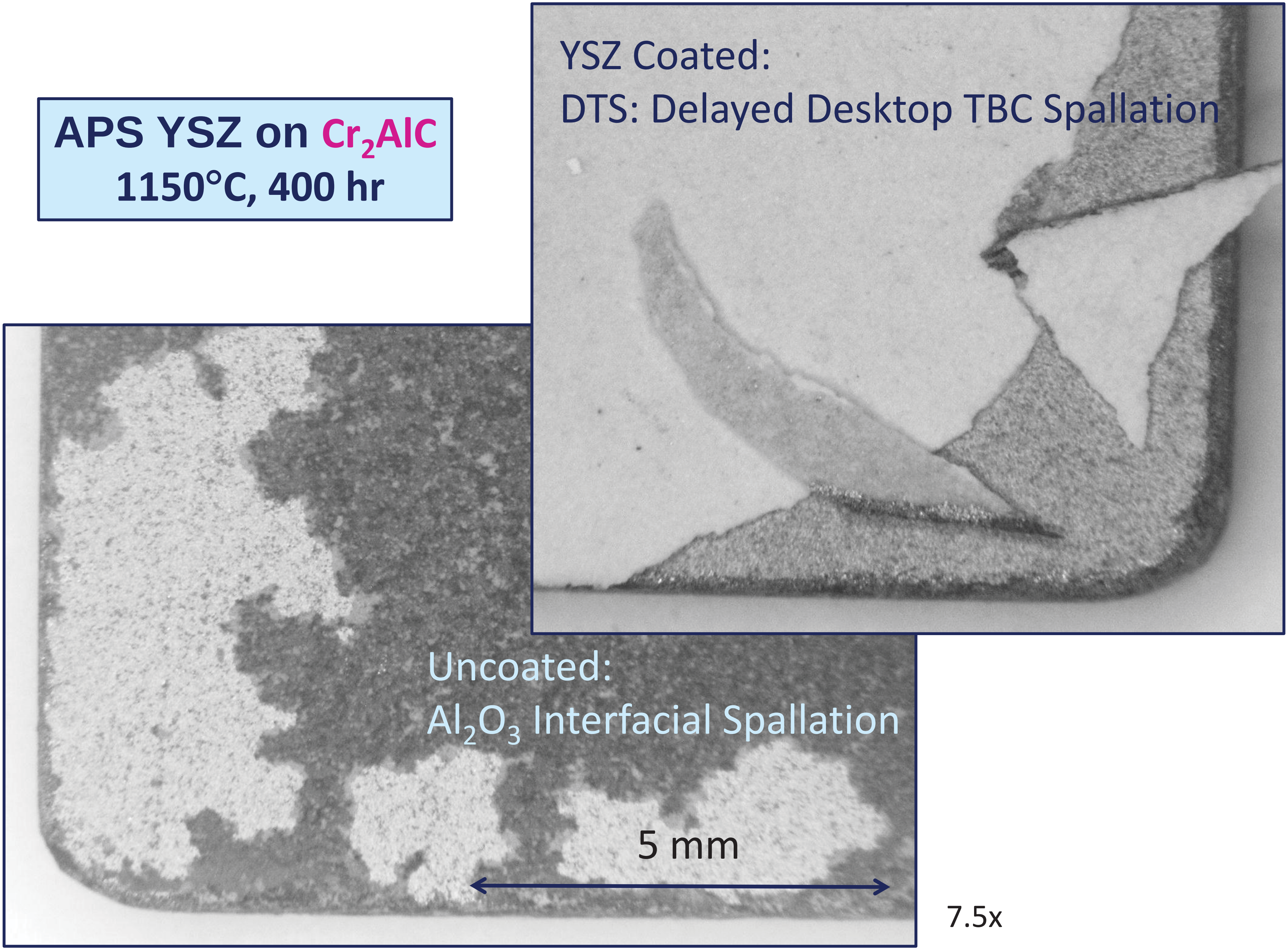
7.5x

Interrupted Oxidation of APS YSZ on Cr_2AlC

(TBC failure starts at 1150°C)



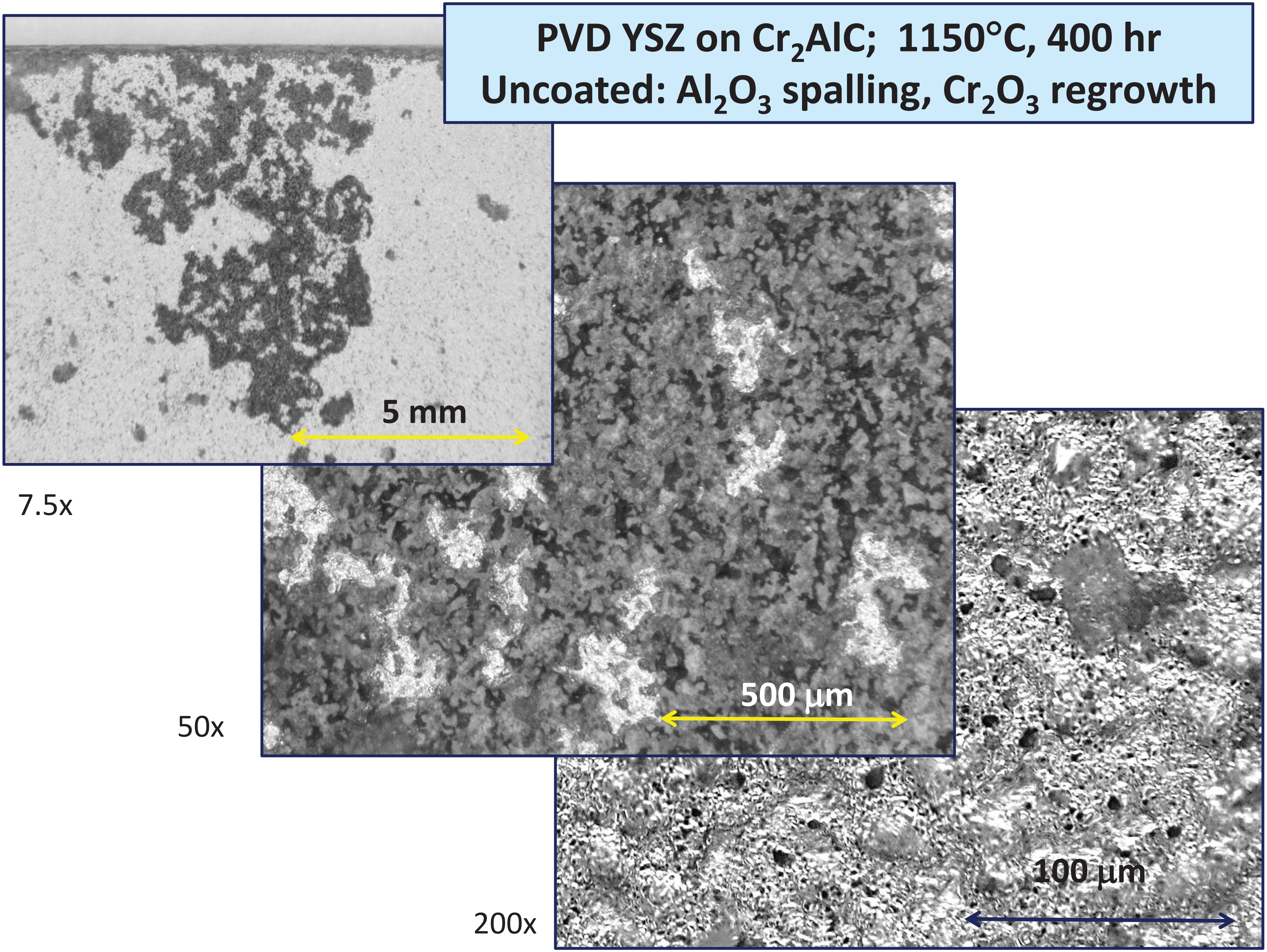
APS YSZ on Cr_2AlC
1150°C, 400 hr


YSZ Coated:
DTS: Delayed Desktop TBC Spallation

Uncoated:
Al_2O_3 Interfacial Spallation

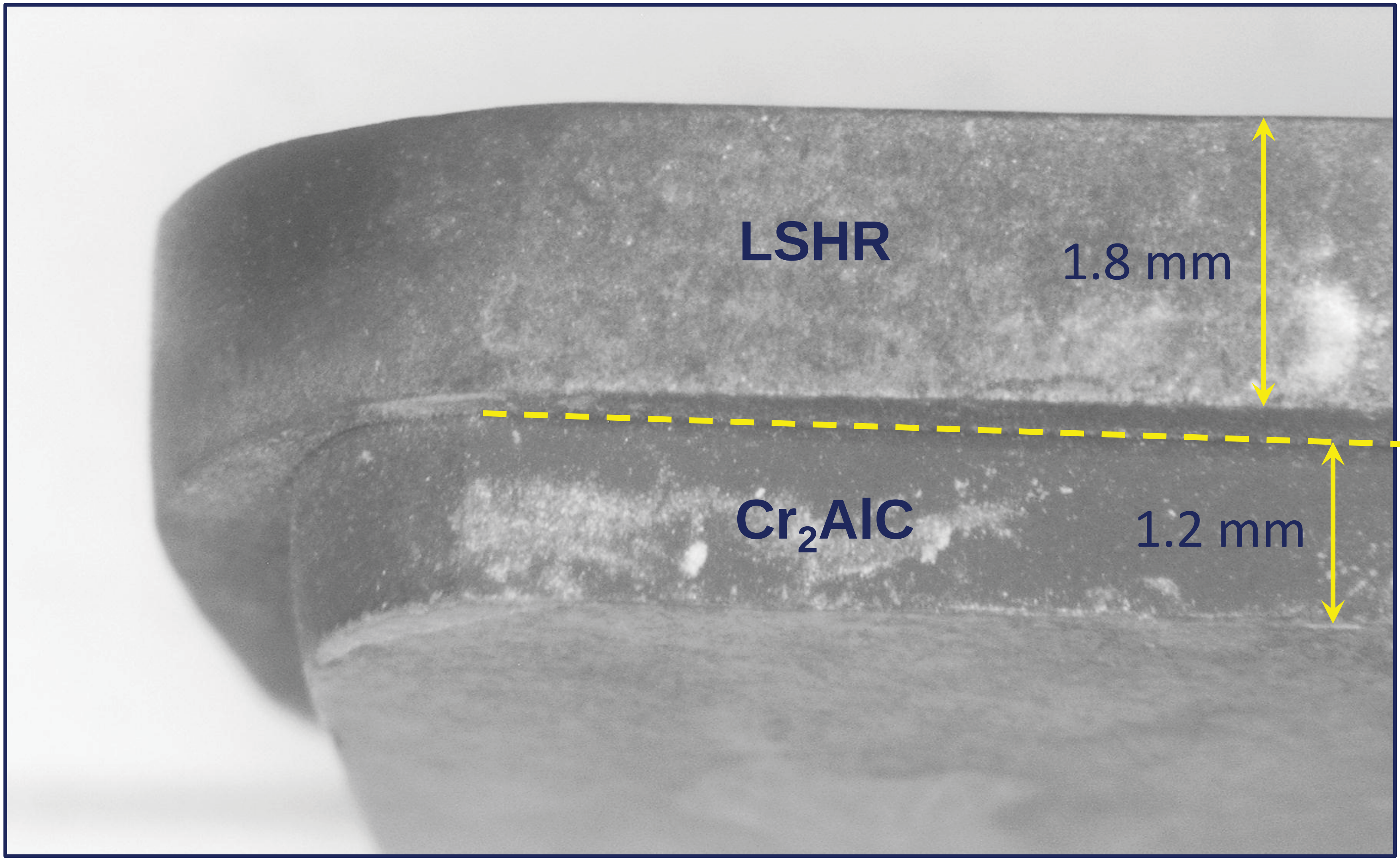
7.5x

PVD YSZ on Cr_2AlC; 1150°C, 400 hr
Uncoated: Al_2O_3 spalling, Cr_2O_3 regrowth

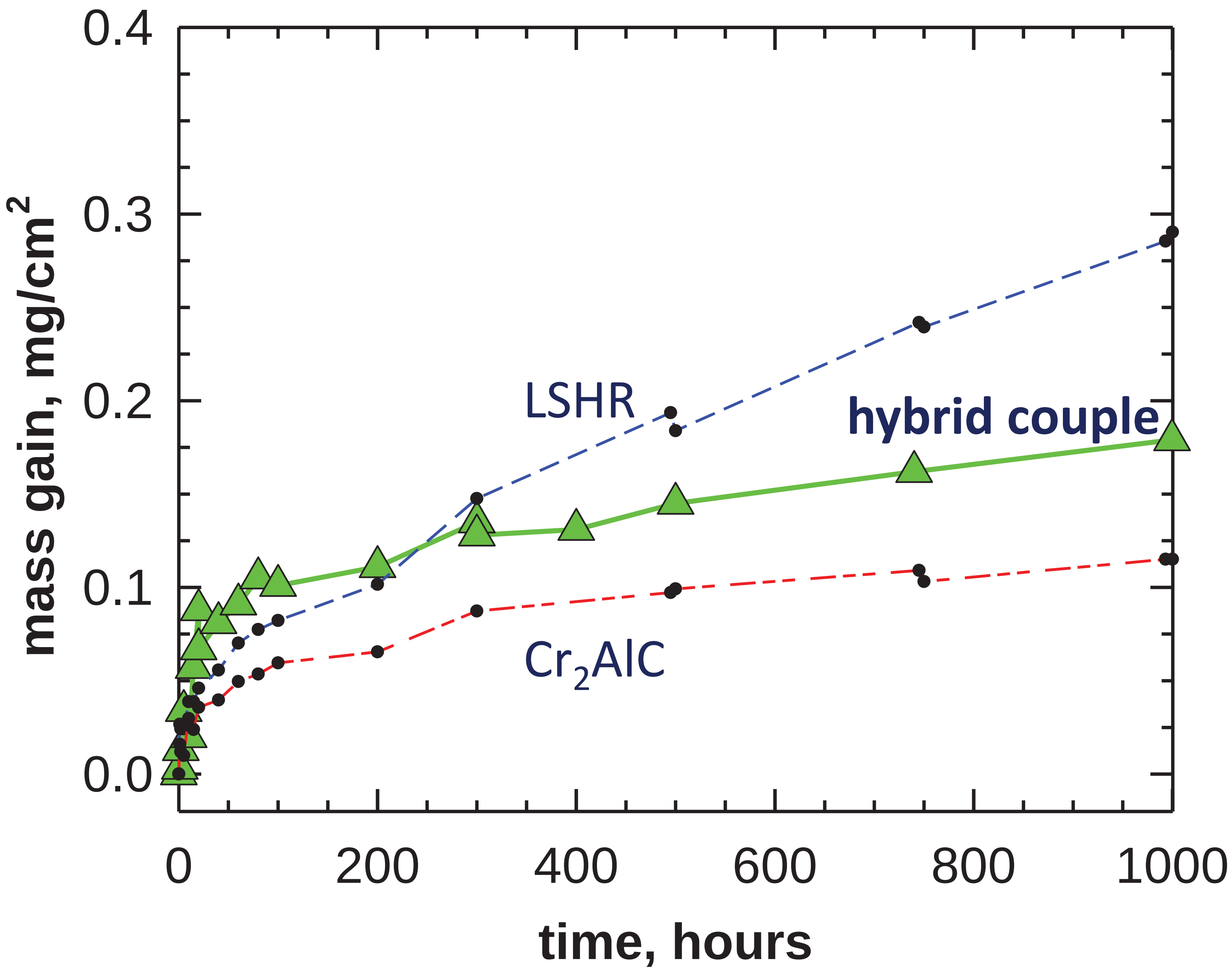


4) Stability of Superalloy/MAX Phase Hybrid

hot pressed 1100°, 2 h, 10^{-6} torr, 30 MPa



800°C Furnace Oxidation
LSHR, Cr_2AlC, and DC3 Hybrid Couple



As-Hot Pressed Cross Section, DC2

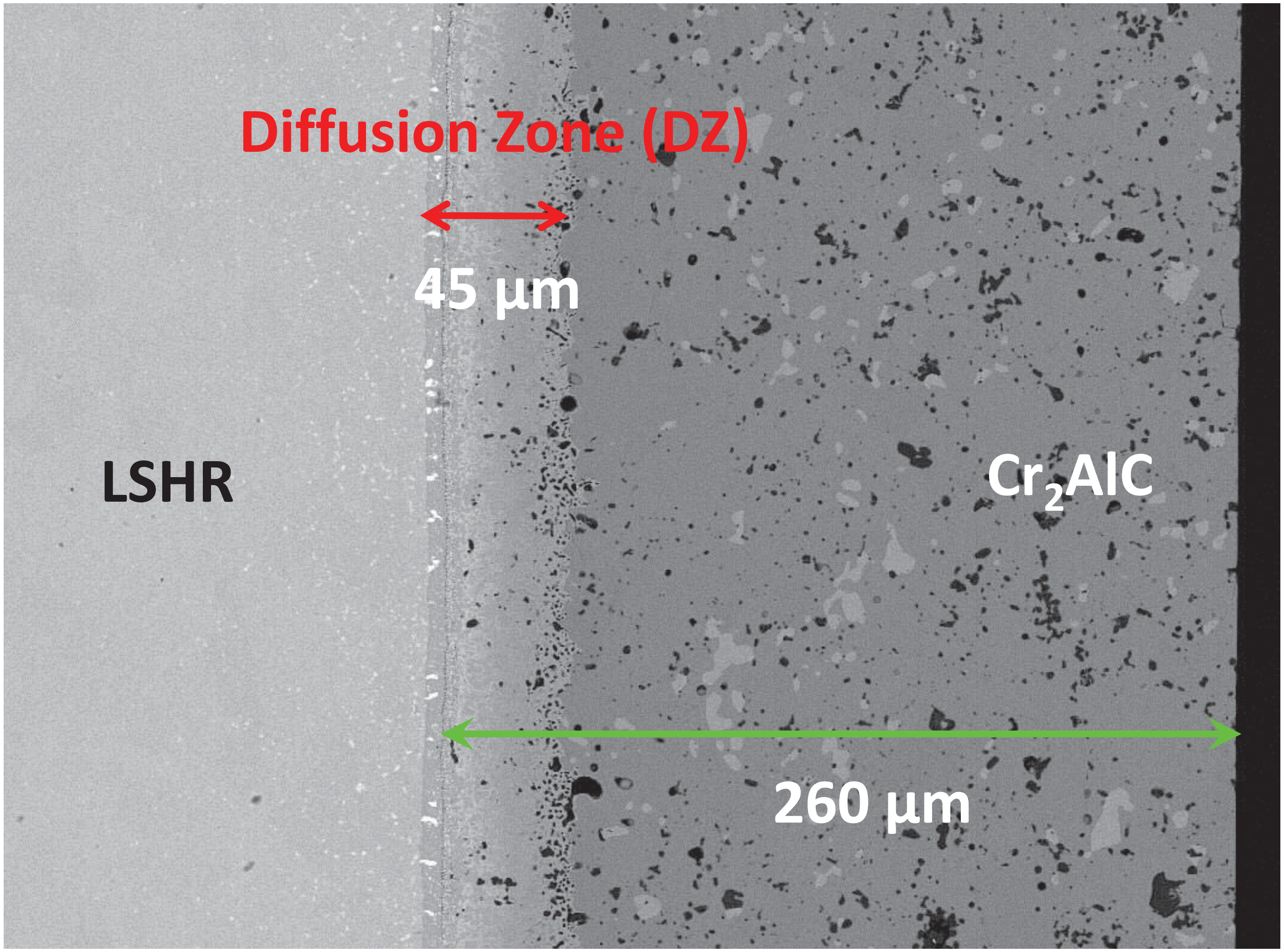


Figure 6

Diffusional Effects after Exposure to 800°C for 100 h

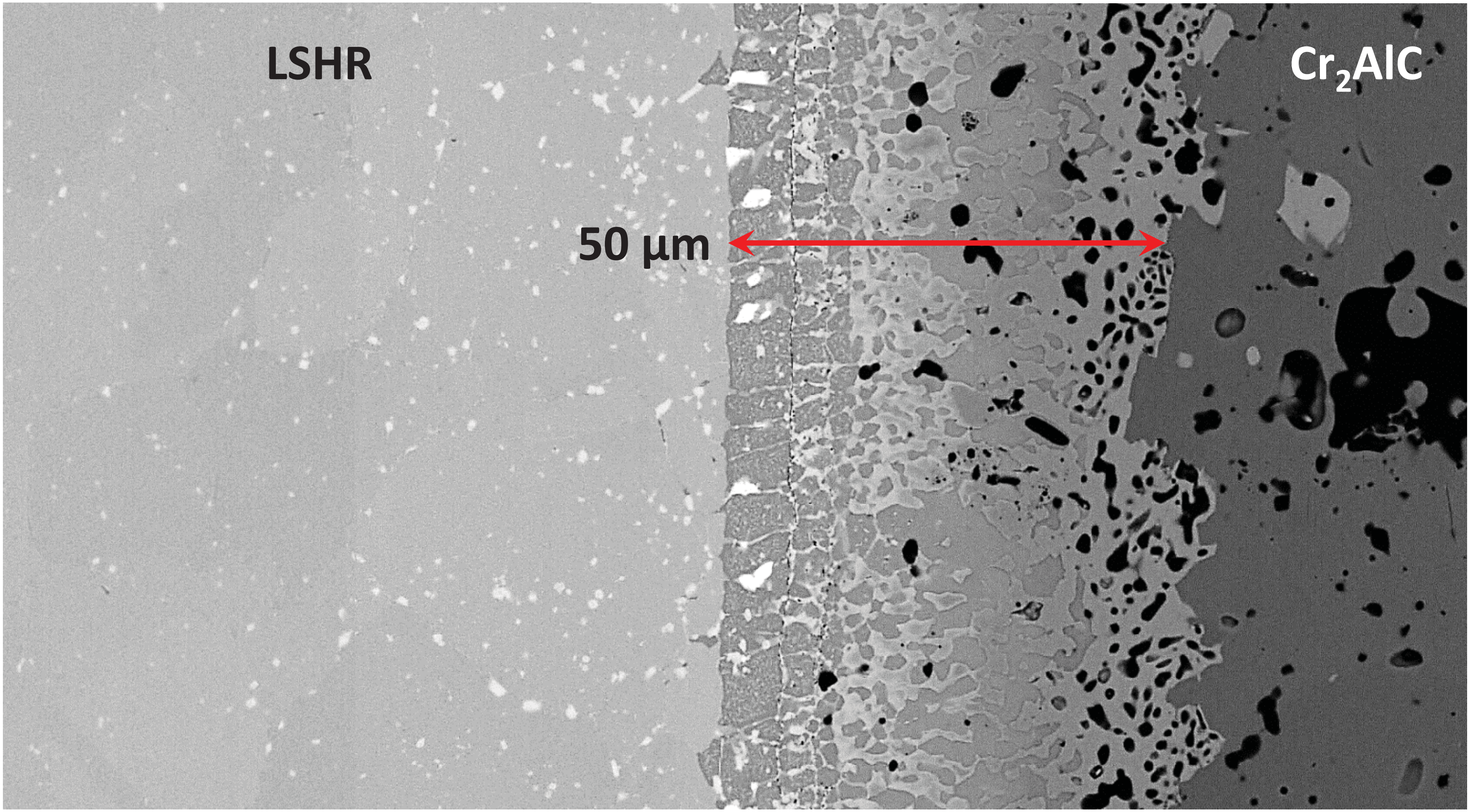
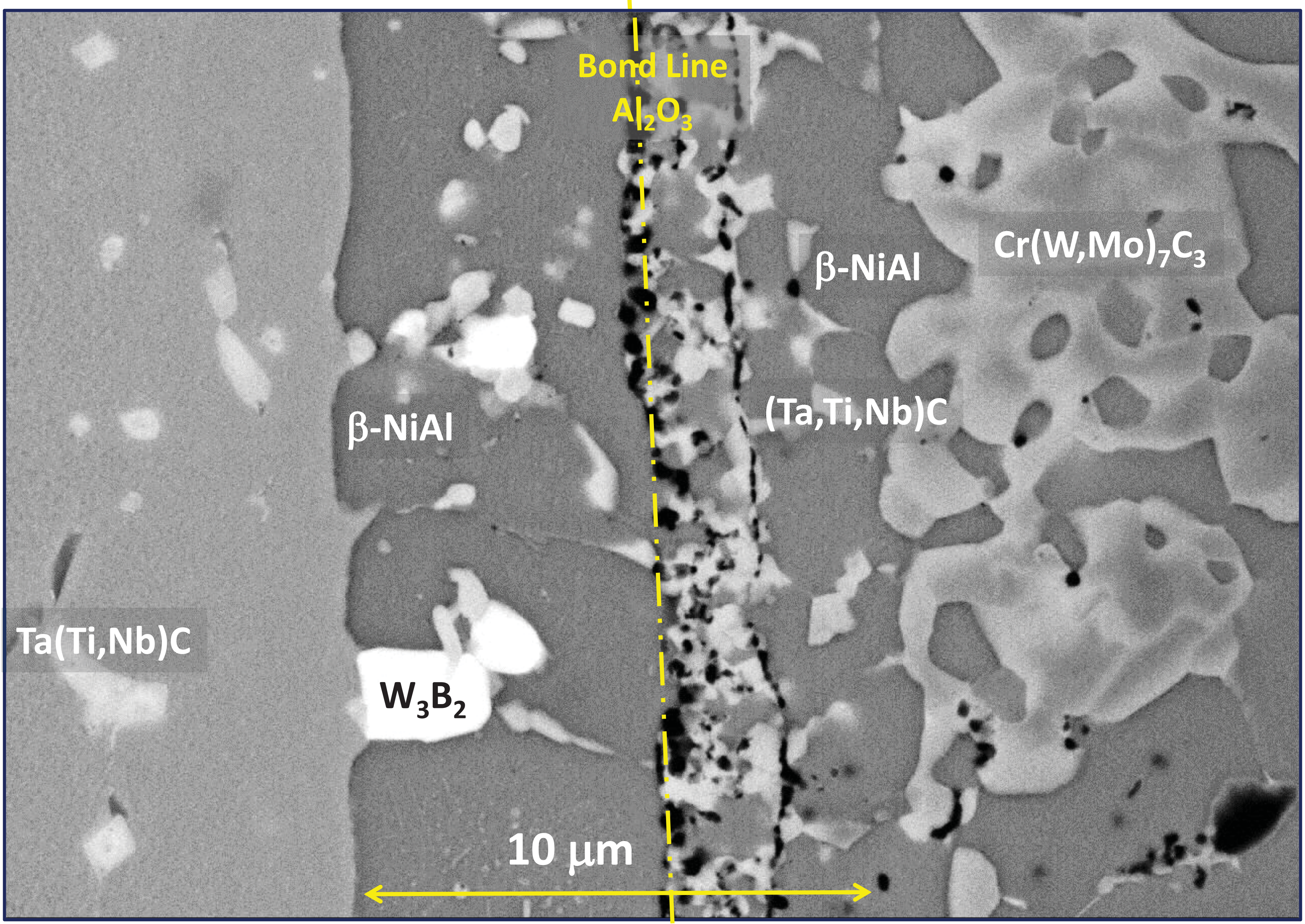


Figure 7

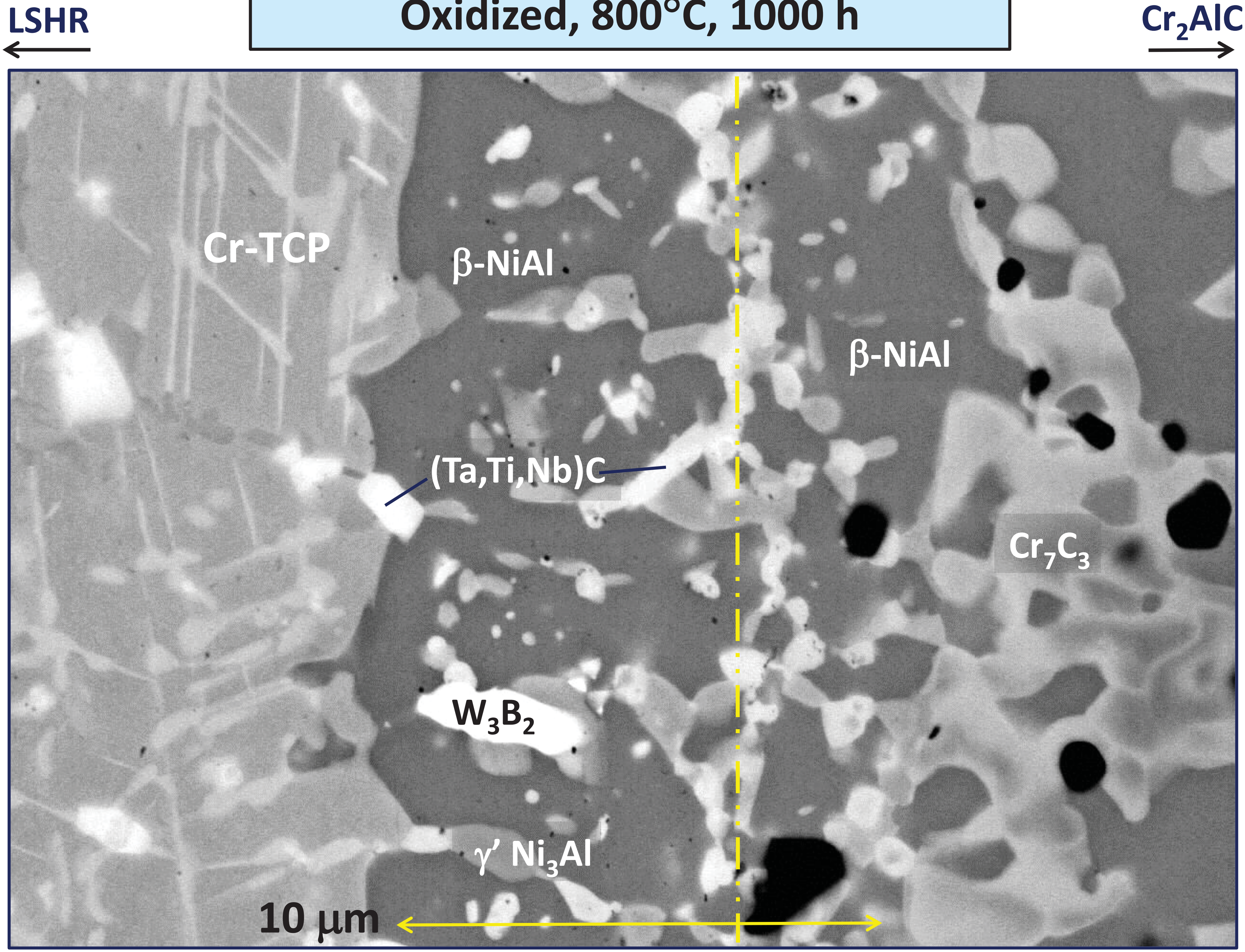
As-Hot Pressed Interface

LSHR ←

Cr_2AlC →

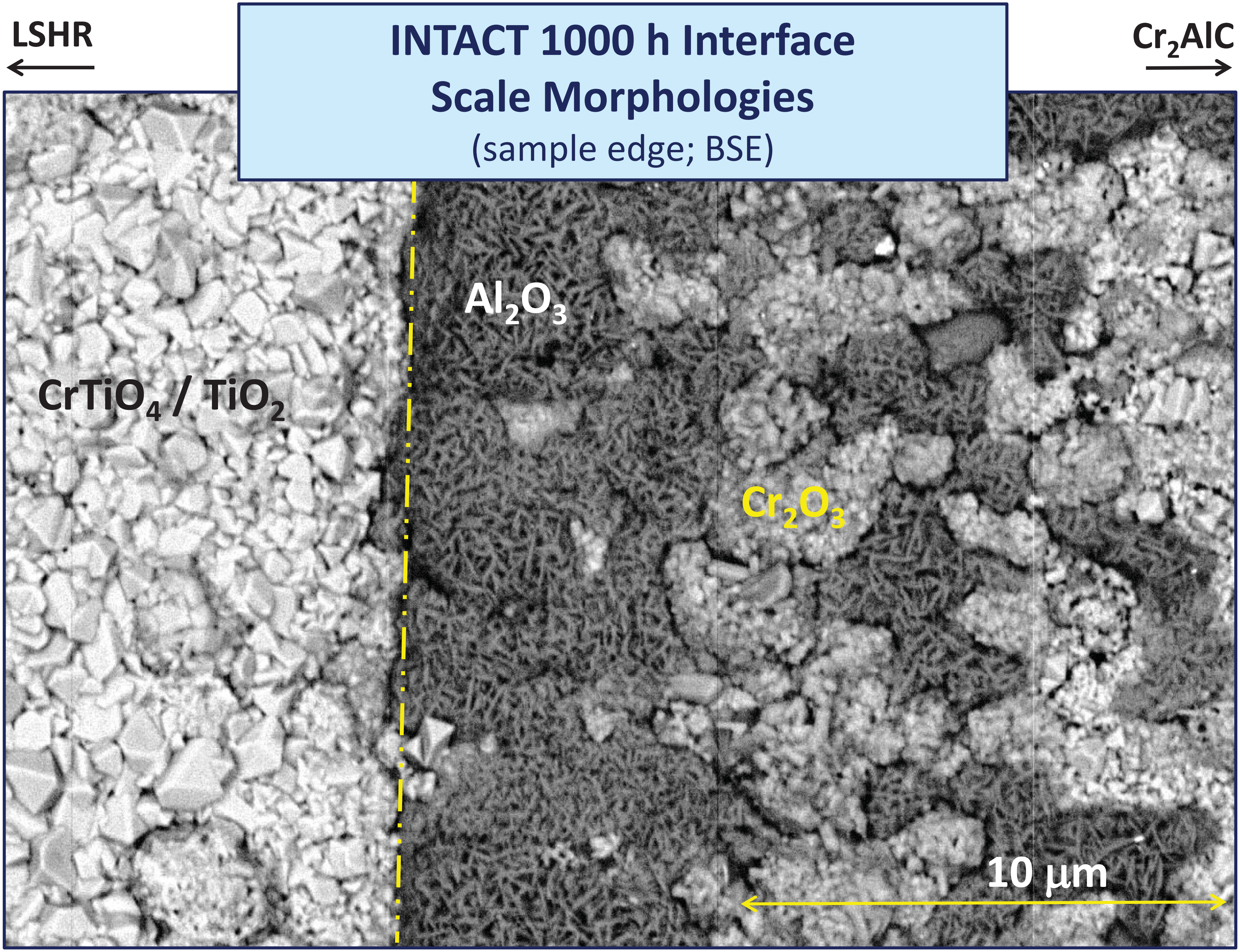


Oxidized, 800°C, 1000 h



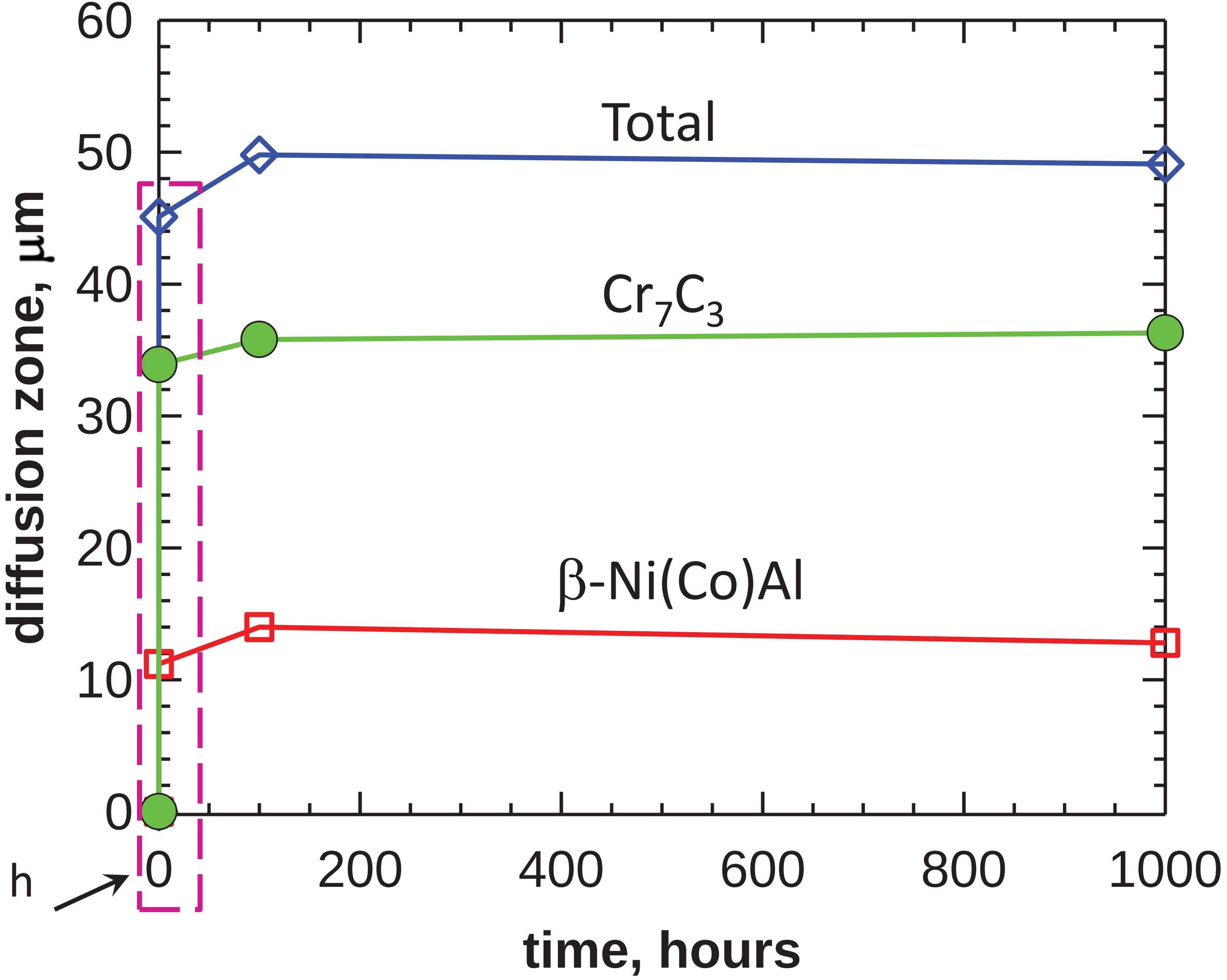
INTACT 1000 h Interface
Scale Morphologies

(sample edge; BSE)



Diffusion Zone Growth at 800^{o}C

LSHR Alloy/Cr_2AlC



1100°C, 2 h
Hot press

Purpose: Relate Al-MAX phases to coatings applications/turbine environment

5) LTHC Hot Corrosion Resistance

- LSHR Superalloy, **Cr_2AlC**, (Ti_2AlC)
- 625°-900°C furnace tests; air, $SO_2/O_2/Ar$
- Li,Mg-Na_2SO_4 eutectic salts (620°, 660°C)

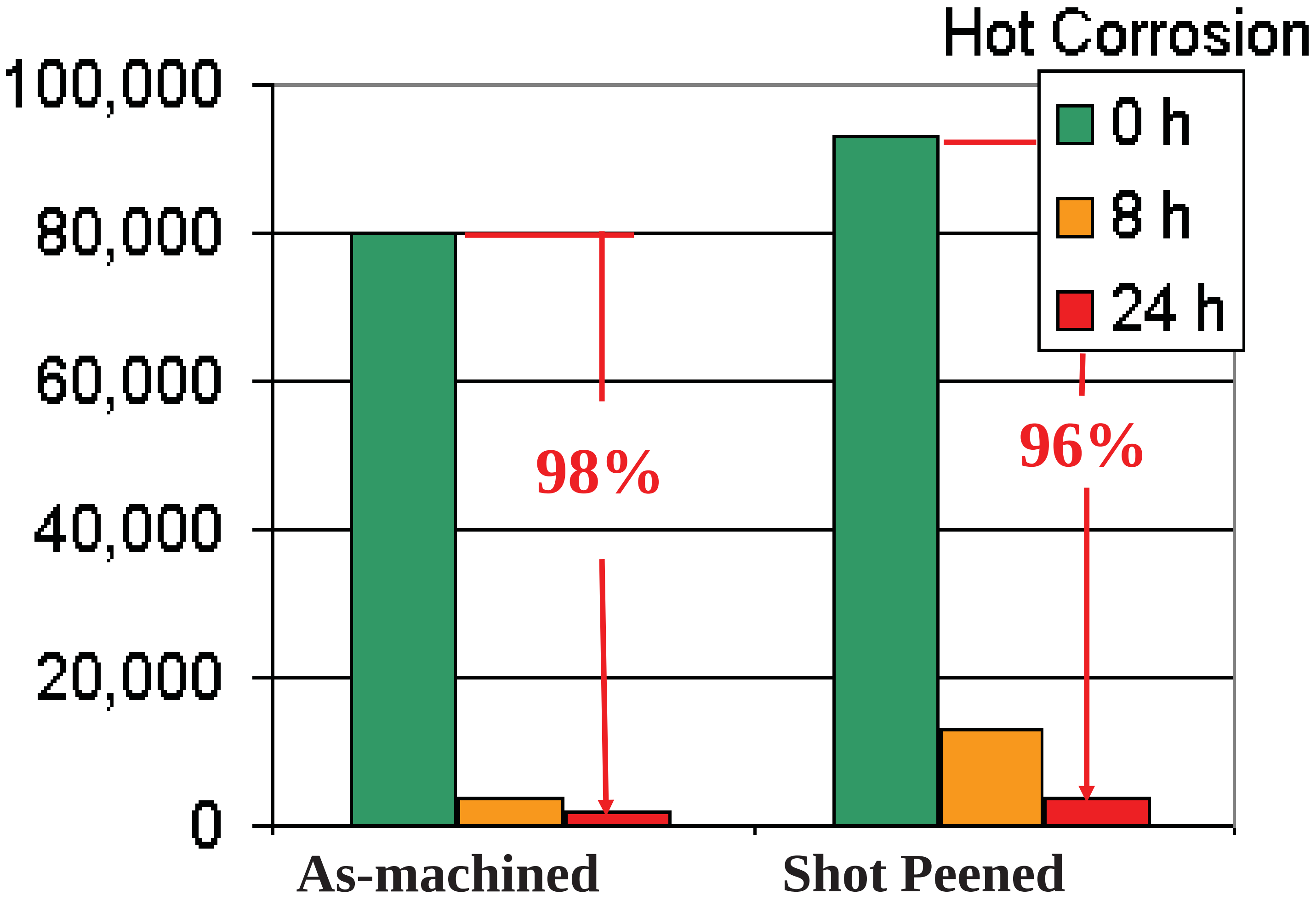
Hybrid Concepts with MAX Phases

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**	← Critical chemistry
Superalloy	**15**	**Substrates**	

704°C Disk Alloy Fatigue Life
Reduced by corrosion pits (and typical coatings)

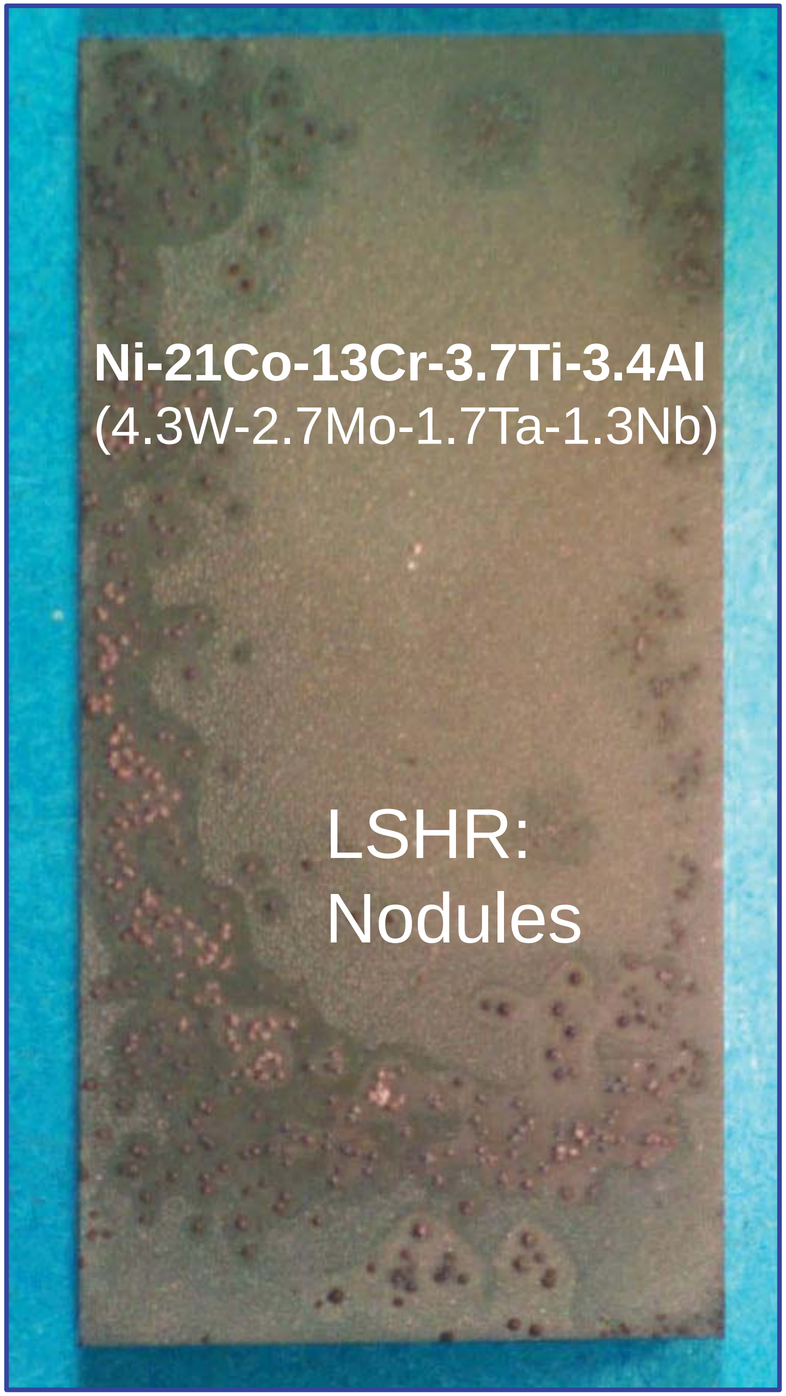


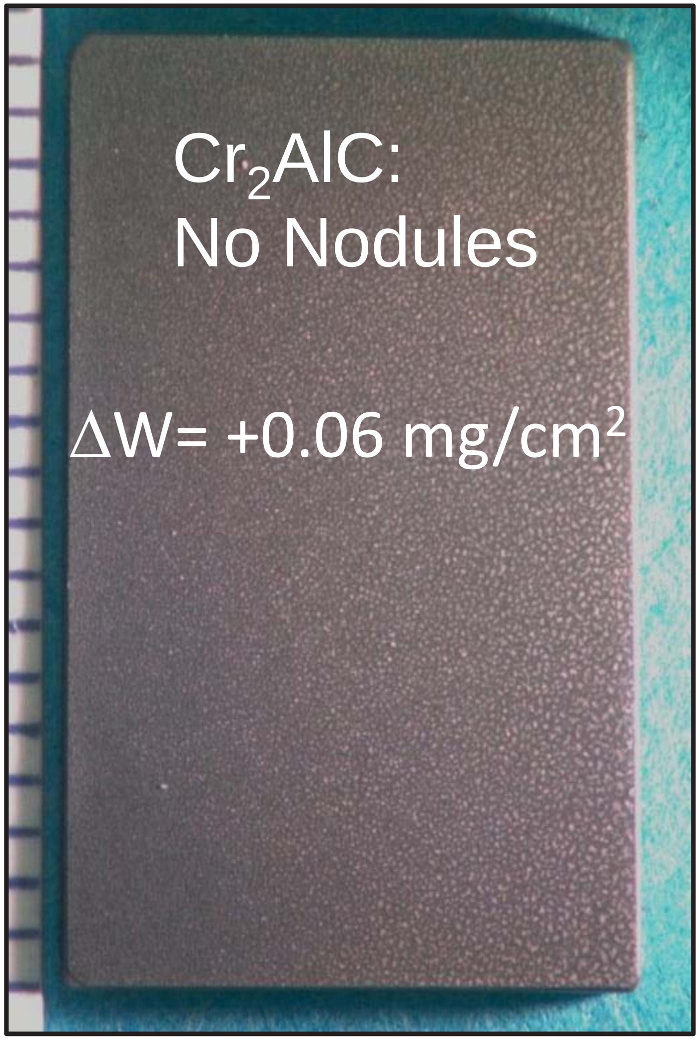
Ref: Gabb, et al., J. of Mat. Engineer. Perf. V. 19, 77, 2010.
“The Effects of Hot Corrosion Pits on the Fatigue Resistance of a Disk Superalloy,”

Pitting Suppressed in Cr_2AlC

1.0 mg/cm², 60 Na_2SO_4- 40 $MgSO_4$

5(0.1 % SO_2/O_2)/95Ar; 700°C, 24 h





Cr_2AlC, Ti_2AlC MAX Phases for Turbines

5) Minimal 700° C Type II LTHC of Cr_2AlC.

(Co,Ni)- Na low melting sulfates precluded.

4) Hybrid Diffusion Couples survive 1000 h at 800C.

β-NiAl-TaC-Cr_7C_3 interdiffusion zone

Little growth at 800°C.

3) YSZ TBCs show extensive furnace life @1200°C for Ti_2AlC

2) Ti_2AlC durable 1100-1300°C high pressure burner tests.

Cubic scale growth, volatile CO/CO_2 , (minimal water vapor losses ?)

1) Rate Control by Al_2O_3 Grain boundary diffusion:

$\delta D_{gb,O}$ MAX phases $\cong$ FeCrAl

Constant $\Pi = k_{p,i}G_i = 12\ \delta D_{gb,O}$

Protective Al_2O_3 with fast TiO_2 transients

Cubic kinetics due to grain growth

Cr_2AlC, Ti_2AlC MAX Phases for Turbines: Recap

1. Rate Control by Al_2O_3 Grain boundary diffusion.
2. Ti_2AlC durable in 1100-1300°C high pressure burner tests.
3. YSZ TBCs extensive furnace life @1200°C for Ti_2AlC.
4. Hybrid Diffusion Couples survive 1000 h at 800C.
5. Minimal 700° C Type II LTHC of Cr_2AlC

Intriguing alumina formers.
Coatings, complete systems need to be verified.