SiC-기반 ATF 개발 현황

2022. 5. 18

김대종, 이현근, 박지연, 김원주

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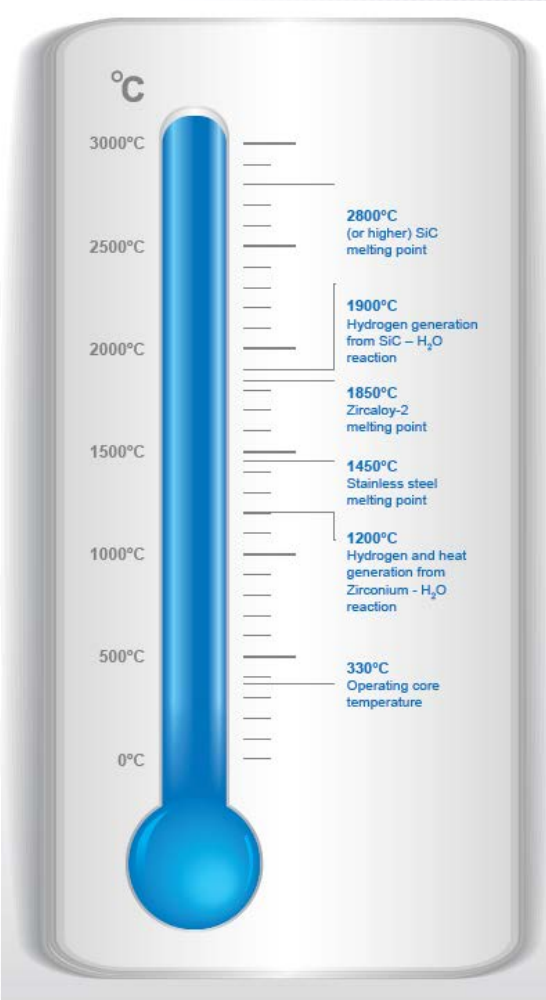
Longer Term Accident Tolerant Fuel Technology

- **U.S. NRC considers longer term accident tolerant fuel concepts**
  - Uranium nitride pellet
  - Extruded metallic fuel
  - **Silicon carbide cladding**
- **Silicon carbide cladding**
  - **The potential benefits** of SiC cladding
    - **Maintains structural integrity at high temperatures**, even beyond the temperature uranium oxide melting
    - **Improved high-temperature steam oxidation**, longer coping times and less hydrogen generation under DBA and Severe Accident conditions
  - **The potential challenges** that need to be overcome
    - Increased permeability of fission gases
    - Corrosion during normal reactor operation
    - Lack of ductility may be a problem for plant power changes, expected operational occurrences
    - Ability to be manufactured



ERI/NRC Final Report, Review of ATF Concepts, ERI/NRC 20-209, 2020

US Industry-led ATF Development

DOE-sponsored, Industry-led Development of ATF Concepts

Framatome

- 'PROtect'
  - *Cr-coated M5 cladding*
  - *Cr Doped UO_2*
- 'Long term'
  - *SiC cladding*

SiC cladding for PWR
: 3 layer system (Zr-SiC-Cr)
SiC channel boxes for BWR

General Electric

- 'ARMOR'
  - *Coated Zr cladding*
- 'Long term'
  - *Iron-based cladding (FeCrAl)*
  - *ODS variants for improved strength*

GE imagination at work

SiC channel boxes for BWR

Westinghouse

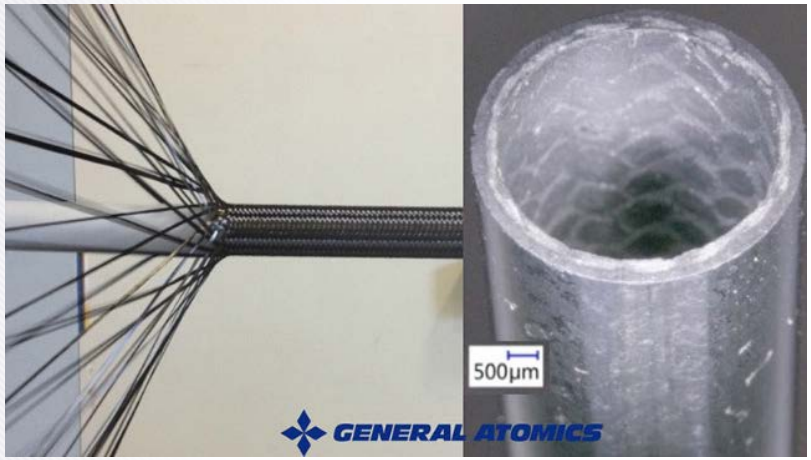
- 'EnCore'
  - *Cr-coated Zirlo/AXIOM cladding*
  - *ADOPT Fuel Pellet*
- 'Long term'
  - *SiC cladding*
  - *High density fuel pellets*

SiC cladding for PWR

D. Wachs, et. al, NWTRB meeting, 2021

Fabrication of Full-length SiC Cladding

- **Full length fiber preform and CVI/CVD facility for SiC cladding processing (General Atomic)**



SiC cladding tubes(1m)

Fiber preformimg

CVD/CVI facility

C.P. Deck, et. al., ANS Transaction, 2019

Irradiation Test Program for SiC Cladding

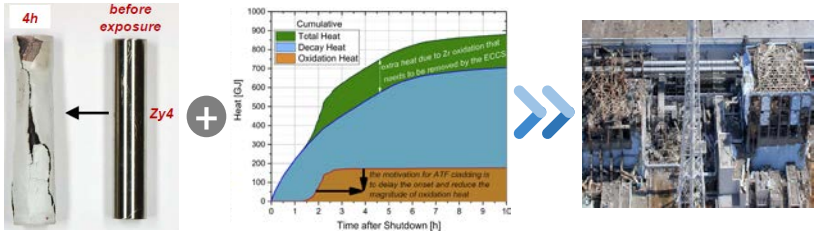
Irradiation Campaign	Irradiation Duration (Discharge Burnup)	Irradiation Condition	Planned PIE, On-line Measurement, and Irradiation Data Acquirement
MITR-1	2013-2014 (0.8 dpa)	PWR, cladding only	2015: corrosion and swelling for tube samples
MITR-2	2015-2016 (0.8 dpa)	PWR, cladding only	2016: corrosion and swelling for joining and tube samples
HFIR-SiC	2016 (~2 dpa)	Dry capsule, representative thermal gradient	2018: PIE for microstructure and hermeticity
MITR-3	2017 (0.8 dpa)	PWR, cladding only	2018: corrosion and swelling for sealed tubes
MITR-4	2019-2020 (0.8 dpa)	PWR, cladding only	Corrosion and qualification tests
ATF-2 irradiation in ATR	2019-2023 (30, 60 MWD/kgU)	PWR with ADOPT first and later U_3Si_2 fuel	2020: Pool-side PIE 2021: PIE for 20 MWD/kgU 2024: PIE for 45 MWD/kgU
IL Travatore BR-2	2019-2020 (2 dpa)	PWR Corrosion	2020: PIE
Halden Replacement	2019-2023 (45 MWD/kgU)	PWR Thermal conditions with U_3Si_2 fuel	2020: Pool-side PIE 2022: PIE for 30 MWD/kgU 2025: PIE for 60 MWD/kgU
2022 LTA	2022-2027 (60 MWD/kgU)	PWR with U_3Si_2 fuel in SiC cladding and coated Zr cladding	2023: Pool-side PIE and hot-cell PIE for 1st cycle fuel 2025: 2nd cycle fuel 2027: 3rd cycle fuel

P. Xu, et. al., ICACC Conference, 2019

국내 사고저항성 SiC 복합체 피복관 개발

경수로 핵연료 피복관 기술적 한계

지르코늄 합금 부식/H_2 ➔ 중대사고



수소발생 → 열방출 → 중대사고

해결방안

사고저항성 핵연료 피복관 ➔ 부식 저항성 향상

- 단기 : 기존 지르코늄 합금 + 사고저항성 코팅
  - 장점: 검증된 소재. 적용이 용이함
  - 단점: 중대사고시 지르코늄의 잠재적 위험 존재, 부족한 사고저항 특성
- 장기 : SiC 복합체 (I) + 내환경 코팅 (II)
  - 장점: 월등히 우수한 사고 환경 구조적 건전성 및 부식저항성
  - 단점: 미세균열에 의한 방사성 물질 담지능 저하, 가동환경 부식

SiC 복합체 기반 사고저항성 핵연료 피복관 개발

초고온 내환경 SiC 복합체 제조 기술 개발

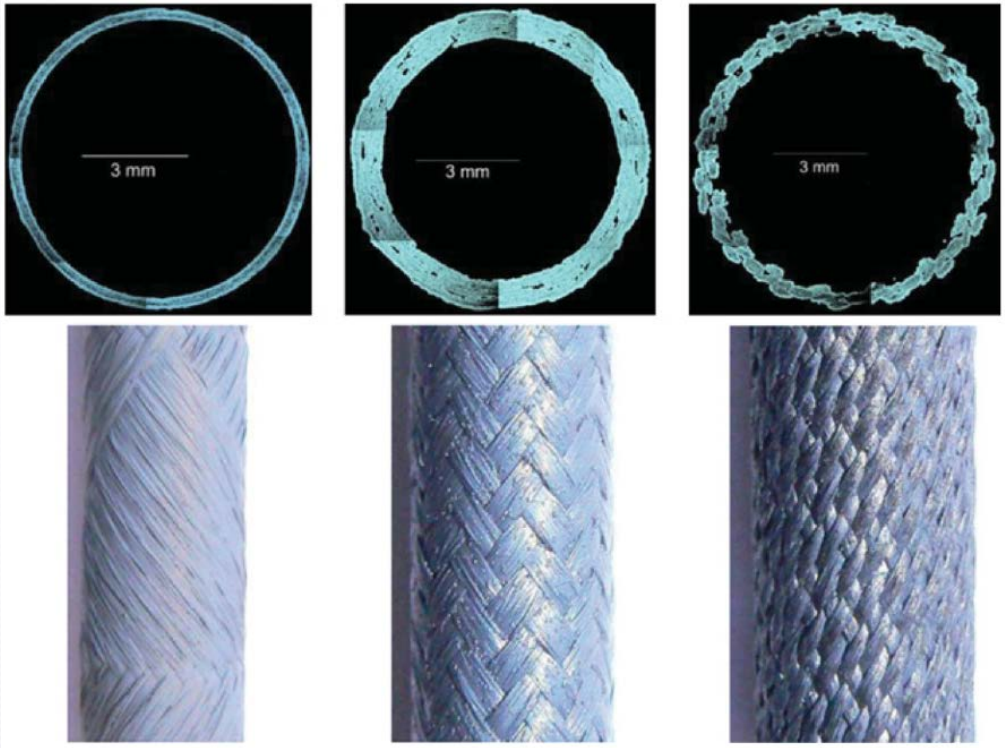
- 고밀도 SiC 복합체 제조 기술 개발을 통한 강도, 열전도도 향상
- 방사성 물질 담지능 향상 + 가동환경 부식성 향상을 위한 내환경코팅 기술 개발
- 내환경 특성이 개선된 접합 소재 및 공정 개발

복합체 피복관 성능 평가

- 가동환경 및 사고환경 성능, 중성자 조사 특성 평가

Fabrication of SiC Cladding

- **Fiber volume fraction in SiC_f/SiC layer**
  - Filament winding > 2D braiding > 3D braiding



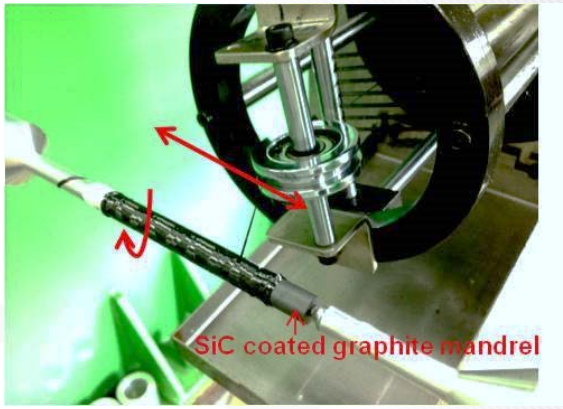
Filament winding (Fiber volume fraction: high)

2D braiding (medium)

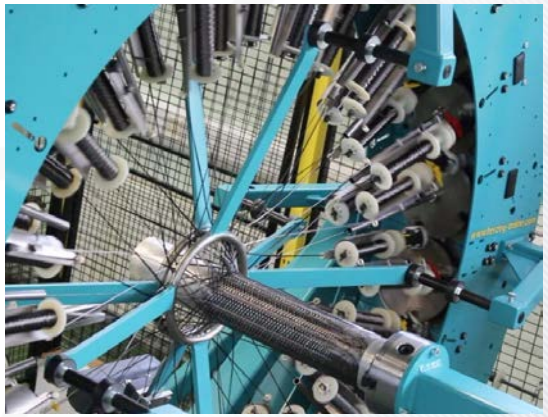
3D braiding (low)

KAERI, CEA

GA, CEA



Filament winding (KAERI)

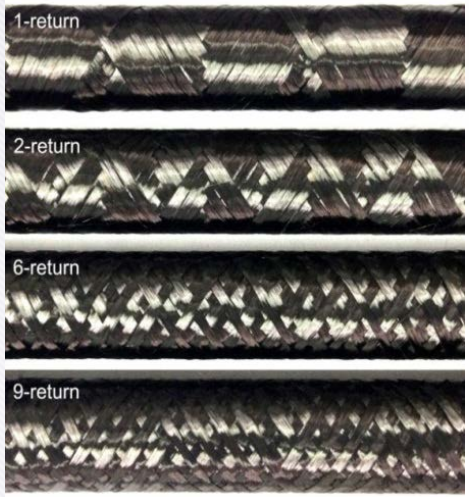


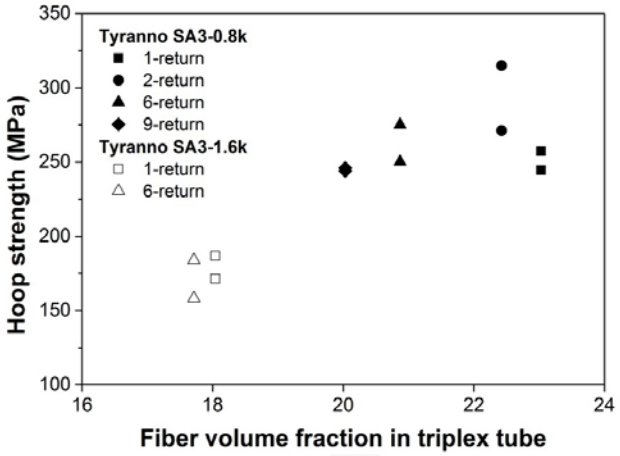
2D braiding

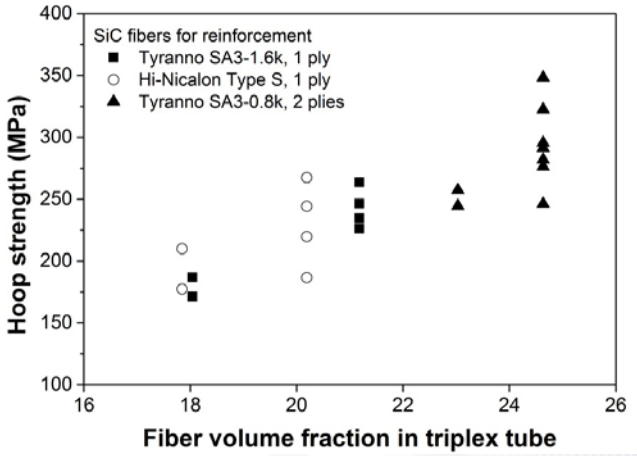
C. Sauder, et. al., Modeling and Technology, 2014

Fabrication of SiC Cladding

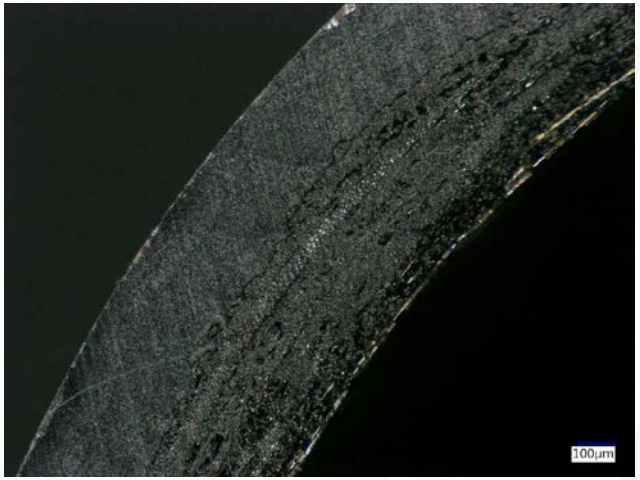
- **Optimization of fiber architecture**

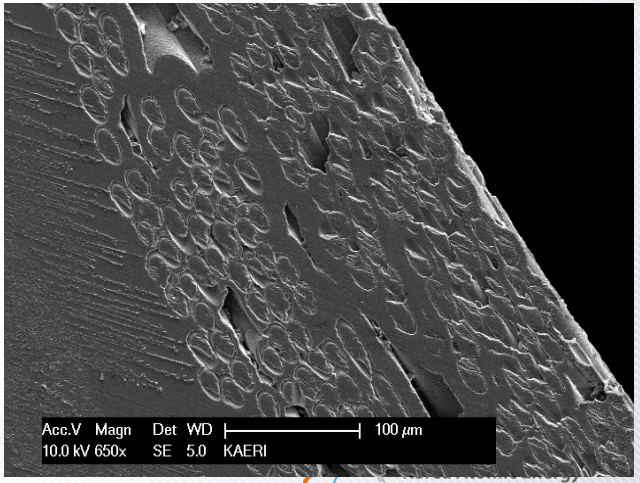






- **Fabrication of duplex SiC cladding**

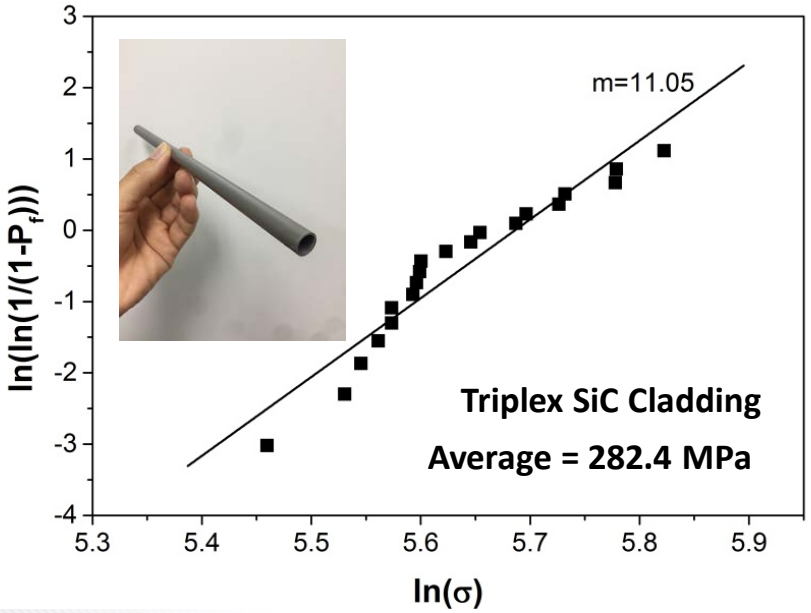


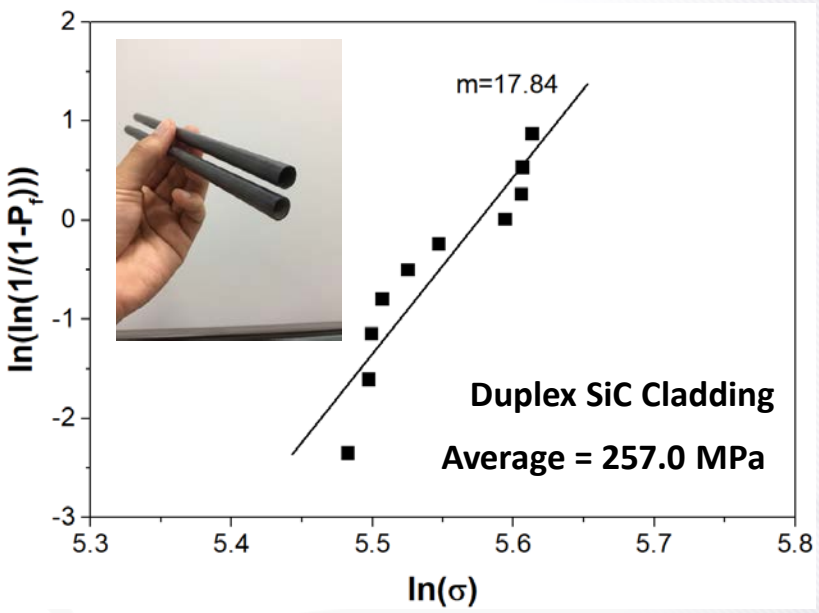


D. Kim, et. al., Journal of Nuclear Materials, 2015

Mechanical Strength of SiC Cladding

- **Triplex and duplex SiC composite cladding ((CVD SiC) - SiC_f/SiC - CVD SiC)**



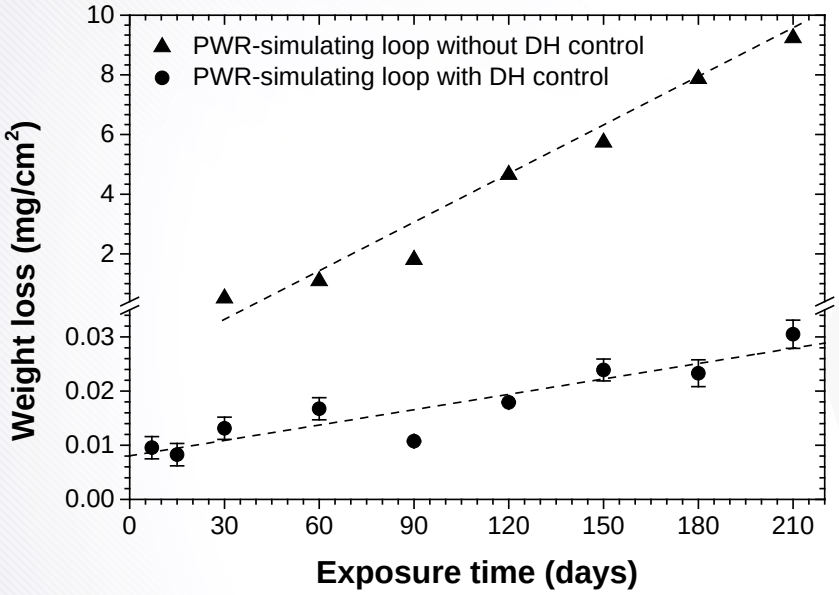


	Test Method	Strength, MPa	Fiber Architecture	
Full SiC/SiC	C-ring	209	Braiding, Axial biased	GA
Full SiC/SiC	C-ring	331	Braiding, Hoop biased	GA
Full SiC/SiC	Internal pressurization	303	Filament winding+Braiding	CEA
Duplex: SiC(inside) and SiC/SiC	Expanding plug	152, 231	Braiding, Axial biased	GA
Duplex: SiC/SiC(inside) and SiC	Expanding plug	271, 332	Braiding, Hoop biased	GA

T. Koyanagi, et. al., ORNL Technical Report, ORNL/TM-2017/385

Hydrothermal Corrosion of CVD SiC

- **Dissolution of SiC in a PWR coolant water condition**

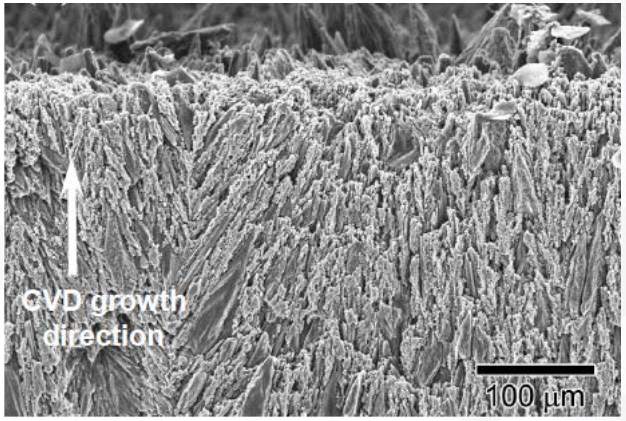


$$SiC + 2H_2O \rightarrow SiO_2 + CH_4$$
$$SiC + 3H_2O \rightarrow SiO_2 + CO + 3H_2$$
$$SiC + 4H_2O \rightarrow SiO_2 + CO_2 + 4H_2$$
$$SiC + 4H_2O \rightarrow Si(OH)_4 + CH_4$$

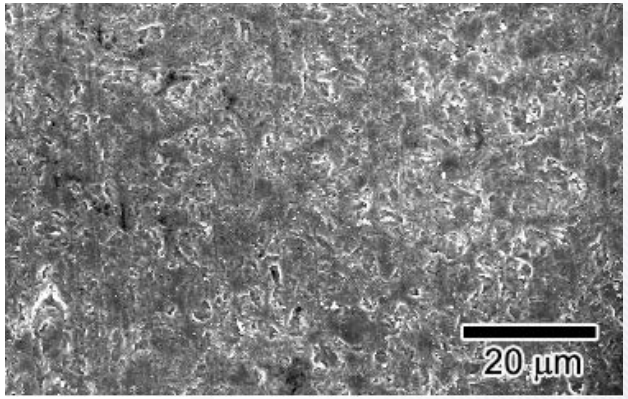
Rate-limiting step

and

$$SiO_2 + H_2O \rightarrow HSiO_3^- + H^+ \rightarrow SiO_3^{2-} + 2H^+$$
$$Si(OH)_4 \rightarrow H_3SiO_4^- + H^+ \rightarrow H_2SiO_4^{2-} + 2H^+$$



DH uncontrolled water

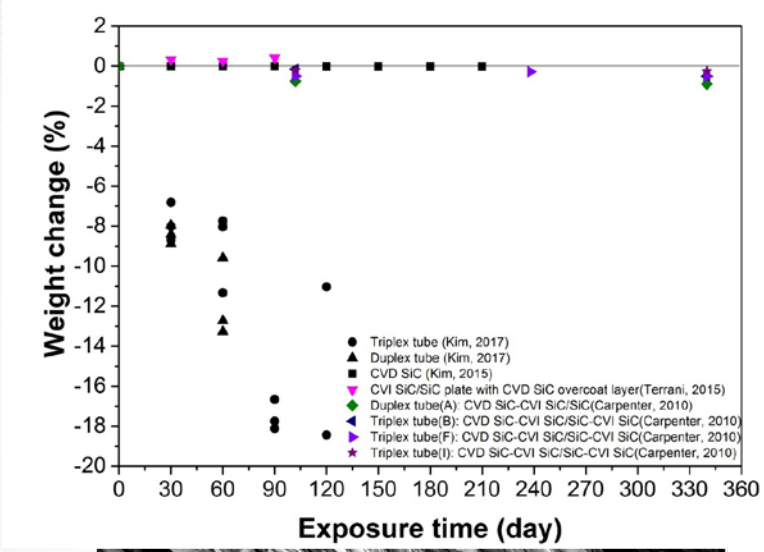


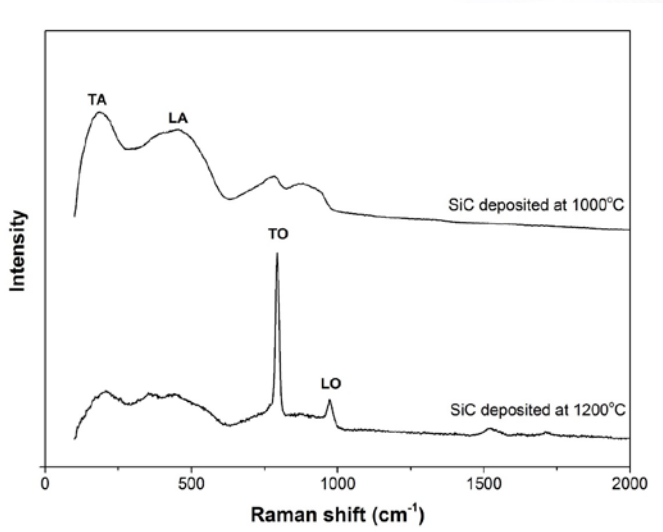
DH controlled water

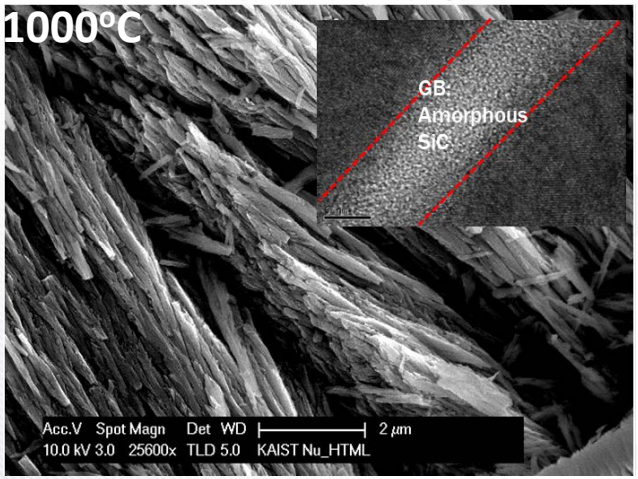
J.-Y. Park, et. al., Journal of Nuclear Materials, 2013, D. Kim, et. al., Corrosion Science, 2015

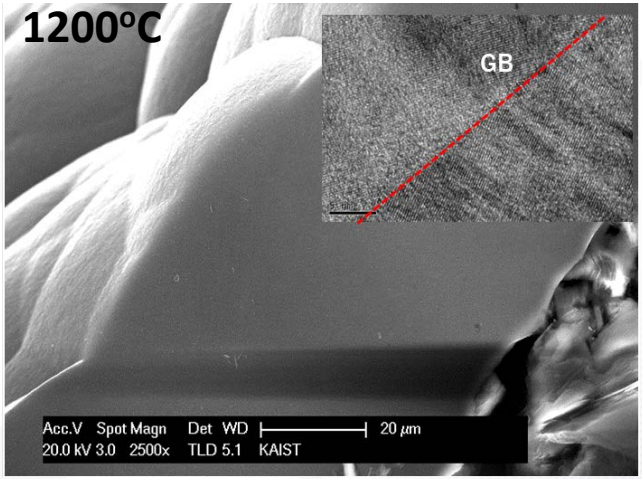
Hydrothermal Corrosion of SiC Composite

- **Rapid dissolution of SiC_f/SiC composite**





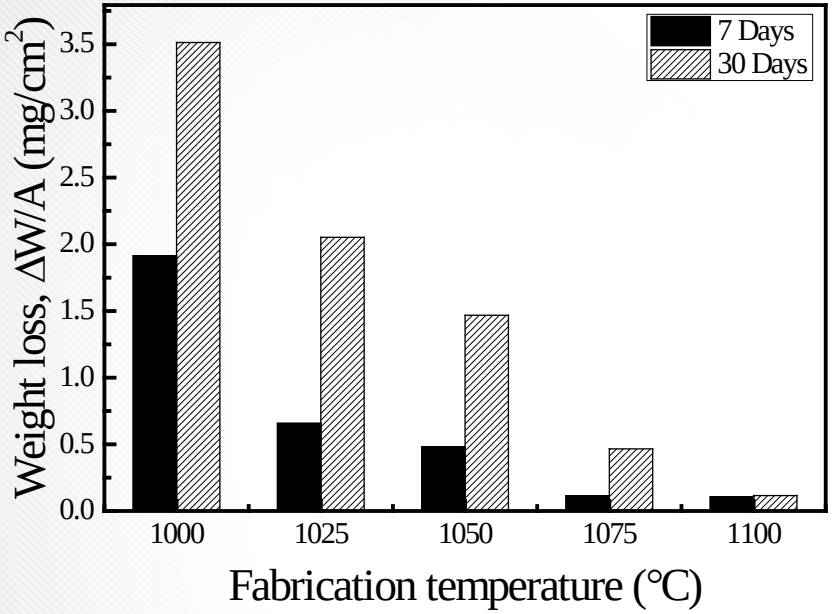


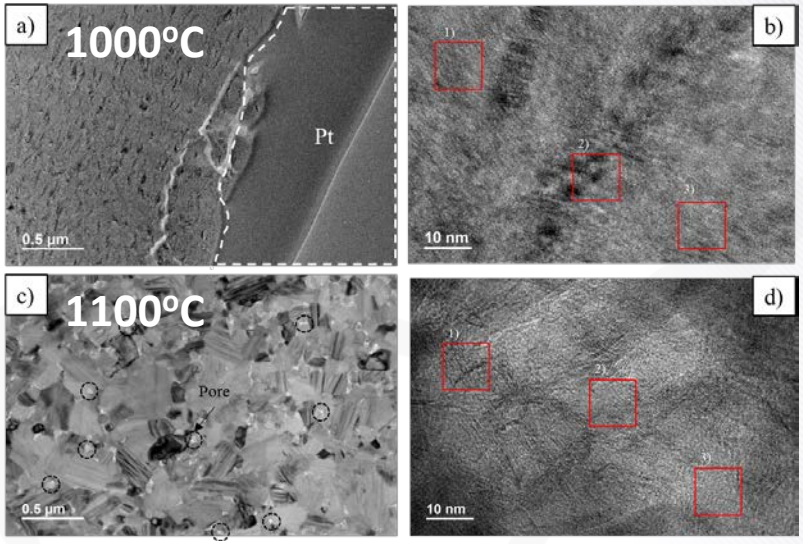


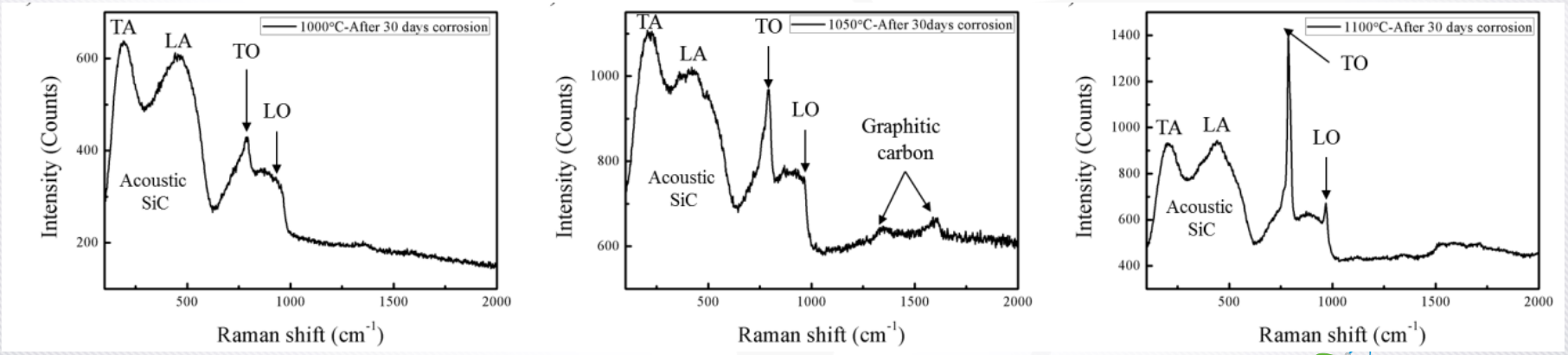
D. Kim, et. al., Journal of Nuclear Materials, 2017

Improvement of Corrosion Resistance of SiC

- **Influence of crystallinity of SiC on hydrothermal corrosion**



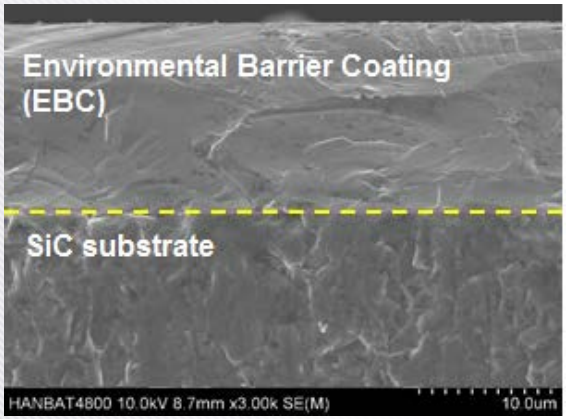


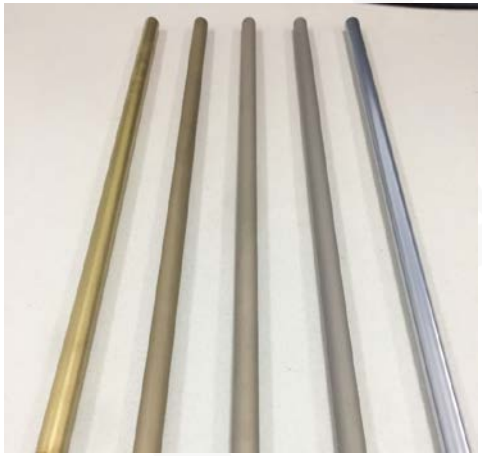


J. Han, D. Kim, et. al., Int. J. Appl. Ceram. Technol., 2021

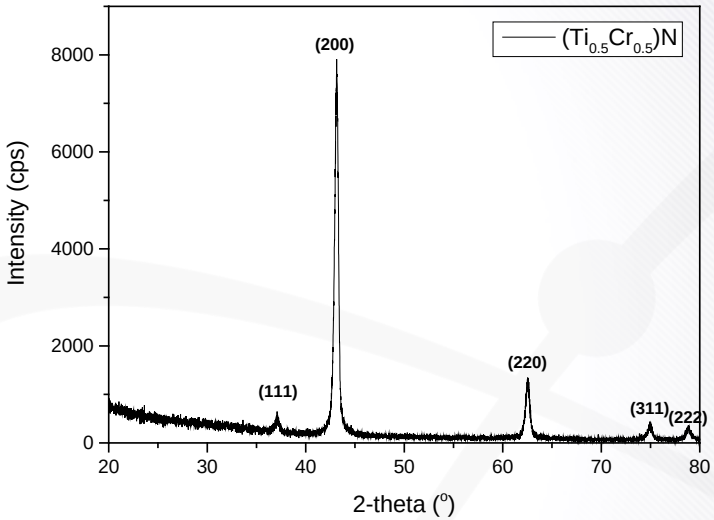
Environmental Barrier Coating

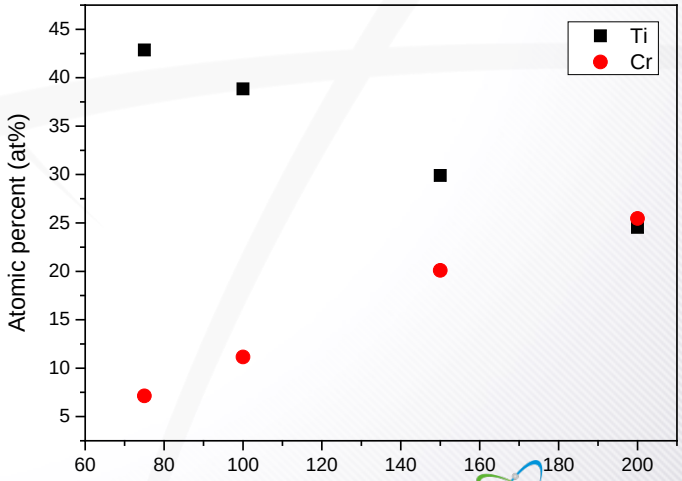
- **Deposition of nitride-based EBC**
  - TiCrN : Ti (Arc ion plating), Cr (Sputtering)
  - CrAlN : Cr (Arc ion plating), Al (Sputtering)
  - Atmosphere : Ar-N_2 mixture (1:1)
  - Coating thickness : 3~5 μm





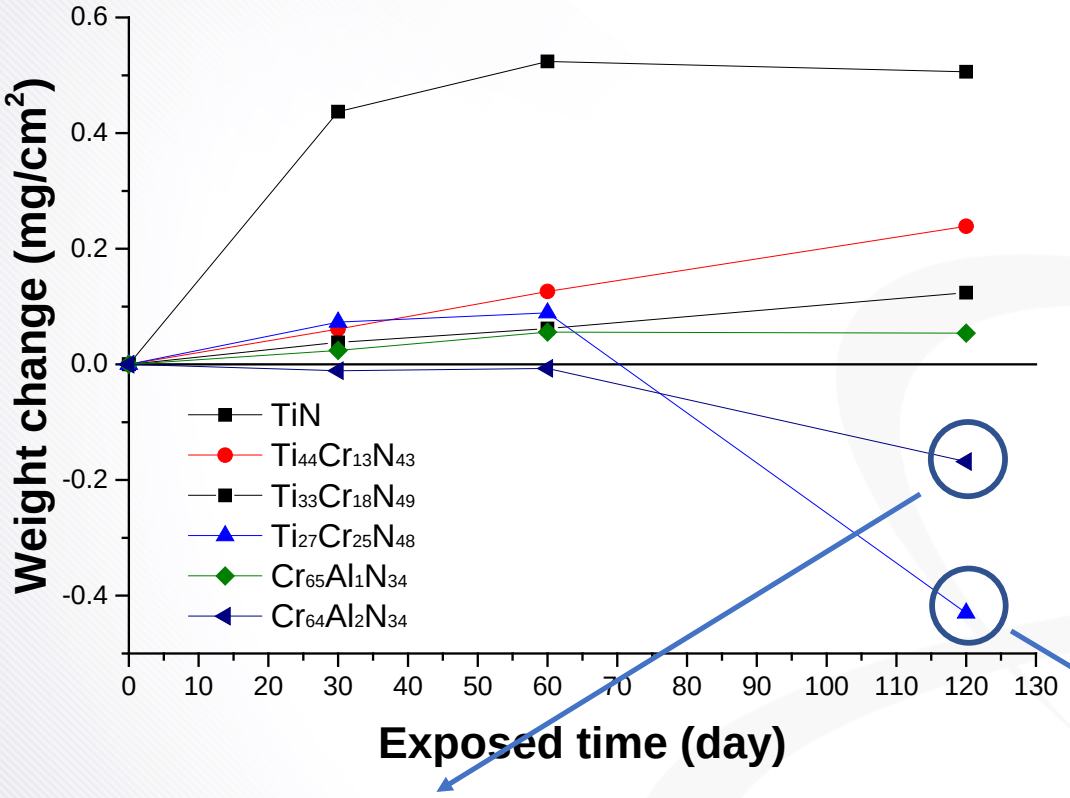
EBC coating using AIP & sputtering

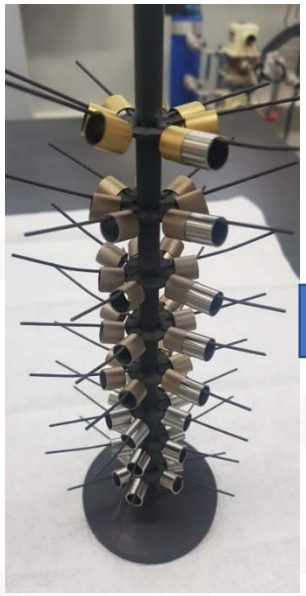


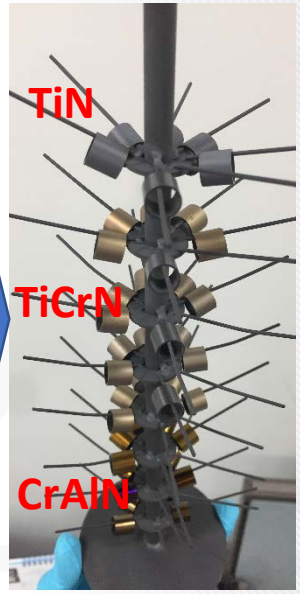


Weight Change after Hydrothermal Corrosion

- **Weight change for 120 days in the simulated PWR coolant environment**







Before

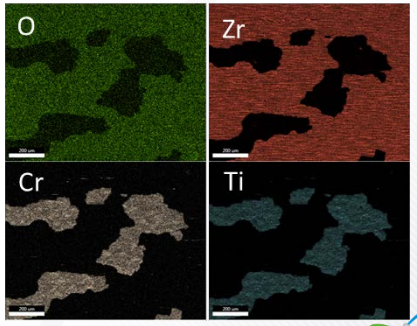
After

➢ **Dissolution of Al_2O_3**

Al_2O_3 (s) + $3H_2O$ (aq) = $2Al(OH)_3$ (aq)

$Al(OH)_3$ (aq) + $3H^+$ (aq) = **Al^{3+} (aq)** + $3H_2O$ (aq)

spallation

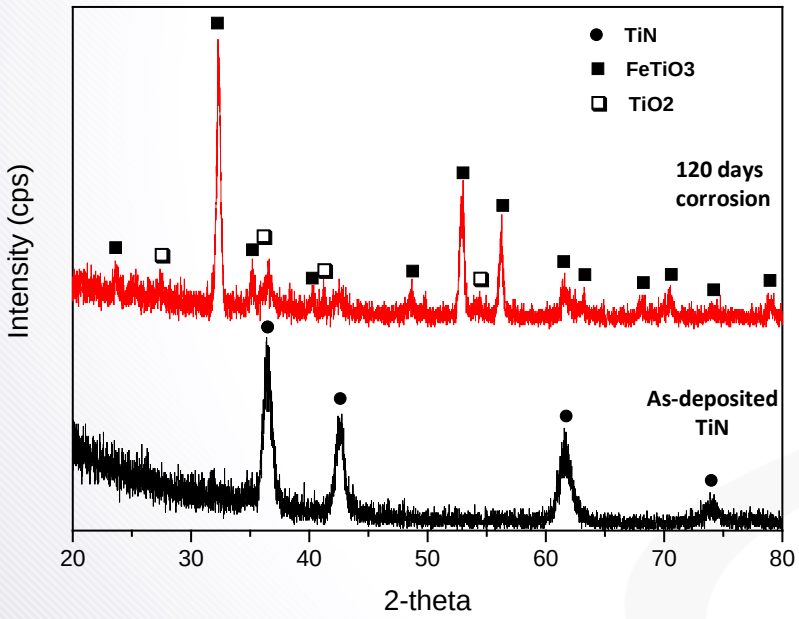


A. Do, D. Kim, et. al., Journal of Nuclear Materials, 2020

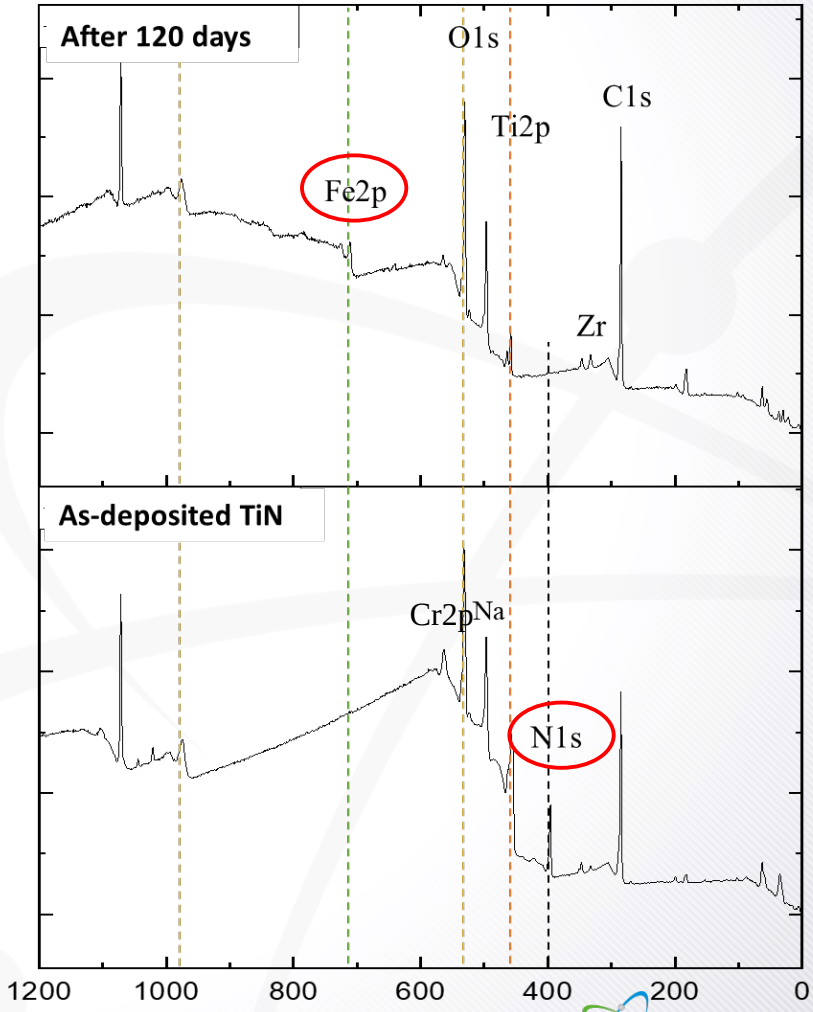
Hydrothermal Corrosion of TiN

- **Formation of Thick $TiO_2/FeTiO_3$ after 120 days**

XRD for TiN before/after 120 days

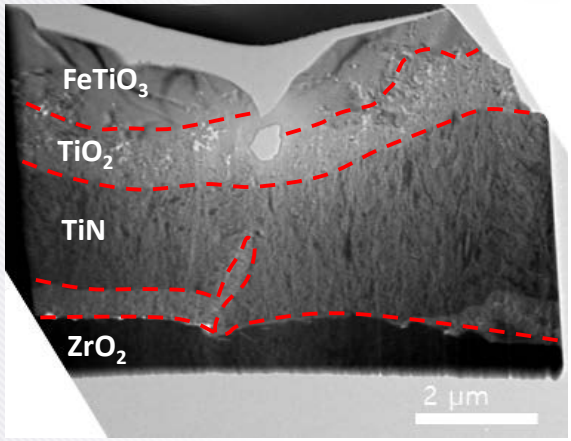


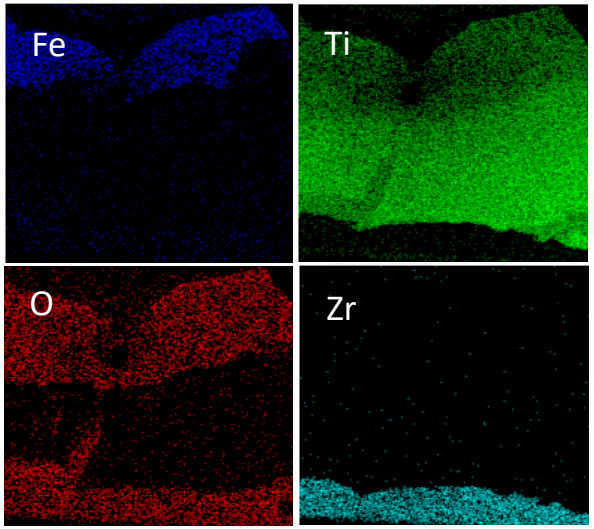
XPS for TiN before/after 120 days



Hydrothermal Corrosion of TiN

- **Microstructure of TiN after 120 days**





Solubility of Fe in PWR

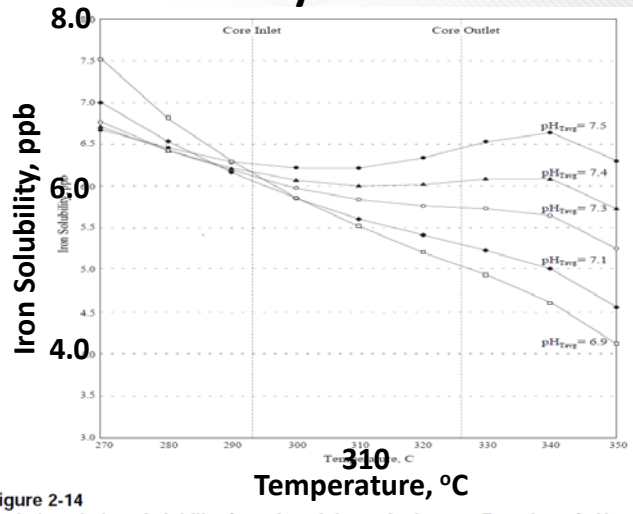


Figure 2-14
Variations in Iron Solubility from Core Inlet to Outlet as a Function of pH_t at the Core Average Coolant Temperature (Boron = 600 ppm, H_2 = 35 cc/kg H_2O)

Constituent	SG Crud	Core Crud	Oxidized SG Tubing
Iron	14 - 22%	39 - 47%	6%
Nickel	20 - 30%	19 - 24%	52%
Chromium	20 - 38%	0.8 - 2.5%	13%
Cobalt	0.24%	0.11%	0.035%

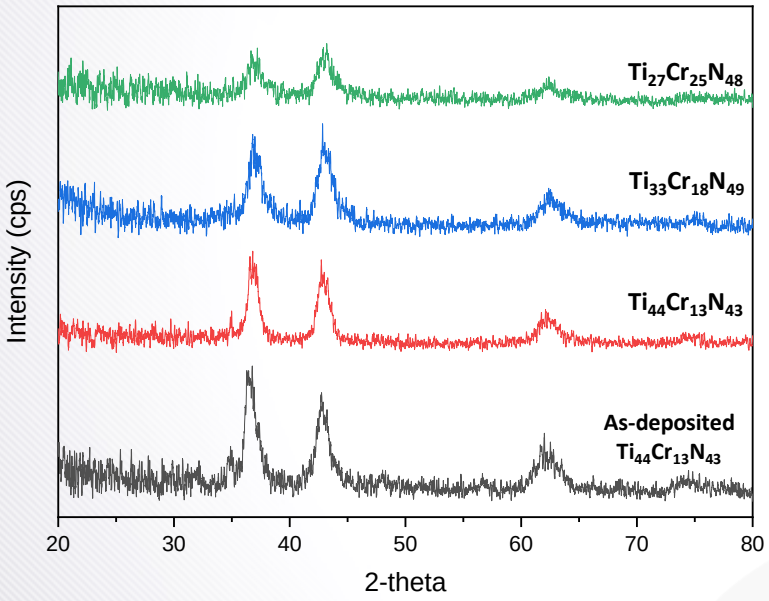
- **$FeTiO_3$ formation by reaction of TiN and Fe in high-temperature pressurized water**

$$2TiN\ (s) + 4H_2O\ (aq) = 2TiO_2\ (s) + N_2\ (g) + 4H_2\ (g)$$
$$2TiN\ (s) + 6TiO_2\ (s) = 4Ti_2O_3\ (s) + N_2\ (g)$$
$$Ti_2O_3\ (s) + 2FeO\ (s) + H_2O\ (aq) = \mathbf{2FeTiO_3\ (s)} + H_2\ (g)$$

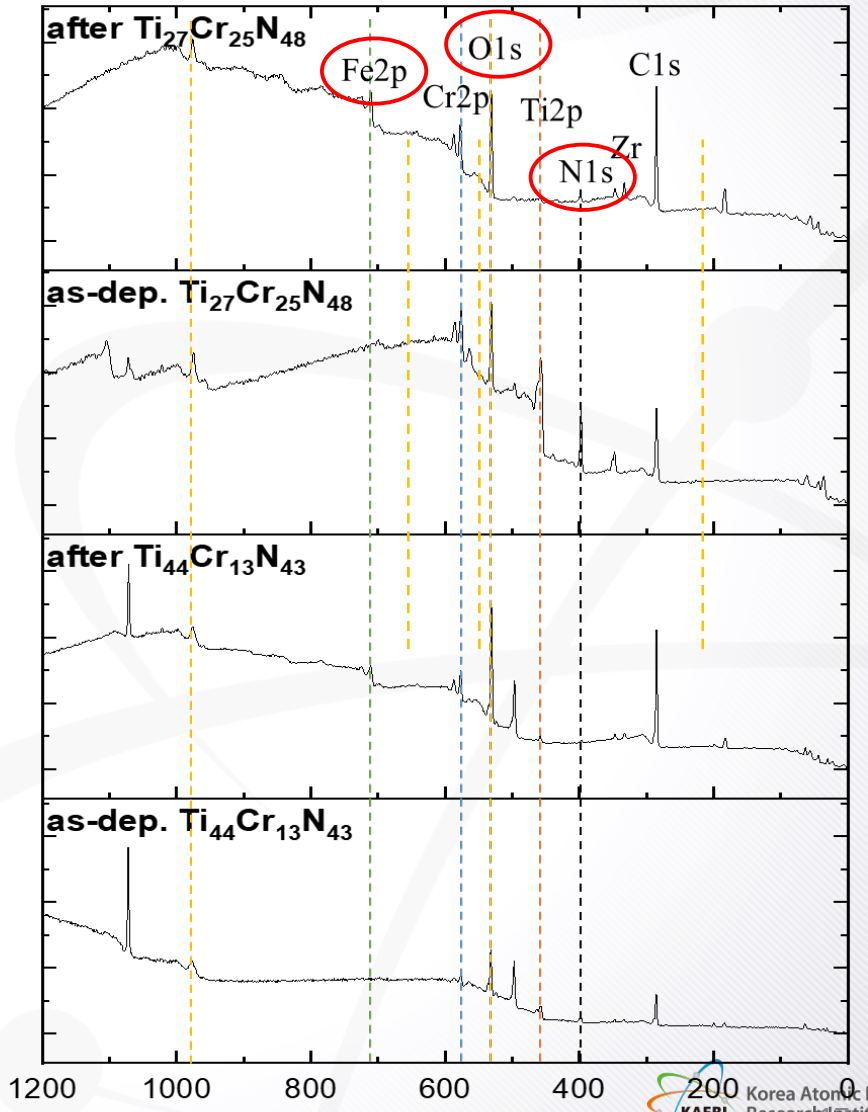
Hydrothermal Corrosion of TiCrN

- **Formation of thin oxide after 120 days**

XRD for TiCrN before/after 120 days

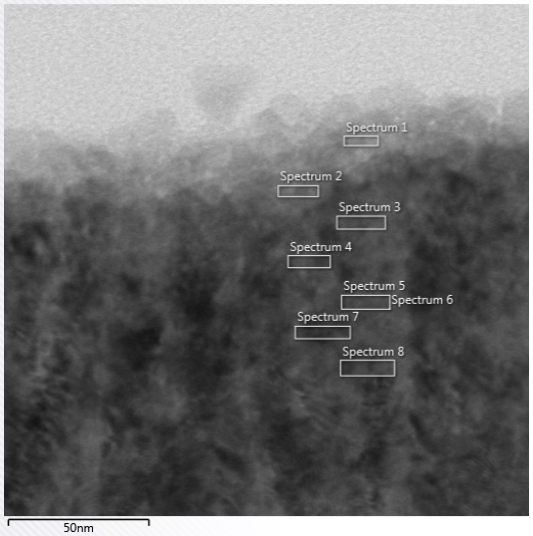


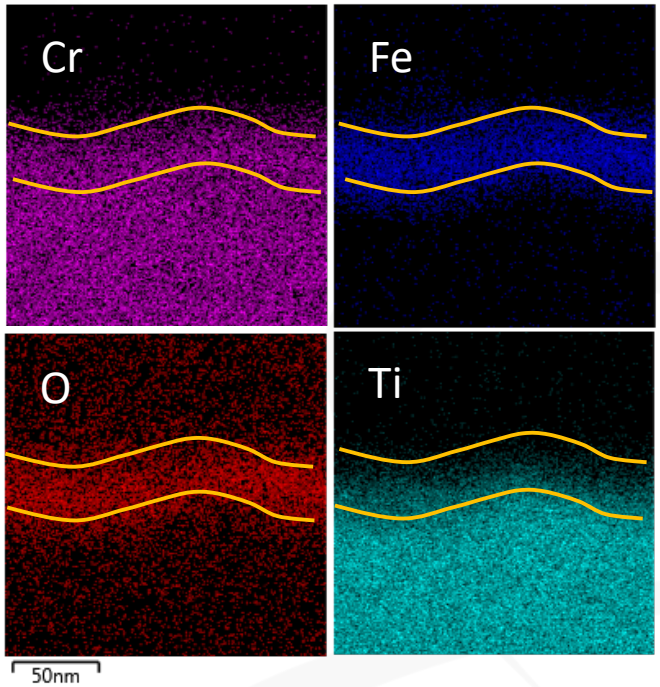
XPS for TiCrN before/after 120 days

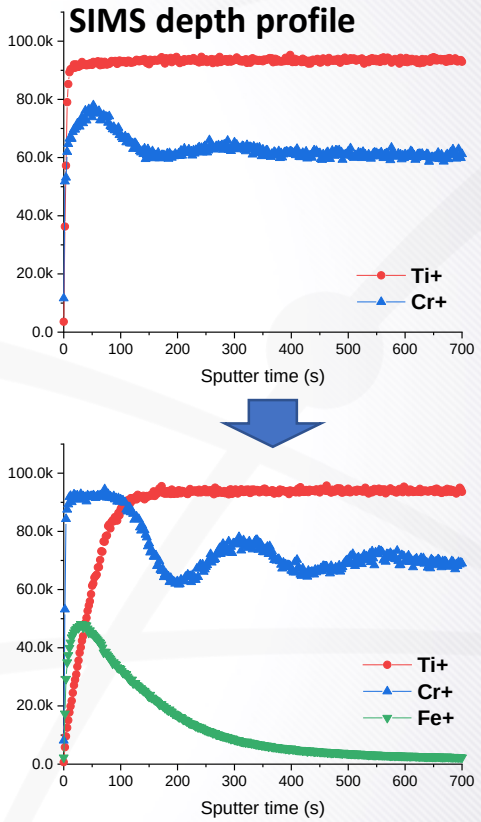


Hydrothermal Corrosion of TiCrN

- **Microstructure of $Ti_{44}Cr_{13}N_{43}$ after 120 days**







- **Formation of $FeCr_2O_4$ in high-temperature and pressurized water**

$$CrN\ (s) + H_2O\ (aq) = CrN_xO_y\ (s) + H_2\ (g)$$

$$2CrNO\ (s) + FeO\ (s) + H_2O\ (aq) = \mathbf{FeCr_2O_4\ (s)} + N_2\ (g) + H_2\ (g)$$

High-Temperature Steam Oxidation

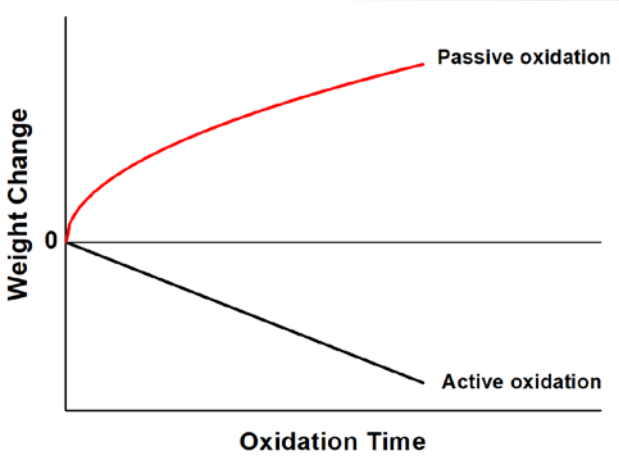
- **Active-passive oxidation of SiC**

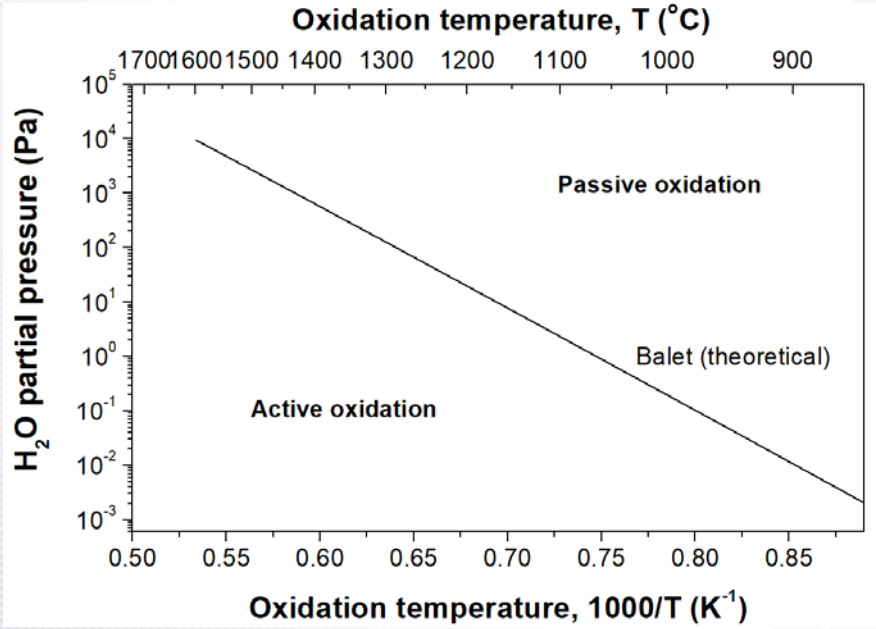
  Active oxidation

  $SiC + 2H_2O(g) \rightarrow SiO(g) + CO(g) + 2H_2(g)$

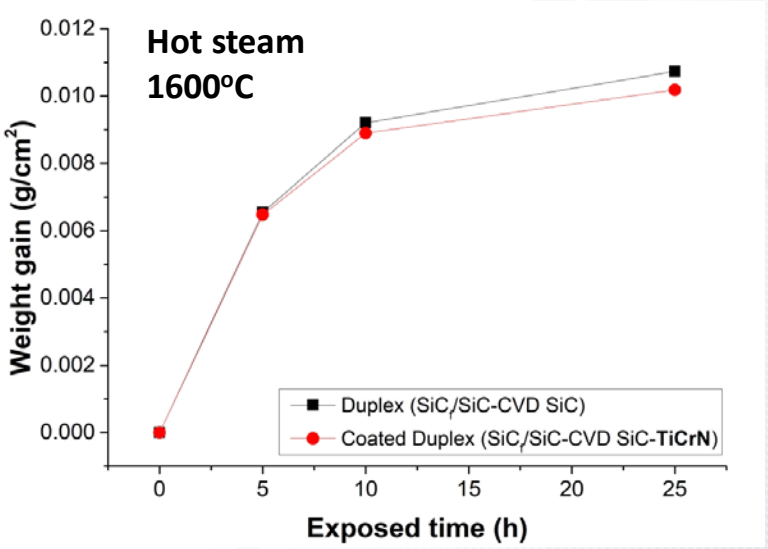
  Passive oxidation

  $SiC + 3H_2O(g) \rightarrow SiO_2(s) + CO(g) + 3H_2(g)$





Transition of active-passive oxidation of SiC

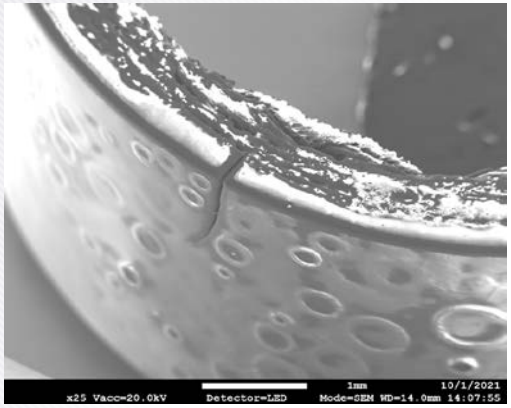


Weight change of duplex SiC cladding

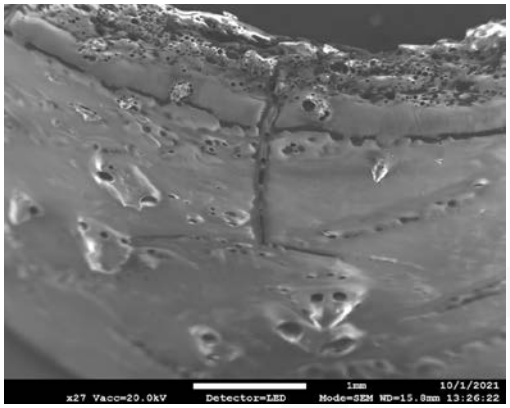
D. Kim, et. al., Oxidation of Metals, 2013

High-Temperature Steam Oxidation

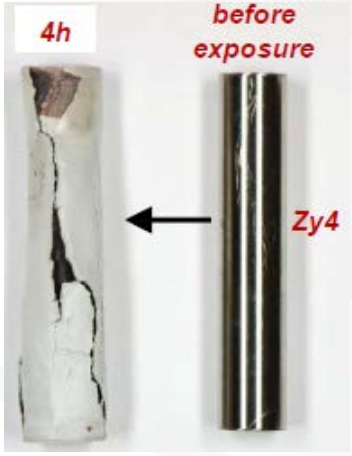
- **Hot steam oxidation at 1600°C for 25 hrs**



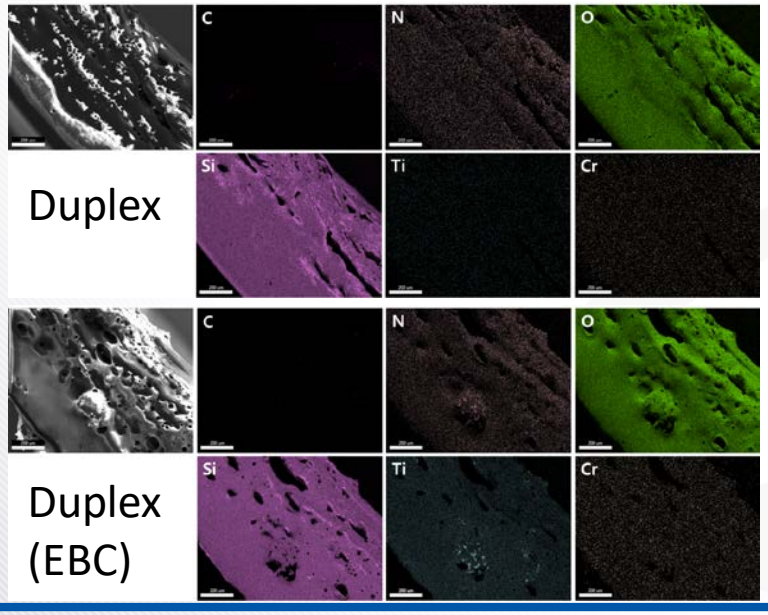
Duplex SiC cladding

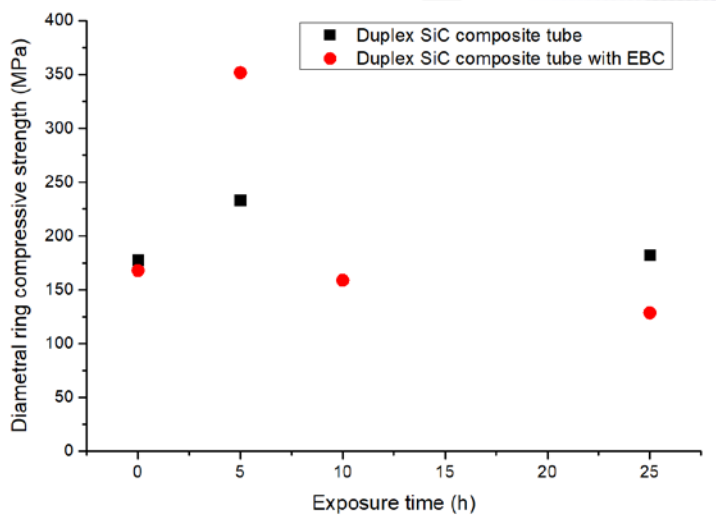


Duplex SiC cladding (with EBC)



Zy4 at 1200°C hot steam

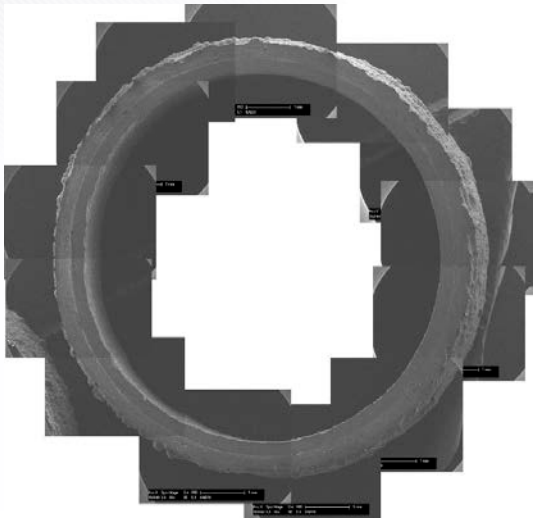


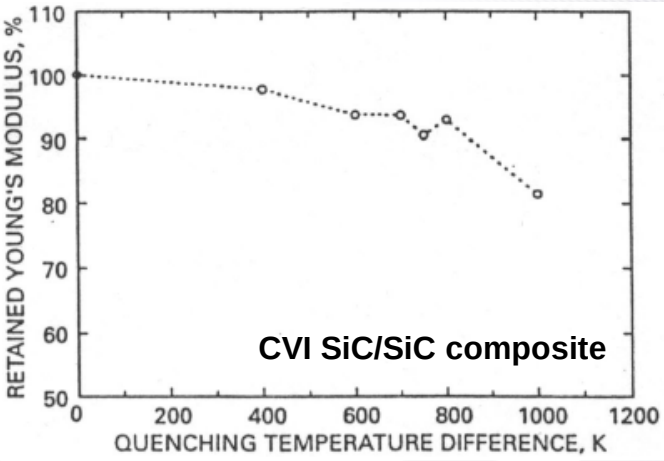


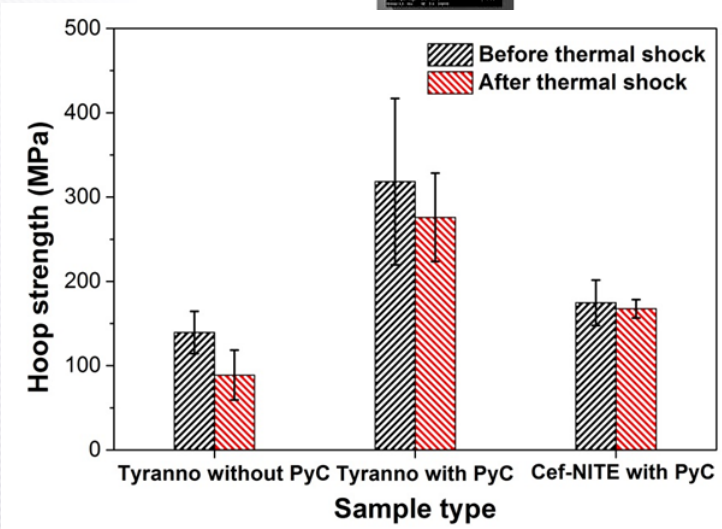
C-ring strength after corrosion for 25hrs

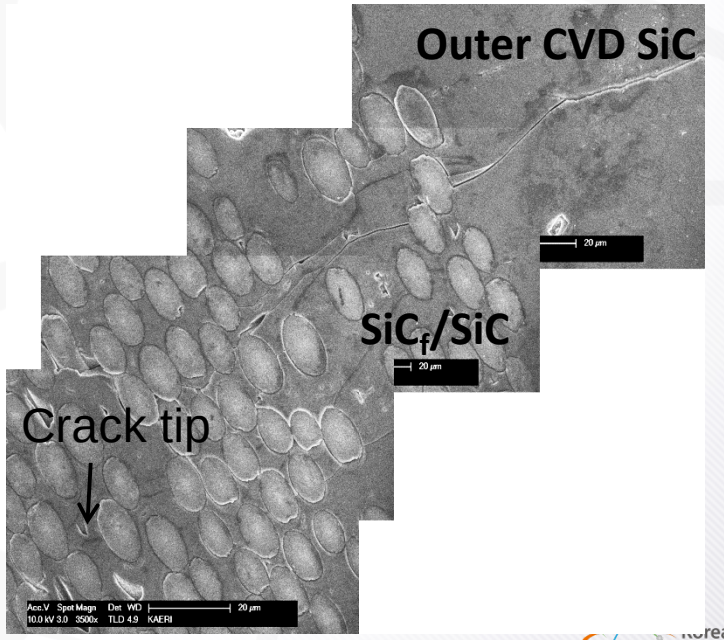
Thermal Shock Resistance

- **Water quenching from 1200°C to RT**







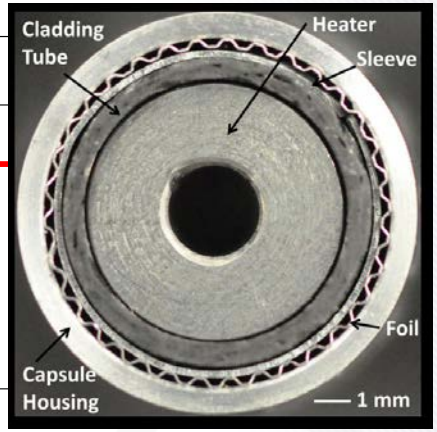


H. Wang, et. al., J. Am. Ceram. Soc., 1996 , D. Kim, et. al., Int. J. Appl. Ceram. Technol., 2017

Neutron Irradiation Experiment at HFIR

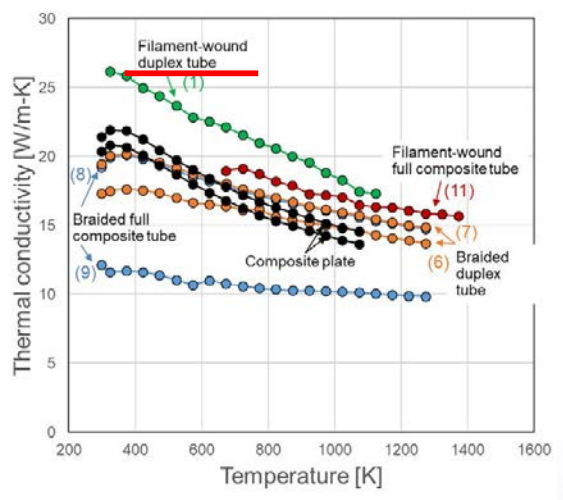
- **Fast neutron fluence : 2.7 x 10^{25} n/m^2 (E > 0.1MeV)**
  - Heat flux : low heat flux (0.08 MW/m^2), high heat flux (0.6 MW/m^2)

Material type	Provider	Matrix	Fiber architecture	Nominal fiber volume fraction [%]	Thickness of PyC interphase [nm]
Filament-wound duplex tube	KAERI	CVI	1 ply, filament winding angle ±55°	20	200
Braided duplex tube	GA	CVI	1 ply, braiding angle ±55°	~20	150
Braided full composite tube	GA	CVI	2 plies, braiding angle ±55°	35–40	150
Filament-wound full composite tube	CEA	CVI	3 plies, filament winding angle ±45°	~35	30
Composite plate	Rolls -Royce	CVI	Satin-weave, 0°/90° stacking	~40	50–160
Monolithic tube	Dow Chemical	CVD	Not applicable	Not applicable	Not applicable

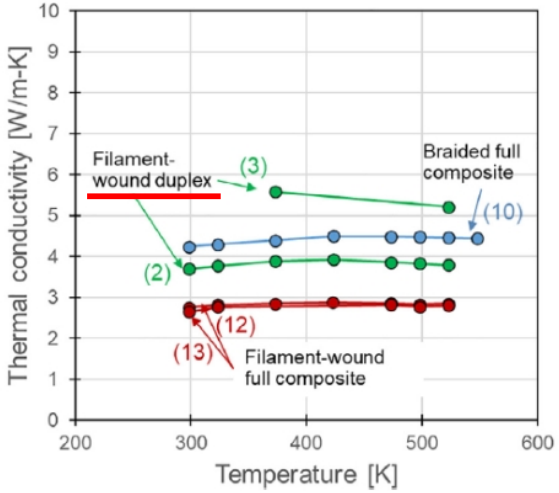


- **Thermal conductivity**

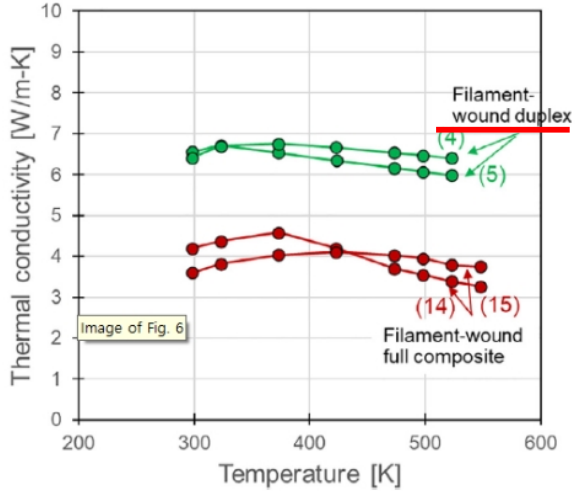
Unirradiated



(a) Irradiated with low heat flux



(b) Irradiated with high heat flux

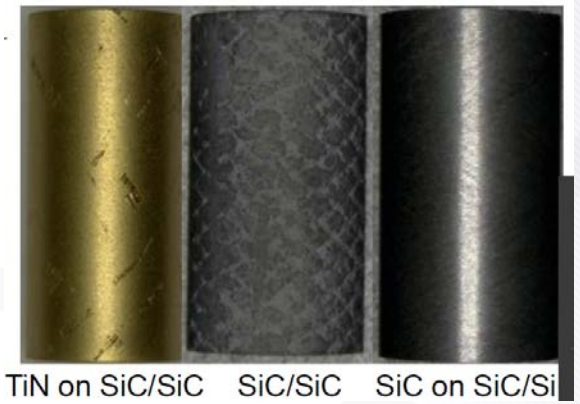


T. Koyanaki, et. al., Journal of Nuclear Materials, 2020

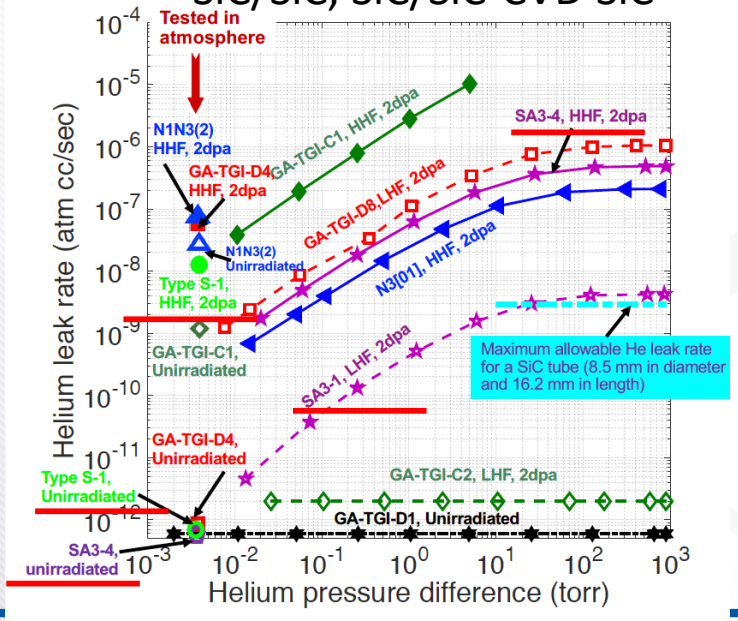
Neutron Irradiation Experiment at HFIR

- **Gas-tightness of SiC cladding**

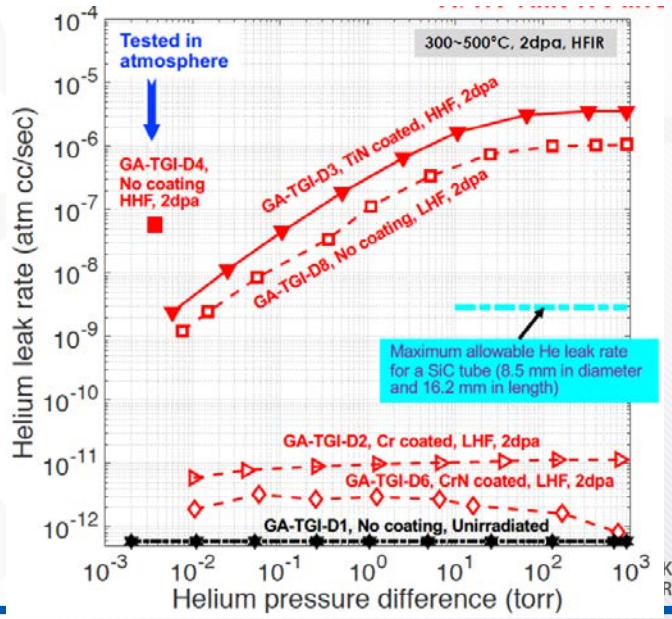
Manufacturer	Type	Coating	Specimen ID	Heat flux	
				High	Low
Dow	Monolith	None	CVD-X (X=E, G, H, L, Q, R)	3	3
GA	SiC/SiC composite	None	GA-TGI-C-1	1	0
GA	Duplex: inner composite, outer monolith	CrN	1-TM-CrN, 3-RP-CrN	1	1
GA	Duplex: inner composite, outer monolith	Cr	6-RP-Cr	0	1
KAERI	Duplex: inner composite, outer monolith	None	TYPE S-1, SA3-1, SA3-2	2	1
CEA	SiC/SiC composite	None	N1N3(1), N1N3(8)	1	1
CEA	SiC/SiC composite	CrN	2-TM-CrN, 4-RP-CrN	1	1
CEA	SiC/SiC composite	TiN	7-TM-TiN	0	1



SiC/SiC, SiC/SiC-CVD SiC

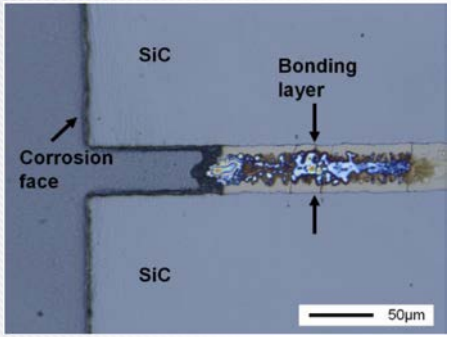


SiC/SiC-CVD SiC-**EBC**

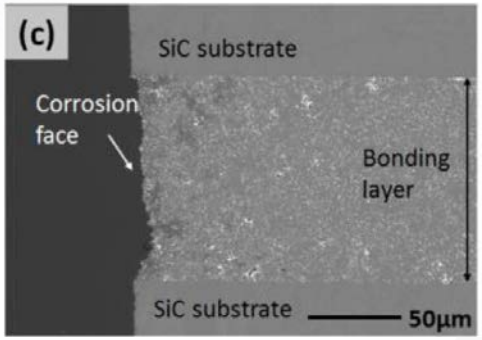


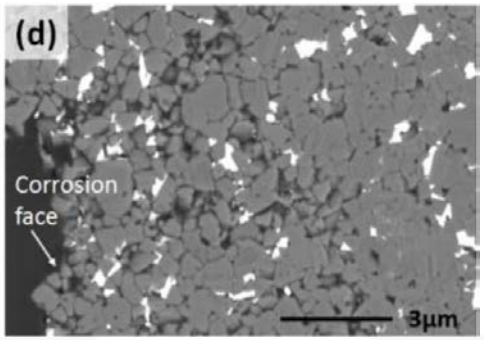
Corrosion Resistant Reaction-diffusion Bonding

- **Dissolution or cracking in bonding area**

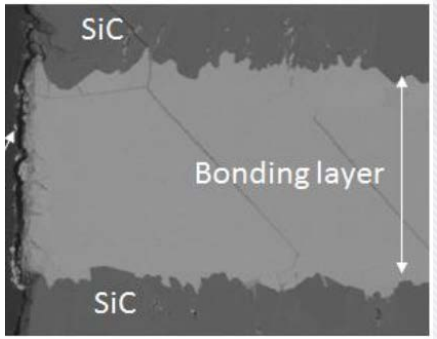


Mo interlayer



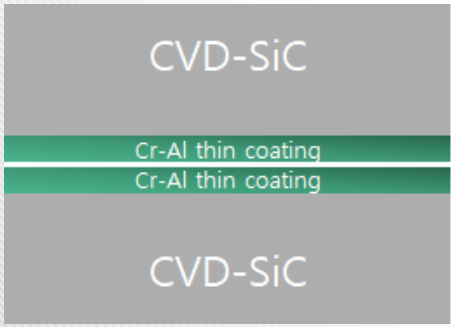


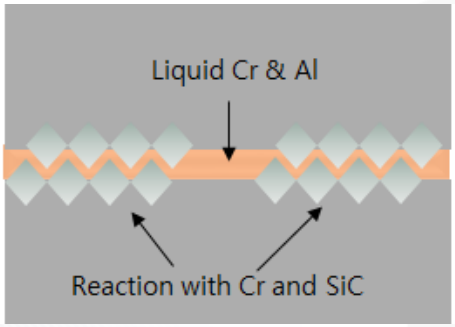
Sintered SiC with additives

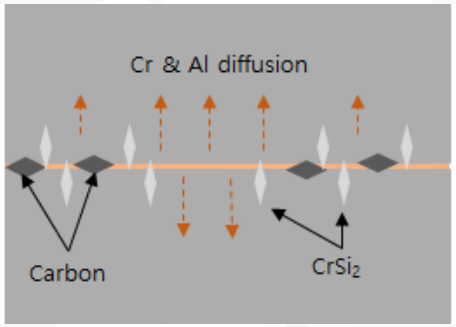


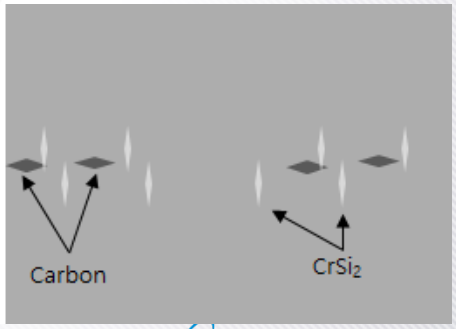
Ti interlayer

- **Corrosion resistant Cr-Al diffusion bonding**
  - ~200 nm Cr-Al (85:15) coating on CVD SiC by PVD
  - Pressureless or 10 MPa HP at 1800°C for 1 hr





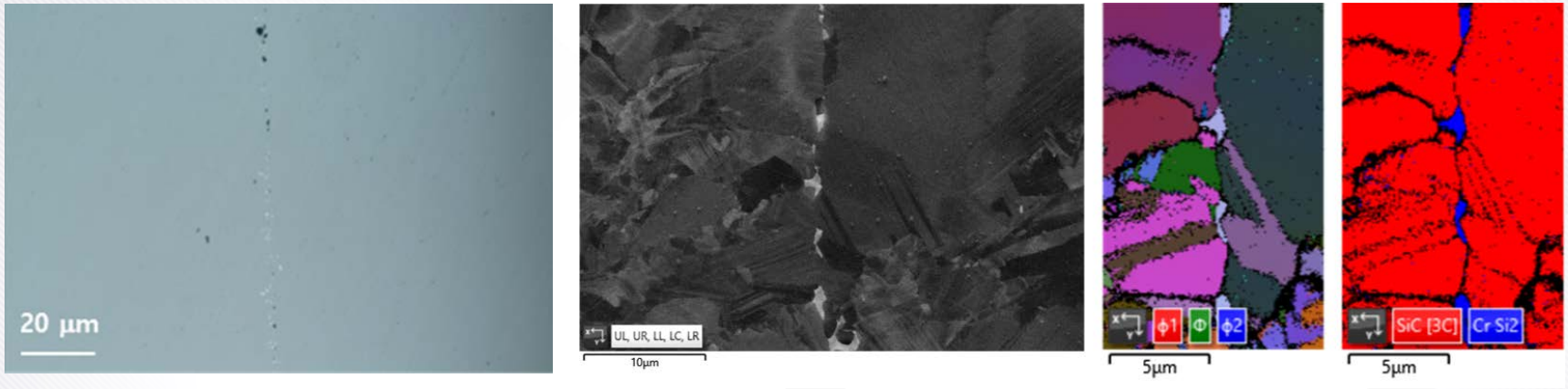




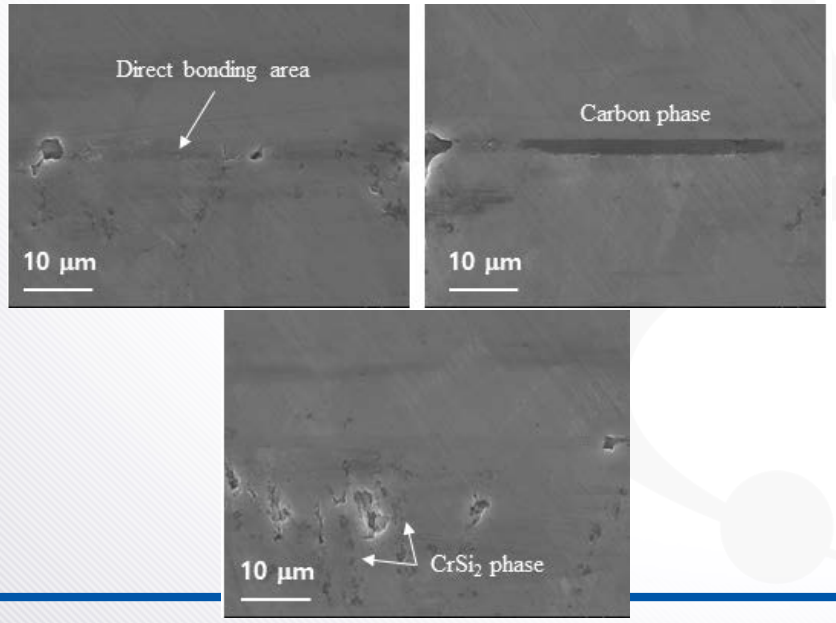
T. Koyanagi, et. al., Journal of Nuclear Materials, 2016

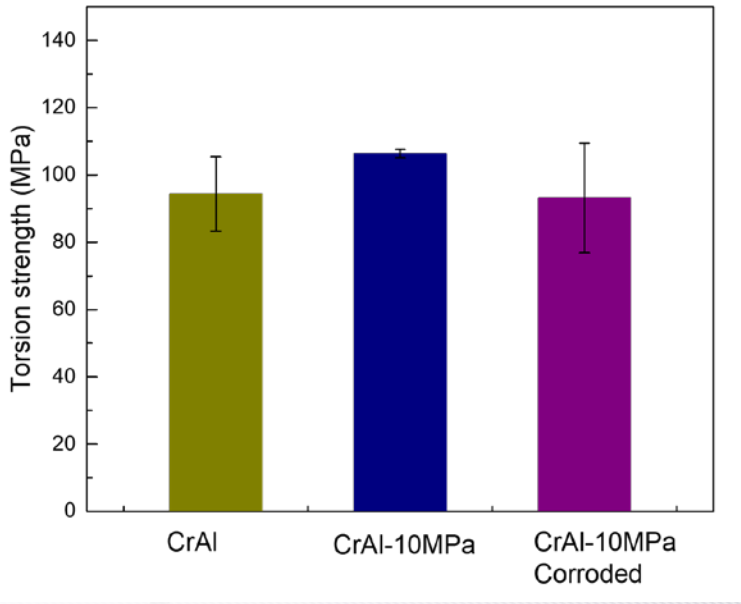
Corrosion Resistant Reaction-diffusion Bonding

- **Microstructure of bonded-SiC**



- **Microstructure and torsion strength after hydrothermal corrosion for 30 days**





Summary

- **SiC composite cladding is a promising longer term ATF cladding concept because of its exceptional accident-tolerance**
  - Excellent resistance to high-temperature steam
  - Structural integrity even in DBA and BDBA

- **Environmental barrier coating is deemed to overcome critical problems such as hydrothermal corrosion and permeability of fission gases, but it still requires a lot of further technical progress**
  - Optimization of chemical composition and deposition process
  - Verification of performance under irradiation conditions

THANK YOU

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