Karlsruhe Institute of Technology

Institut für Angewandte Materialien

Magnetron-sputtered Al-containing MAX phase carbide thin films and their application as oxidation-resistant coatings

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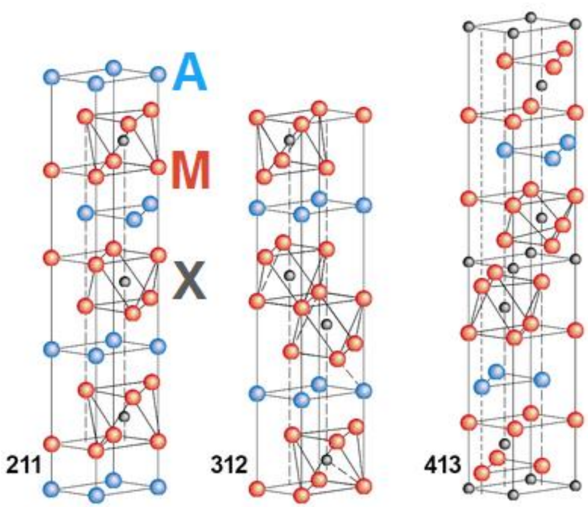
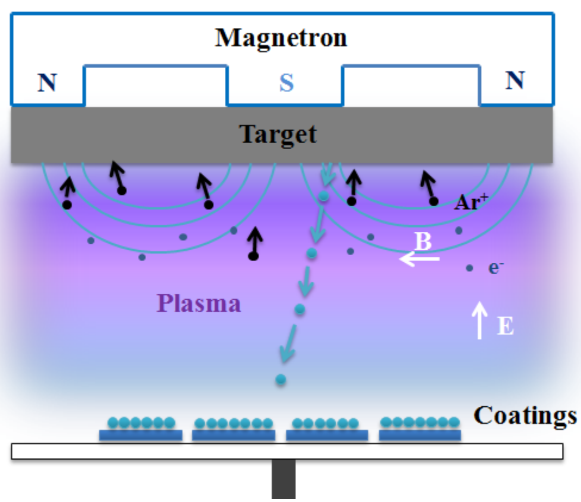
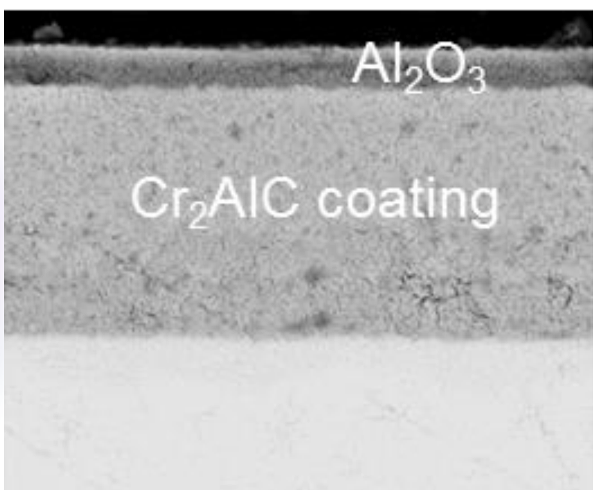


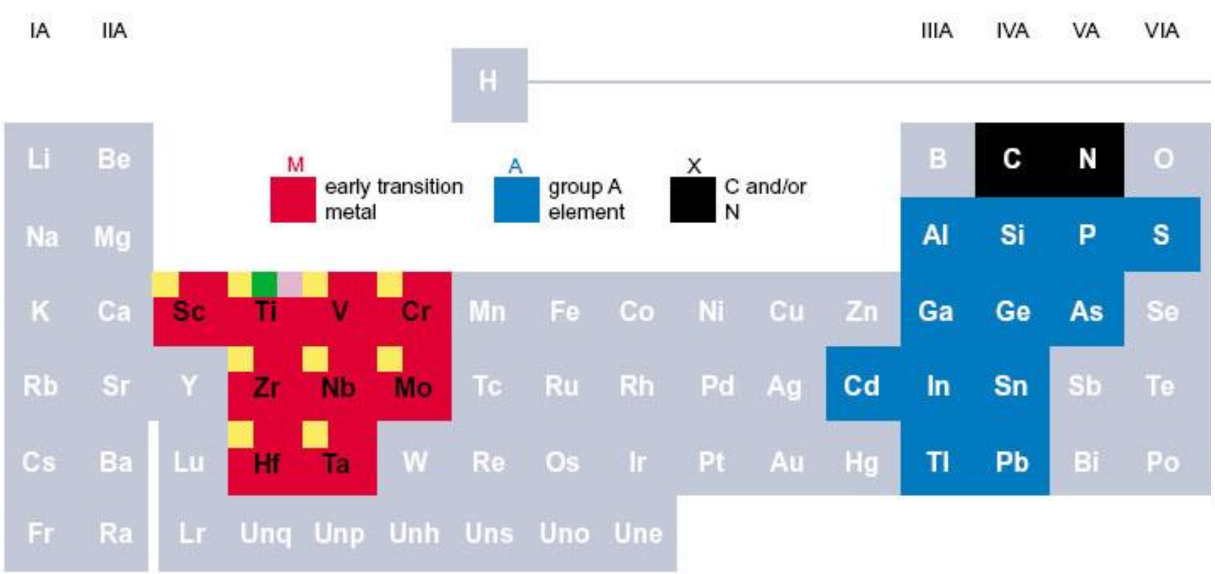


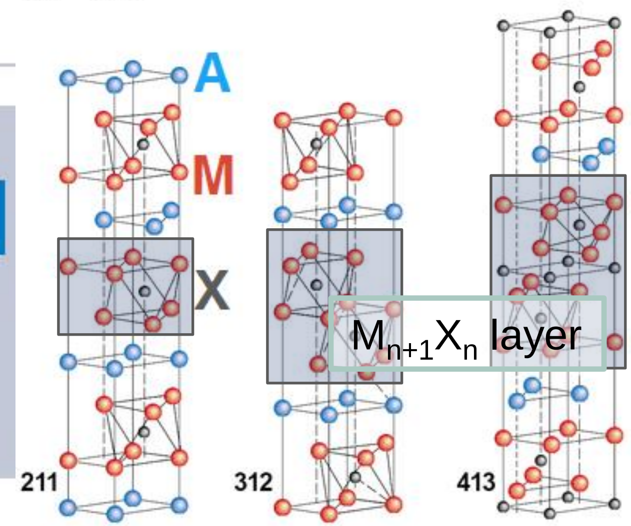


Introduction

- MAX phases: ternary carbide and nitride compounds described by the general formula $M_{n+1}AX_n$, where n typical is 1, 2, 3
- Nanolaminated crystal structure: M_6X octahedral interleaved with A layers

$M_{n+1}AX_n$ (MAX) phase





Nanolaminated crystal structure

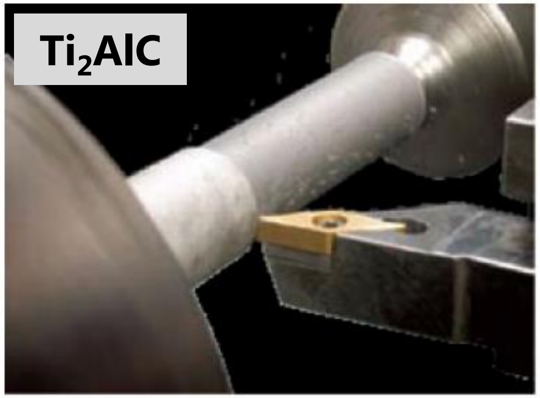
M-X: strong covalent-ionic bonds

M-A: weak metallic bonds

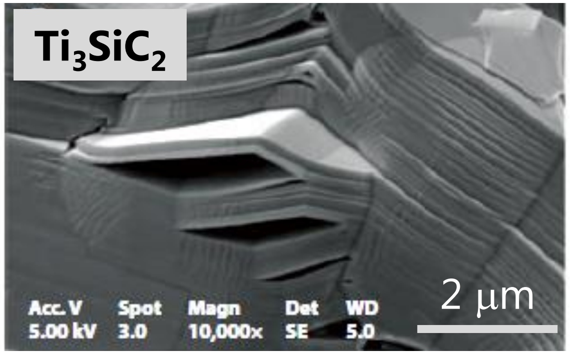
 M.W. Barsoum, MAX phases: properties of machinable ternary carbides and nitrides, John Wiley & Sons, 2013.

Introduction

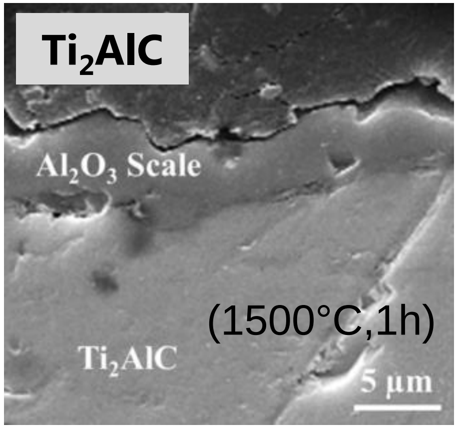
- Unique combination of physical, chemical, mechanical properties of both metals and ceramics



Machinability



Damage tolerance



Oxidation resistance

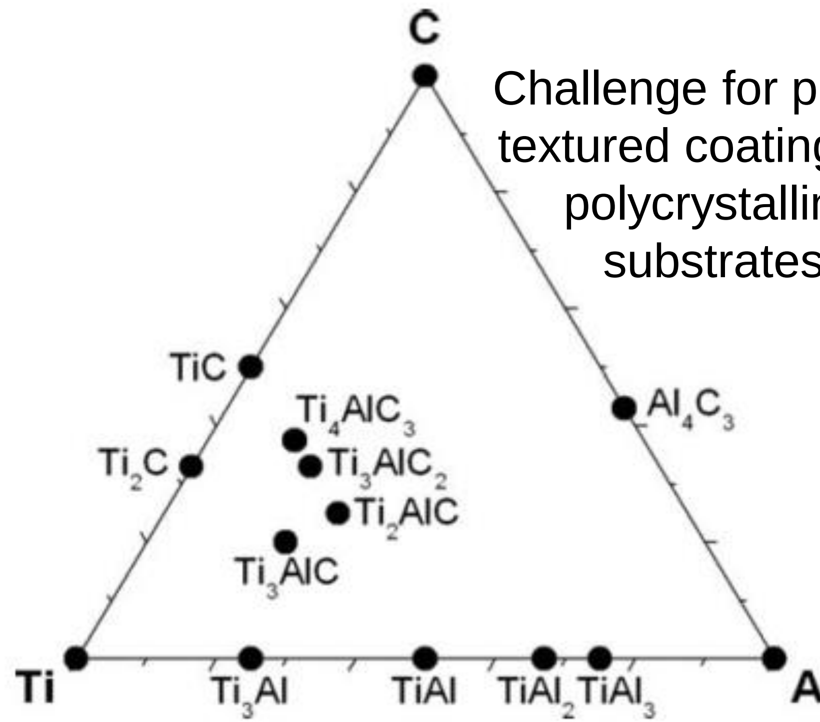
Low density | ***High melting/decomposition temperature*** | ***Thermal conductivity***

- Promising application prospects as structural materials and protective coatings in harsh environments

Motivation

Karlsruhe Institute of Technology

- **MAX phase coatings**
  - Spraying
    - High velocity oxy-fuel spray
    - Cold spraying
  - Physical vapor deposition (PVD)
    - Cathodic arc evaporation
    - Pulsed laser deposition
    - Magnetron sputtering
      - sputtering with 3 element sources
      - sputtering with compound targets
      - reactive sputtering
      - sputtering-solid state reactions



Challenge for pure, textured coatings on polycrystalline substrates

Impurities degrade the oxidation performance of MAX phases

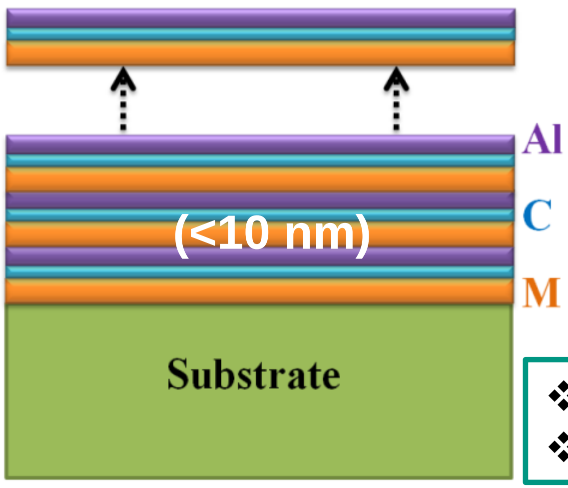
Magnetron sputtering and evaluation of Ti_2AlC, Cr_2AlC and Zr_2AlC as oxidation resistant coatings (phase-pure)

 M. Sonestedt et.al, J. Mater. Sci. 45 (2010) 2760–2769.

Experimental arrangement

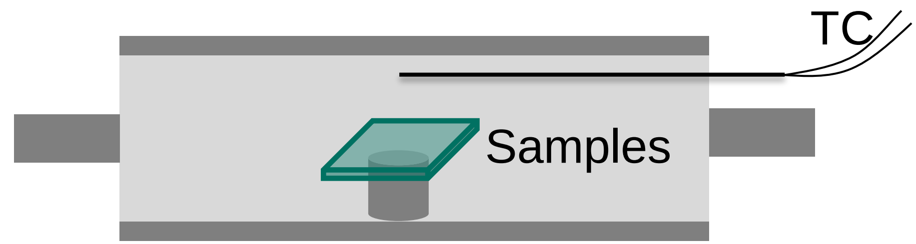
A two-step approach

Film design



Square: 10 × 10 mm

Ex-situ annealing



- ❖ Reduced diffusion length
- ❖ Precisely stoichiometry control

Magnetron Sputtering

Film thickness:

~ 3 µm on Al_2O_3, SiO_2/Si

~ 5.5 µm on Zircaloy-4 (~98wt%Zr)

(fuel claddings in nuclear reactors)

Annealing parameters

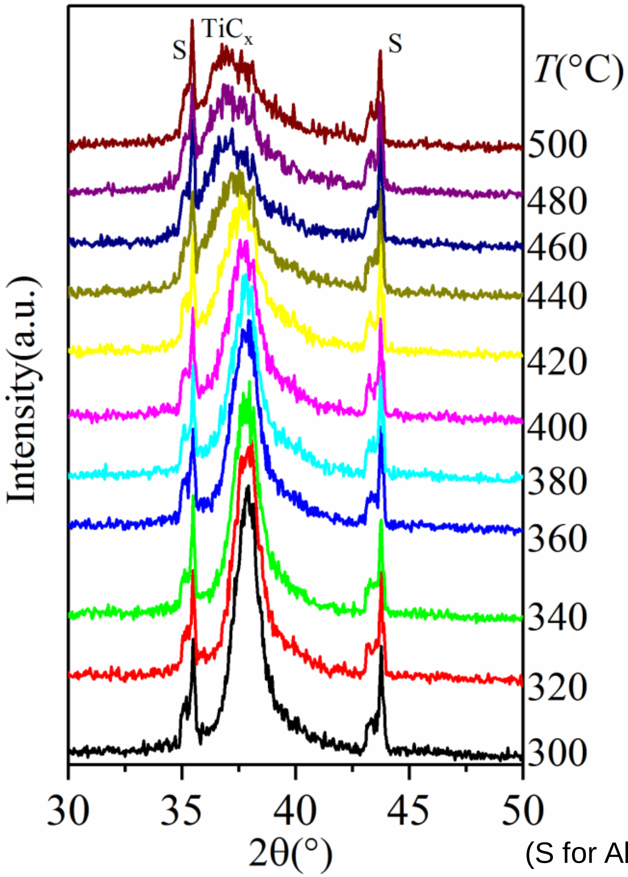
Annealing in pure Ar

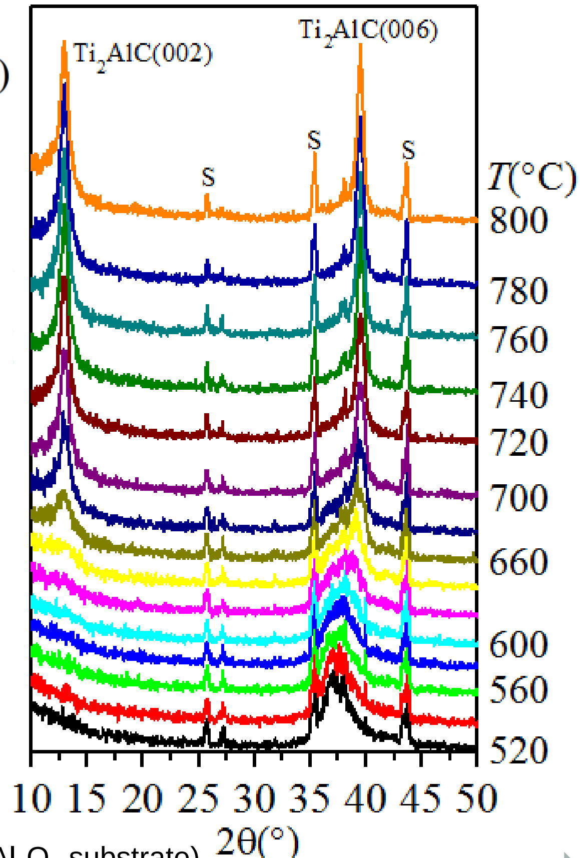
400°C-1200°C @10 min

Heating/cooling rate: 10 K/min

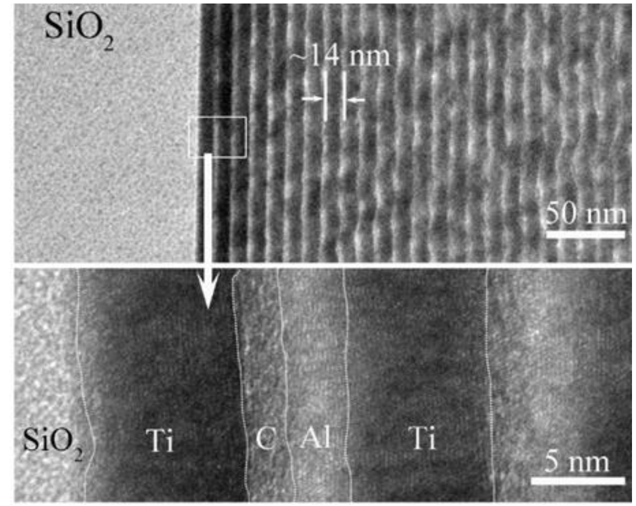
Synthesis of MAX phase coatings

- Ti_2AlC

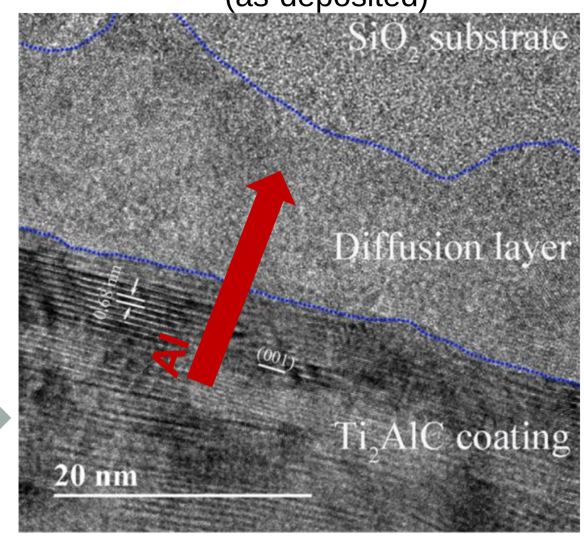




(S for Al_2O_3 substrate)



(as-deposited)

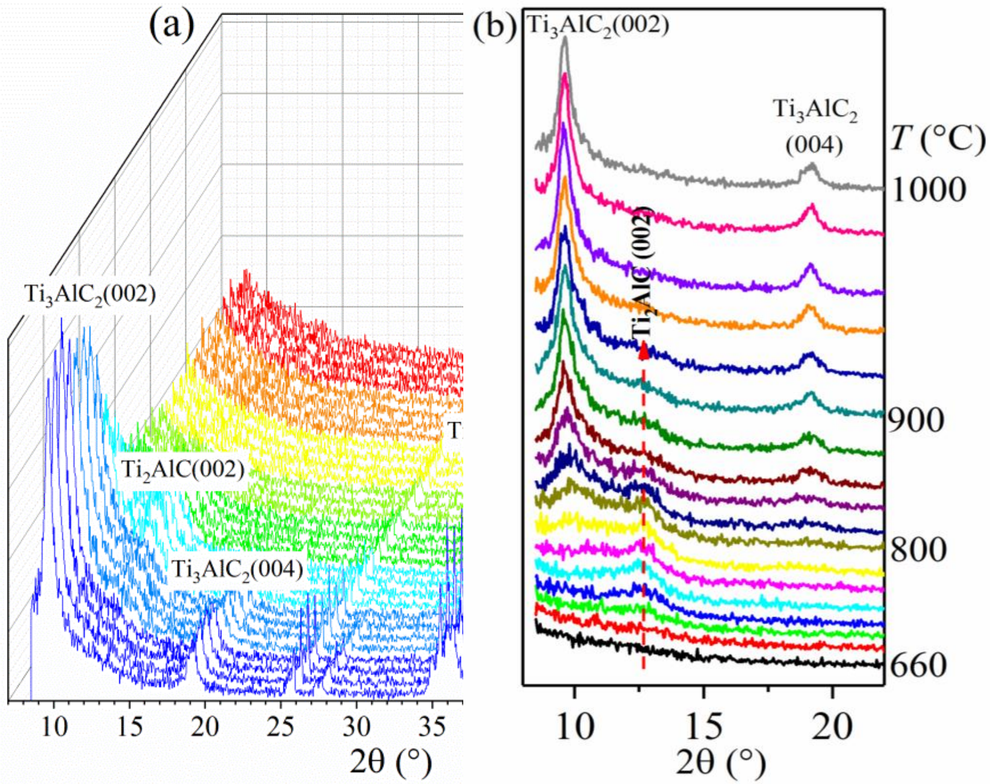


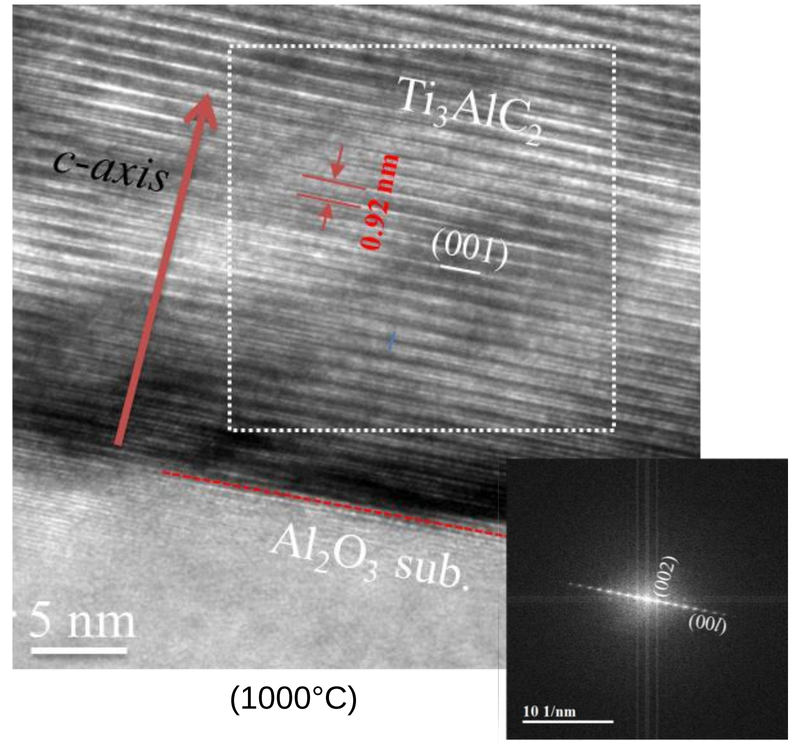
(800°C, 10min)

As-deposited	440°C	660°C	800°C
Ti/C/Al multilayers	$Ti(Al)C_x$	Ti_2AlC crystallization	Single-phase Ti_2AlC (00l) basal plane preferred orientation

Synthesis of MAX phase coatings

- Ti_3AlC_2



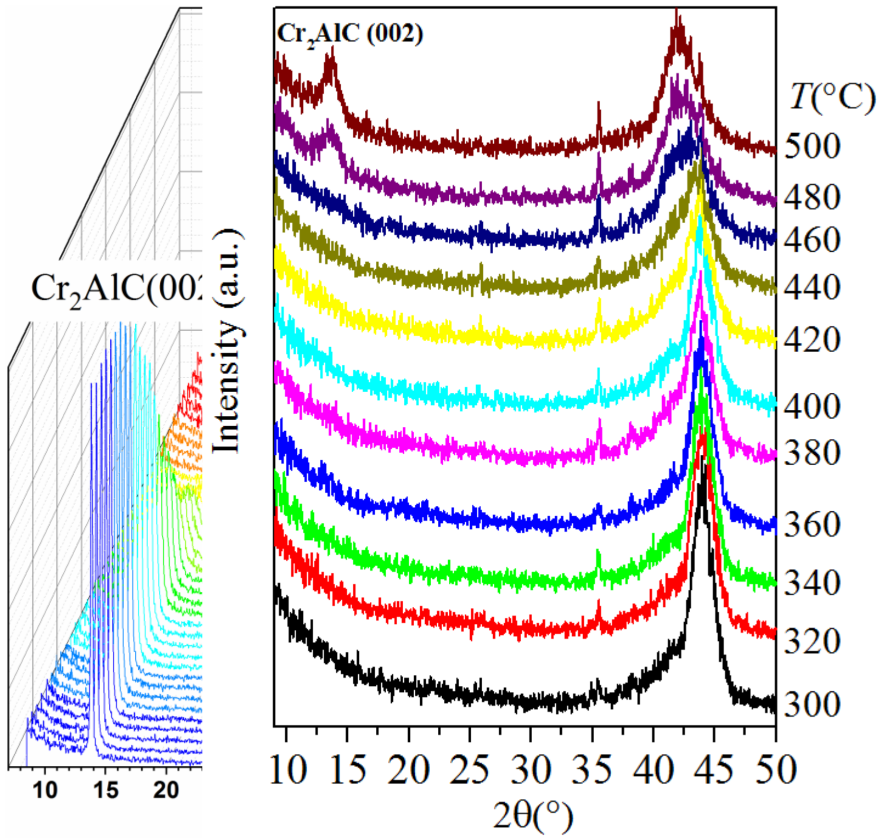


(1000°C)

As-deposited	440°C	660°C	800°C	920°C
Ti/C/Al multilayers	$Ti(Al)C_x$	Ti_2AlC crystallization	Ti_3AlC_2 crystallization	Single-phase Ti_3AlC_2 (00l) basal plane preferred orientation

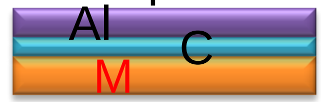
Synthesis of MAX phase coatings

- Cr_2AlC coating



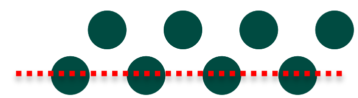
- Texture analysis

As-deposited

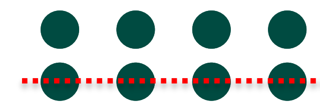


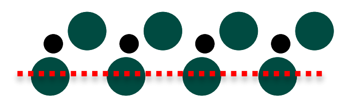
M layers: Textured growth

Ti, hexagonal, (002)



Cr, cubic, (110)





MAX phase (00l)

d-spacing misfit

$Ti(002)/Ti_2AlC(00l)$: 3.3%

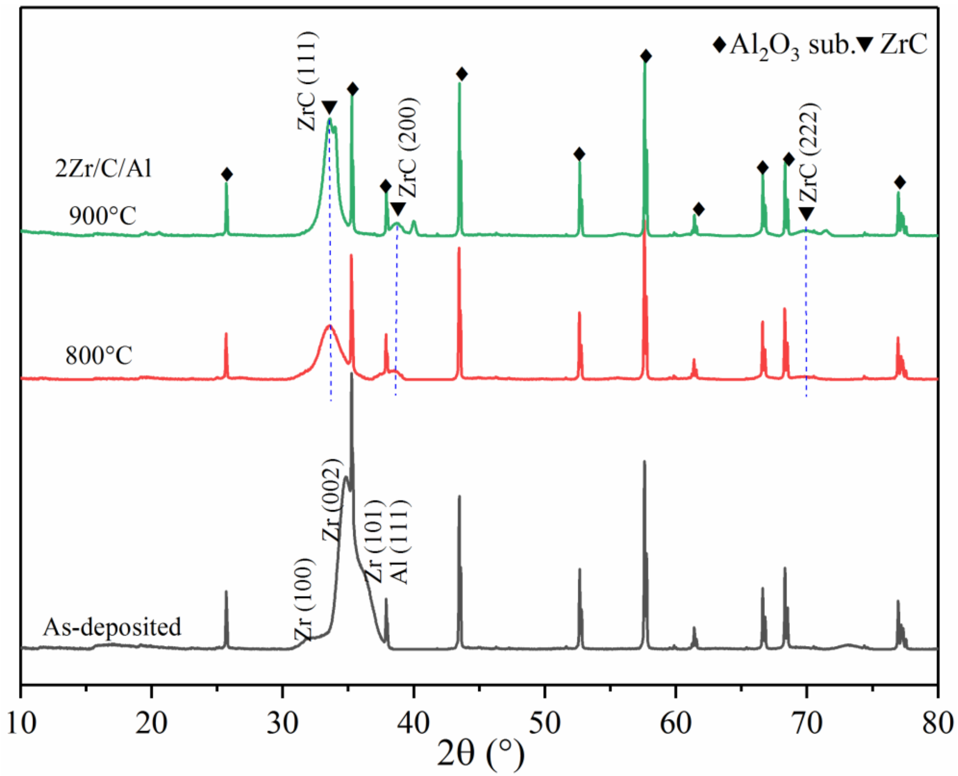
$Cr(110)/Cr_2AlC(00l)$: 4.5%

Crystallographic orientation relationship prompts textural growth of MAX phase grains.

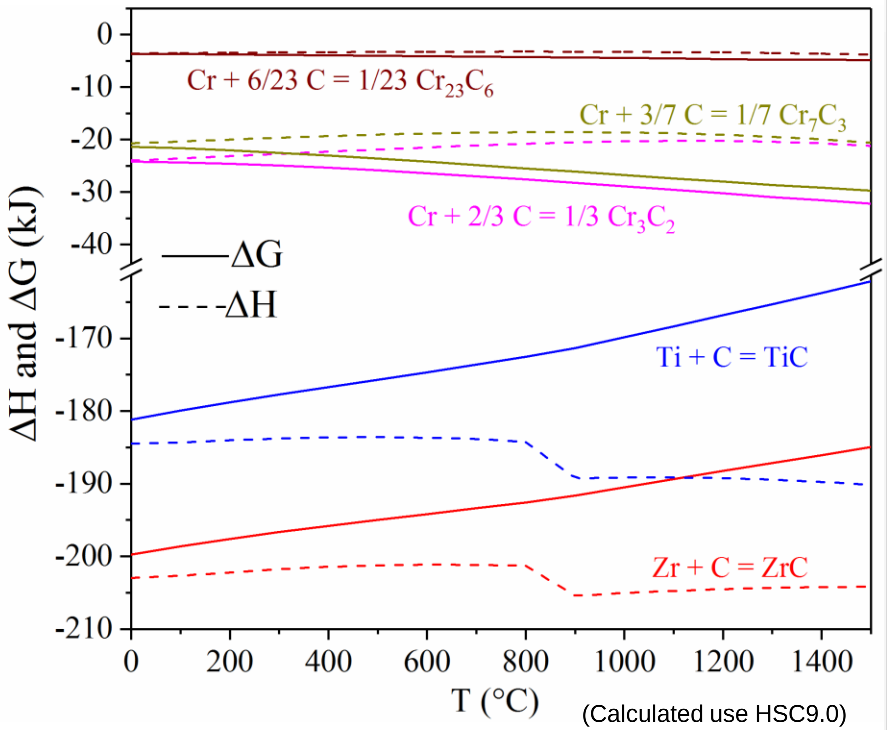
As-deposited	440°C	480°C	550°C
Cr/C/Al multilayers	$Cr(Al)C_x$	Cr_2AlC crystallization	Single-phase Cr_2AlC (00l) basal plane preferred orientation

Synthesis of MAX phase coatings

➢ Zr-C-Al coating



- Zr(Al)C carbide formation, rather than ternary nanolaminated MAX phase after 600-1200°C annealing.



(Calculated use HSC9.0)

➢ Thermodynamic metastable of Zr_2AlC

➢ Stability: ZrC > TiC > CrC_x

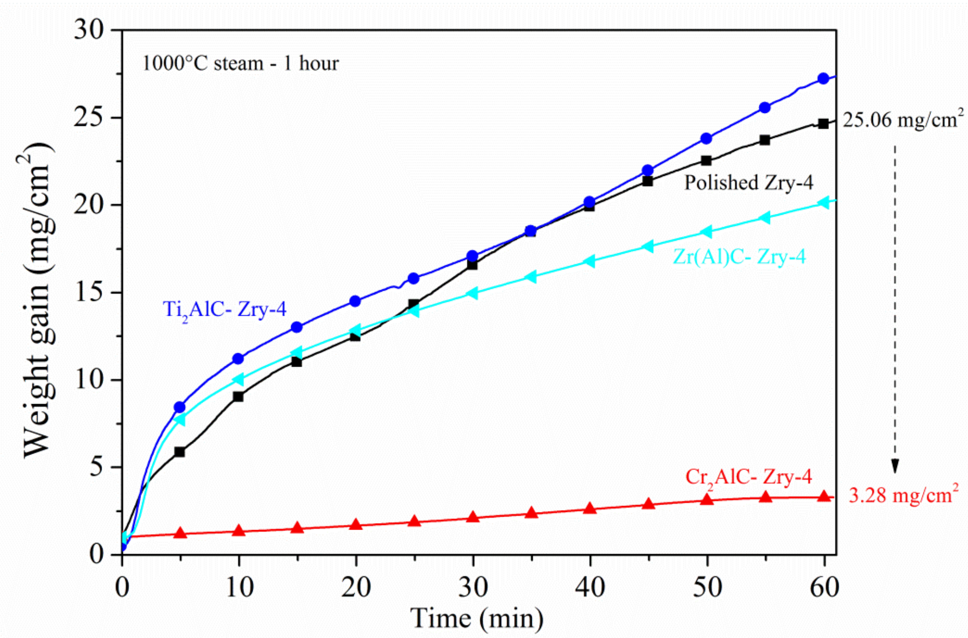
➢ Crystallization temperature of MAX phases

Ti_2AlC (~ 700°C) > Cr_2AlC (~ 500°C)

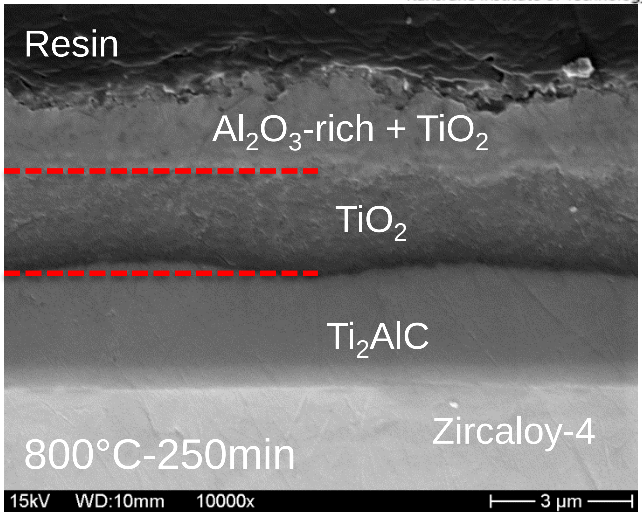
Ti_3AlC_2 (~ 800°C) > Ti_2AlC (~ 700°C)

Oxidation of coated Zircaloy-4

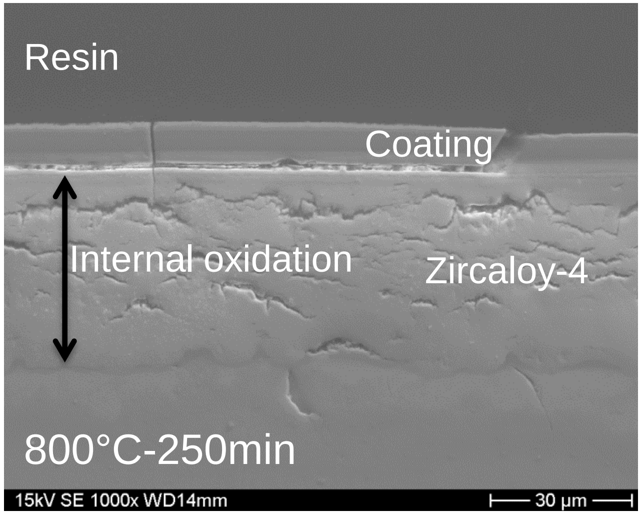
- Isothermal 1000°C 60 min in steam



(Annealing: 800°C for Ti_2AlC, 550°C for Cr_2AlC, 600°C for Zr(Al)C)



Ti_2AlC-Zircaloy 4

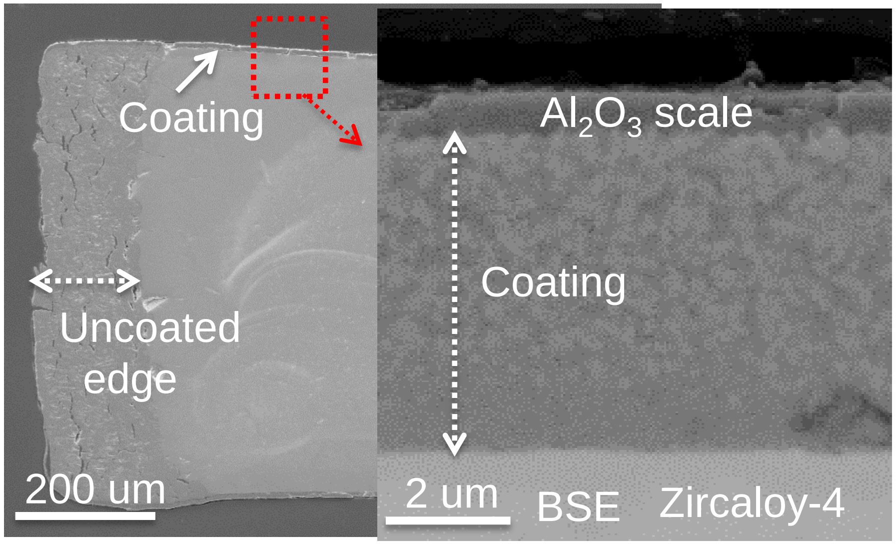


Zr(Al)C-Zircaloy 4

- Significant spallation of Ti_2AlC and Zr(Al)C coatings after oxidation at 1000°C.
- Formation of Al_2O_3-rich layer with TiO_2 or ZrO_2 layer beneath at low temperatures, rather than dense alumina layer.

Oxidation of coated Zircaloy-4

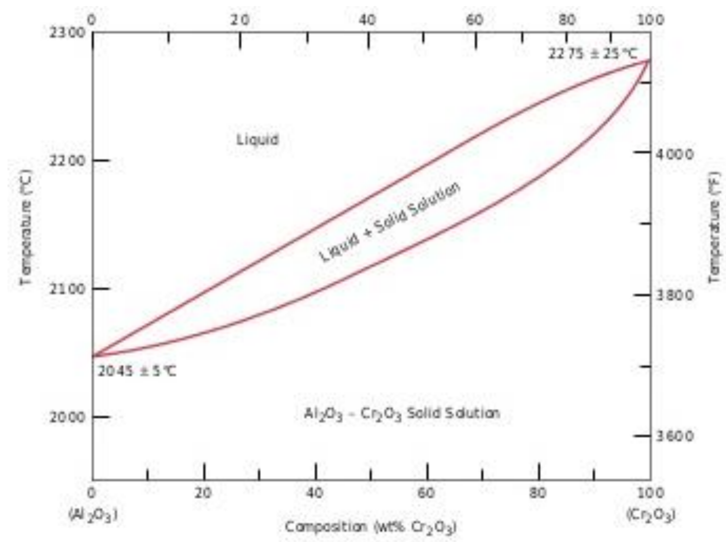
➢ Isothermal 1000°C 60 min in steam



Cr_2AlC-Zircaloy 4

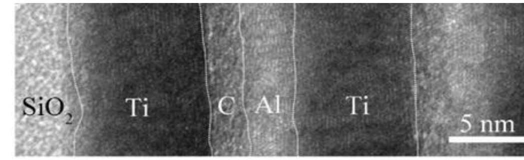
- Growth of dense alumina scale during high-temperature oxidation of Cr_2AlC coating.
- High adherence without spallation.

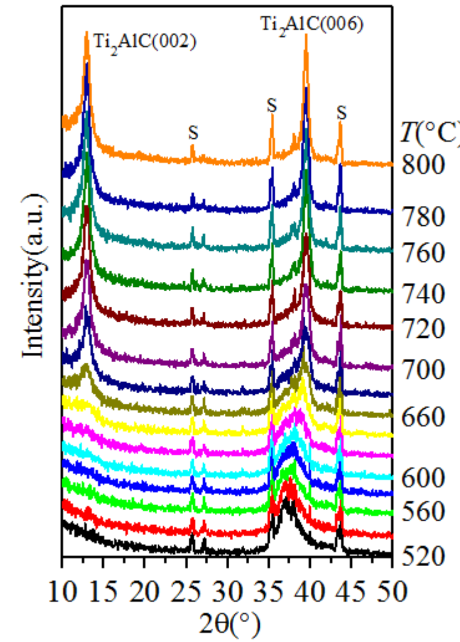
- Low protective effect of TiO_2 and ZrO_2 scale
- Phase transformation of TiO_2 and ZrO_2, prone to cracking
  - TiO_2: anatase, rutile
  - ZrO_2: monoclinic, tetragonal, cubic
- Cr_2O_3 and α-Al_2O_3: similar crystal structure, completely miscible
  - Cr_2O_3 as nucleation sites for α-Al_2O_3

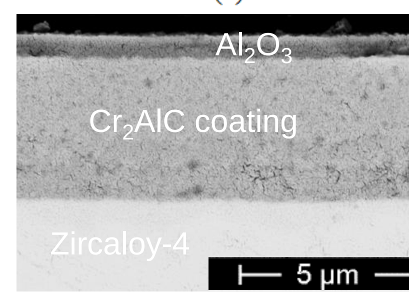


Conclusions

- A two-step approach to synthesize MAX phase coatings
  - Nanoscale multilayer stacks+ thermal annealing in Ar
  - Pure Ti_2AlC(800°C), Ti_3AlC_2 (900°C) and Cr_2AlC(550°C) MAX phases obtained with textured structure independent of substrates
  - Zr(Al)C formation in the system Zr-C-Al
- Oxidation of coated Zircaloy-4
  - Growth of Al_2O_3-rich layer with TiO_2 or ZrO_2 layer beneath for Ti_2AlC and Zr(Al)C coatings with low oxidation resistance
  - Growth of a dense Al_2O_3 scale for Cr_2AlC coatings with excellent HT oxidation resistance
- Phase-pure and highly textured MAX phase coatings can offer benefits for some specific applications







Many thanks to:

High-temperature chemistry group, Thin film group

China Scholarship Council (CSC)

Thanks for your attention !