

INVESTIGATION OF TAILORED SIC/SIC COMPOSITES FOR SODIUM-COOLED FAST REACTORS

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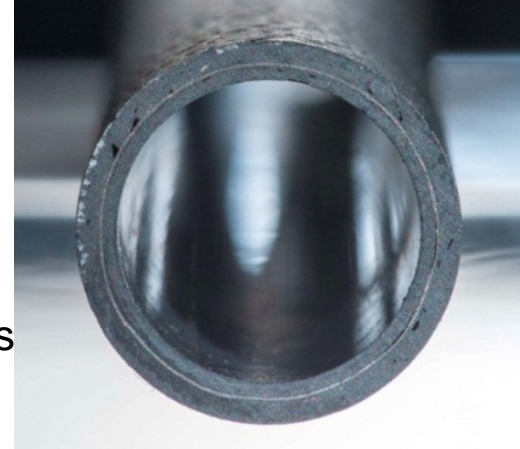


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- SiC/SiC as **core materials** for fission nuclear reactor applications
- **Na - SiC compatibility**
- **Experimental procedure** for Na-SiC compatibility tests at 550°C
- Mechanical behavior of SiC/SiC **before** immersion
- **Chemical surface analyses** after immersion
- Mechanical behavior of SiC/SiC **after** immersion
- **Conclusions and perspectives**

Cladding applications

- Stability under neutron irradiation for high dose (in dpa)
 - > few dpa for thermal neutron applications (LWR, HTR)
 - > 100dpa for fast neutron nuclear applications (GFR, SFR)
- ➔
- Dimensional stability (no large swelling)
 - No degradation of thermal and mechanical behaviors
 - Low irradiation induced creep



→ Gas tightness for cladding applications (French patent – Sandwich concept)

- Low neutron absorption (depending energy of neutrons)
- Resistance to accidental situations (For GFR, $T > 2000^{\circ}\text{C}$)
- Ideally low activation materials
-

High benefits possible but :

- (i) very high level requirements
- (ii) very long term application (> 20 years)
- (ii) demonstration of feasibility still to be proven



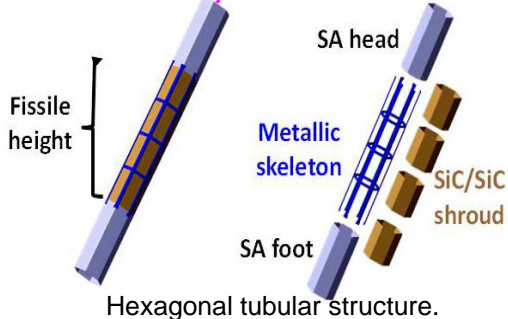
Non-Cladding applications (Mainly lower benefits ?)

- Sub-assembly (SA) duct in SFRs

- Channel box in BWRs

- Control rods in VHTRs

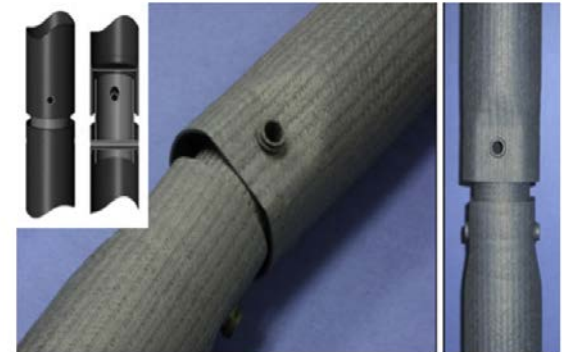
Mixed CMC/metal SA-duct



Patent WO 2011/042406 A1



Yueh et al, TOP FUEL 2012.



Y. Katoh, L.L. Snead, I. Szlufarska and W.J. Weber, *Current Opinion in Solid State Materials Science*, 16 [3] 143-152 (2012).

Easier requirements applications (ex : hermeticity is not a requirement)

more accessible for demonstration of SiC/SiC interest for nuclear applications

Specific requirements for SiC/SiC composites

- Reproducible dimensional tolerance (easier than for cladding) to ensure
- Good mechanical and thermal properties up to high temperature
- Good chemical compatibility with environment (coolant and core structures) event under accidental situation

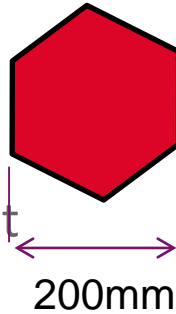
Probably the fastest route to acquire operational experience of SiC/SiC for nuclear applications

Large diameter hexagonal tubular structure

→ Texture issues

- Use of conventional techniques (Filament winding and braiding) difficult
 - low diameter of tows (~ 1 mm)
 - presence of sharp edges leading to thickness differences along circumference with filament winding or braiding

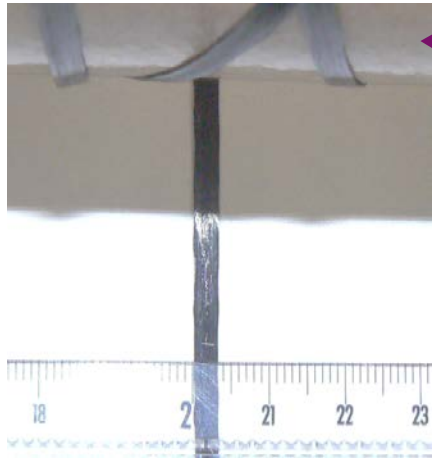
- Weaving is possible but needs expansive tools to ensure rigorous shape during densification (CVI process)



Choice:

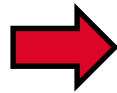
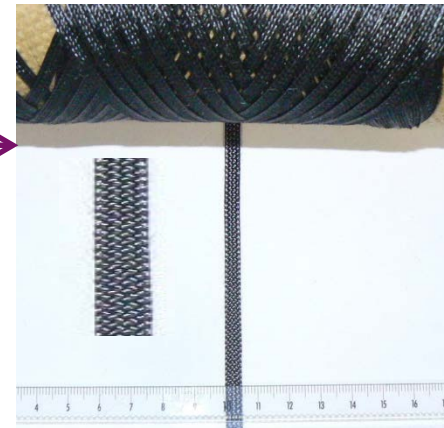
- Experience obtained on filament winding
 - Solution: SiC rebuild tow

➡ 2 approaches have been explored



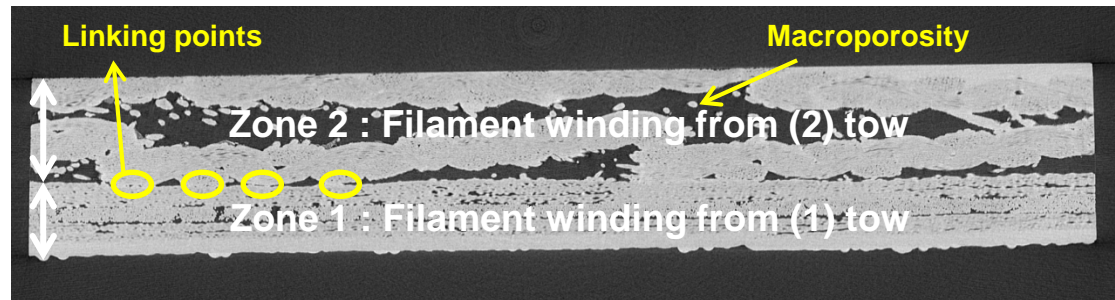
← (1) Production of larger tows (3-4mm)

(2) Production of flat braid (3-4mm) →



Production of a mixed sample by filament winding

- Inner part made from (1) tow
- Outer part made from (2) tow



Solution (1) is promising

Several possible interactions :

SiC – Na_(l) and its impurities:

- Mainly oxygen

- Nominal : [O] ≤ 3 ppm
- Incidental : [O] ~ 200 ppm

- Presence of SiO₂ : Formation of Na₂SiO₃
([Cook, 60], [Kano, 95])



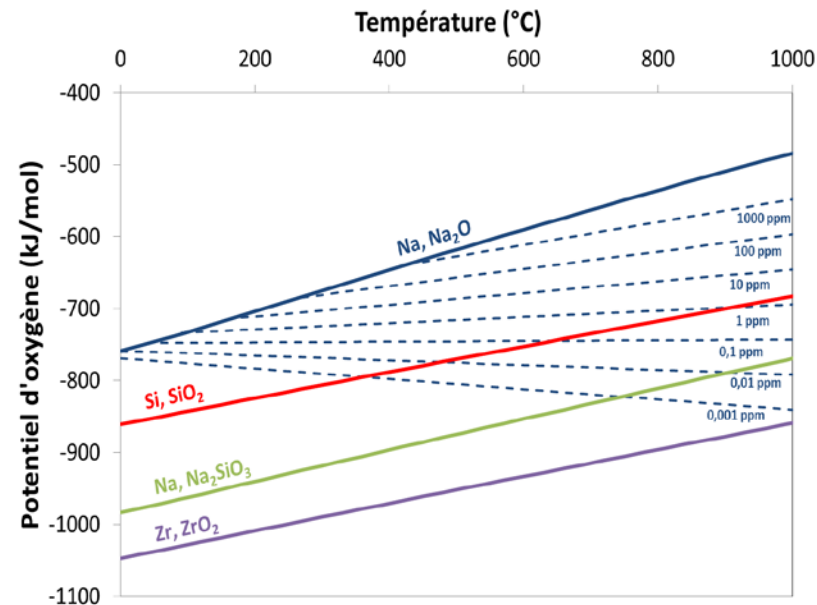
- Na₂SiO₃ ? Solubility in Na_(l) ?
- Oxidation of SiC ?

C (PyC interphase) – Na_(l) :

- Formation of C₆₄Na is possible ([Asher, 59])
- Poor behavior of graphite carbon in Na_(l) ([Gill, 61], [Davidson, 65])
- Modification of lattice parameters → Expansion → Mechanical stresses

Few studies on SiC, no studies on SiC/SiC composites.

What is the behavior of pyrocarbon (interphase in SiC/SiC) ?



Immersion procedure

- **2 Main objectives: Influence of**
 - liquid sodium
 - oxygen concentration in liquid sodium

- **2 experiences: 550°C, 2000h (with partial extraction at 1000h), static sodium:**
 - Purified sodium by a zirconium foil ($[O] < 10$ ppm) – **Na(p)**
 - Sodium with Na_2O/Na_2O_2 to reach $[O] \sim 1000$ ppm) – **Na(O)**

- **2 types of samples:**
 - **CVD SiC**
 - **SiC/SiC Composites (CVI process)**

- **Cleaning of samples after tests:**
 - Ethanol (3x)
 - Distilled water
 - Acetone

- **Analytical techniques :**
weight evolution, XPS surface analysis, SEM,
mechanical tests after immersion



Materials of the Study

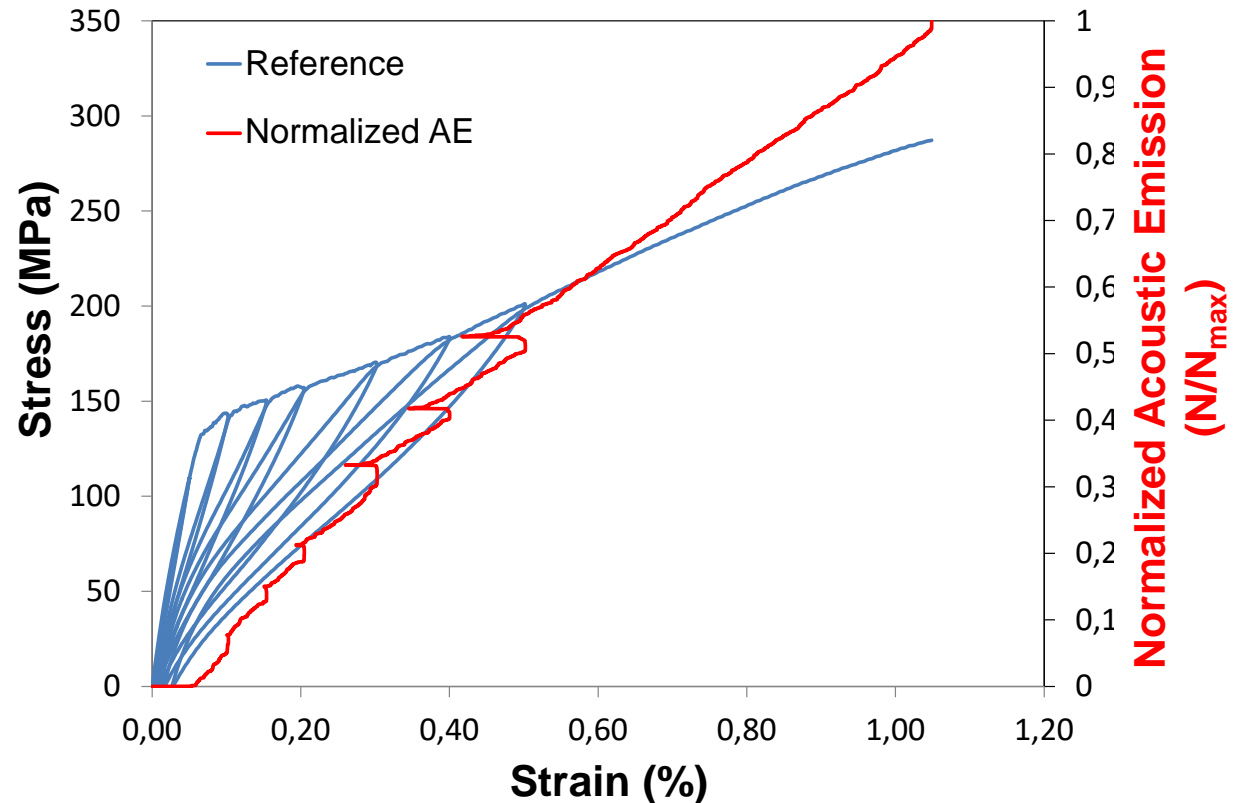
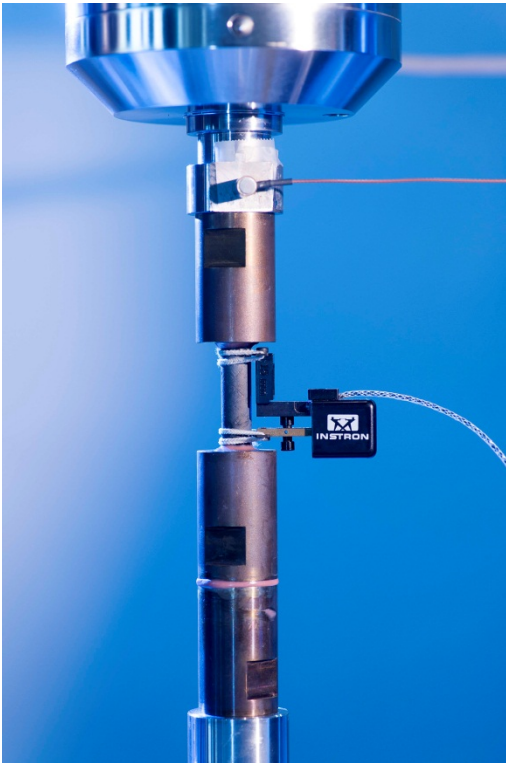
- CVD β -SiC : High purity
- SiC/SiC composites tubes:
 - 1 layer of filament winding (45°) + 2 layers of 2D braiding (45°)
 - 50 nm Pyrocarbon interphase
 - Internal and external grinding



- Intact tubes
- Pre-damaged tubes before immersion
 - ➔ **Possible access to the pyrocarbon interphase**

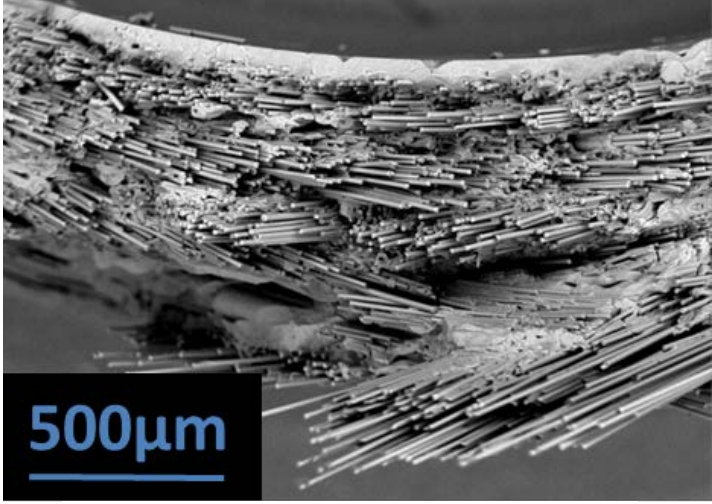
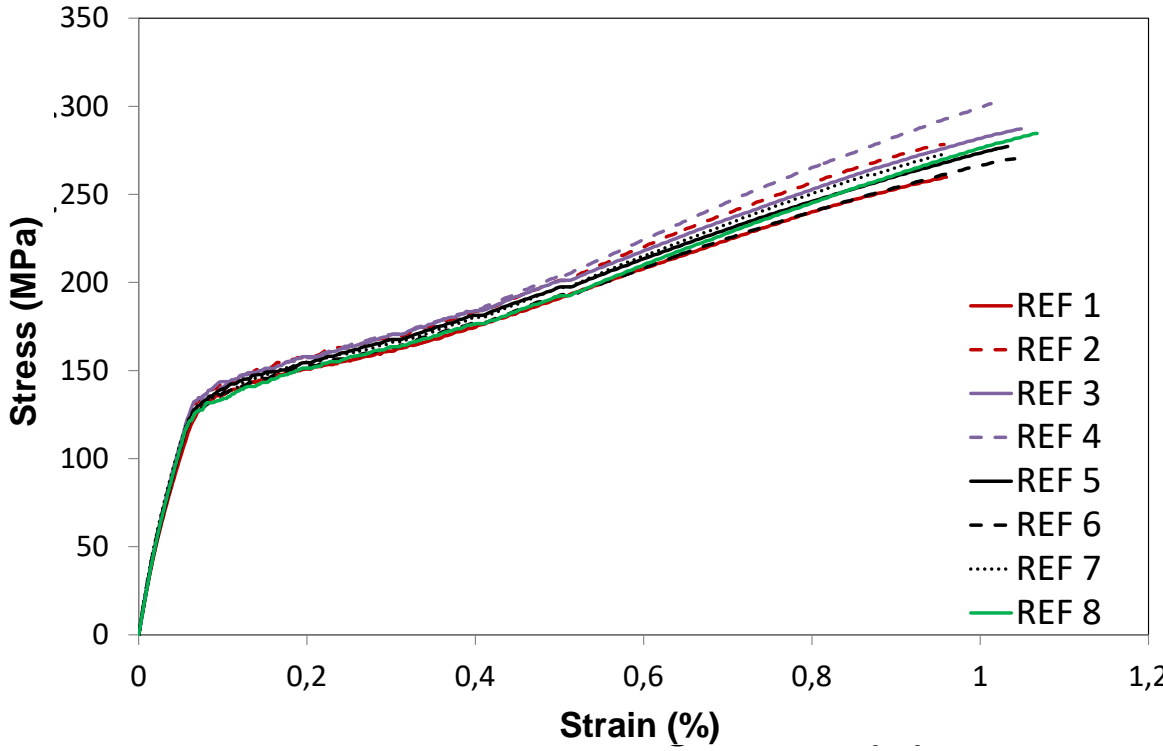
Mechanical tests before immersion

Uniaxial tensile tests with loading-unloading sequences



Analysis of mechanical behavior (loading-unloading sequences)

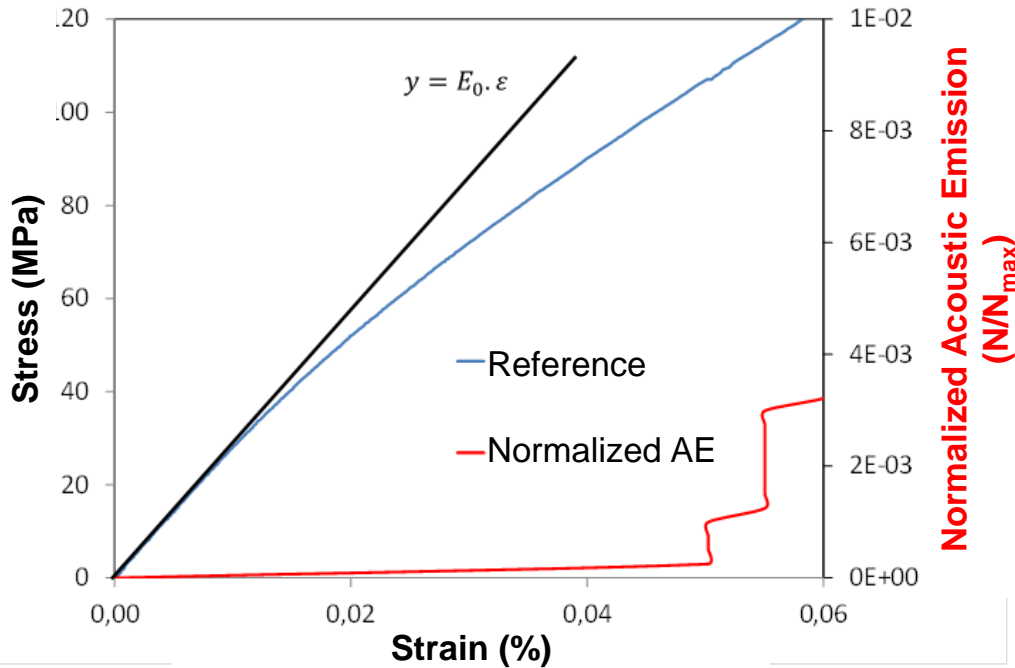
TENSILE MECHANICAL BEHAVIOR OF SIC/SIC PRIOR TO IMMERSION



Fracture surface

■ Very good reproducibility of mechanical behavior

E_0 (GPa)	ϵ_R (%)	σ (MPa)
281	1,010	279



■ AE → Matrix cracking

■ Deviation from linearity before matrix cracking

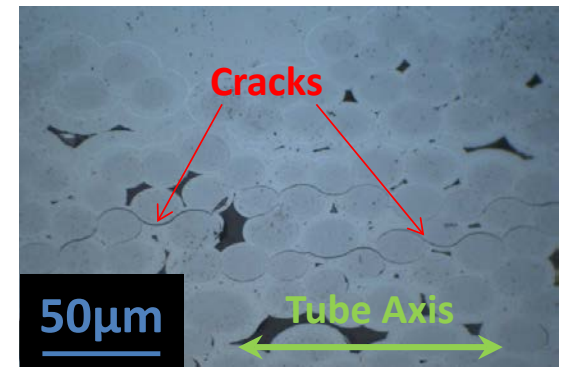
⇒ never observed on this kind of SiC/SiC composites

■ Processing route:

- Filament winding and braiding on a mandrel
- Deposition of Interphase and CVI matrix
- Mandrel withdrawal

Linear elastic range		First Acoustic emission signal	
ϵ_l (%)	σ_l (Mpa)	ϵ_{EA} (%)	σ_{EA} (Mpa)
0,012	35	0,053	110

Conclusion: Deviation from linearity before damaging the matrix is the consequence of pre-existing matrix cracks (due to residual thermal stresses induced by mandrel during processing)



Chemical analysis of CVD SiC before and after immersion

Weight changes

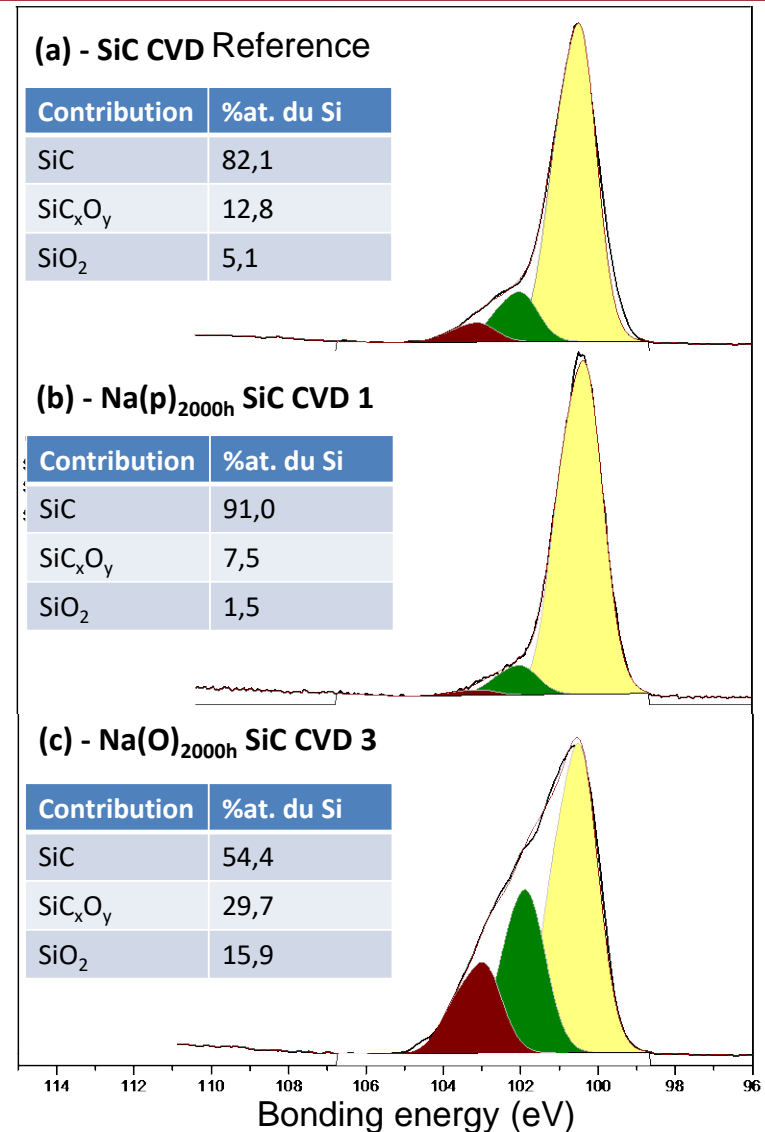
- Na(p): no significant evolution
- Na(O): weight loss (0,63%)

XPS: 3 contributions (SiC, SiO₂, SiC_xO_y) Surface analysis (few nm)

- Reference
- Na(p) : decrease of SiO₂ et de SiC_xO_y amount.
- Na(O) : increase of de SiO₂ et de SiC_xO_y amount ⇒ surface oxydation

Question on the influence of the possible formation of Na₂SiO₃ that would have been dissolved during the cleaning of samples !

Conclusion : Very limited reaction as silicon carbide is still the major phase at the extreme surface.

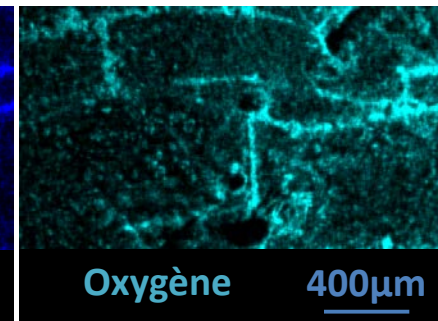
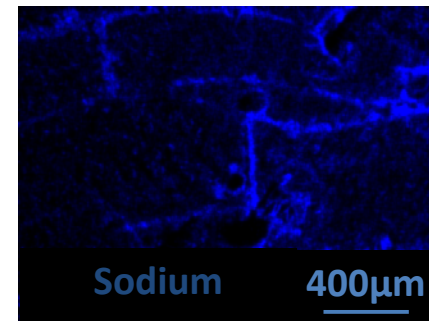
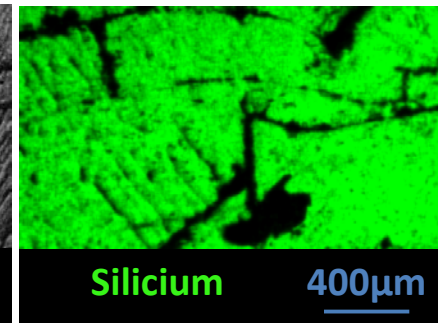
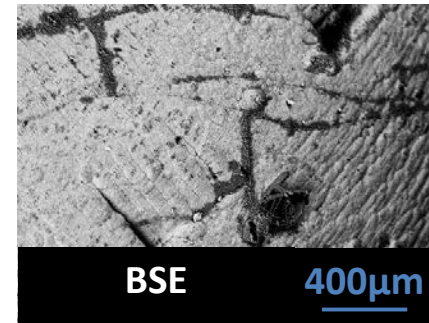
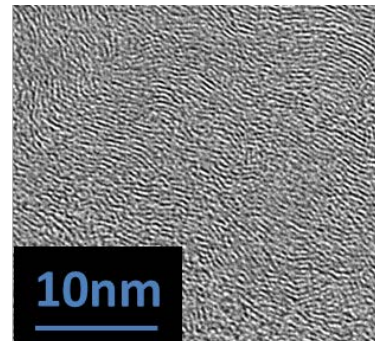
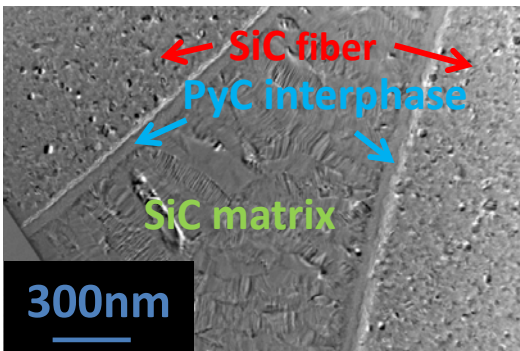
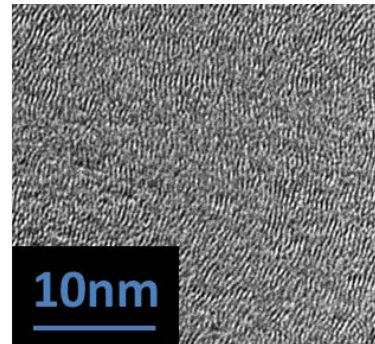
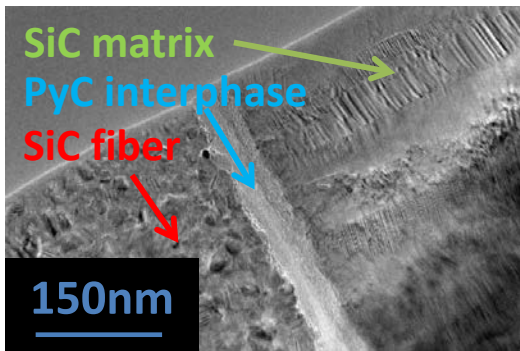


- Weight change for SiC/SiC composites : Positive !
Porous material
→ residual sodium which reacts with air and water
- Surface morphology doesn't allow XPS analysis
- TEM analyses

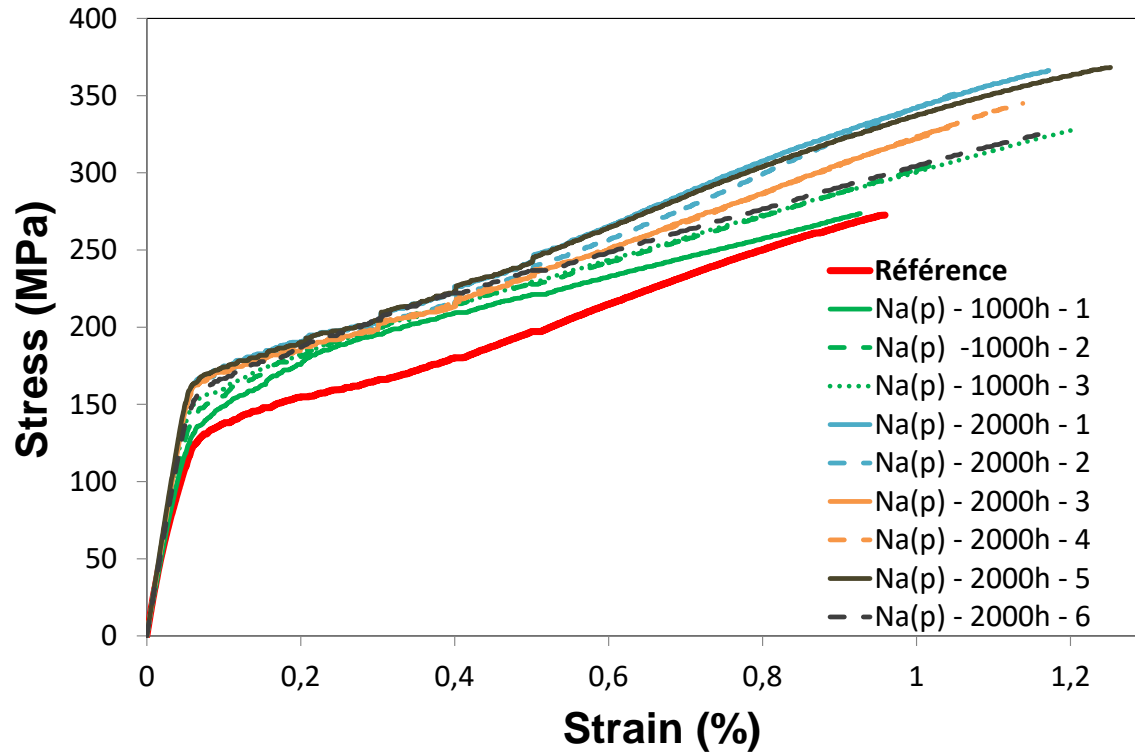


8 months after experiments and cleaning

PyC interphase is not affected



Presence of sodium in crack lips



Mechanical behavior after immersion in purified sodium (Na(p))

Same results after immersion Na(O)

Increase of :
 Rupture strain
 Rupture stress

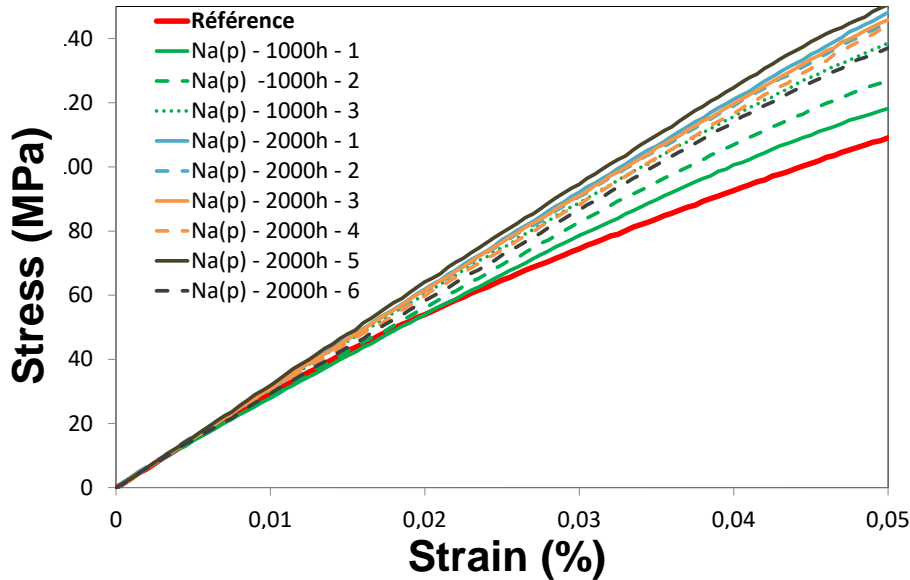
Slight increase of Young modulus

Slight Influence of duration of immersion ?

	E_0 (GPa)	ϵ_R (%)	σ (MPa)
References	281	1,010	279
Na(p) 1000h	296	1,053	303
Na(p) 2000h	308	1,145	349

Higher dispersion of mechanical behavior is noted after immersion

Zoom on mechanical behavior at low strain after immersion in purified sodium(Na(p))



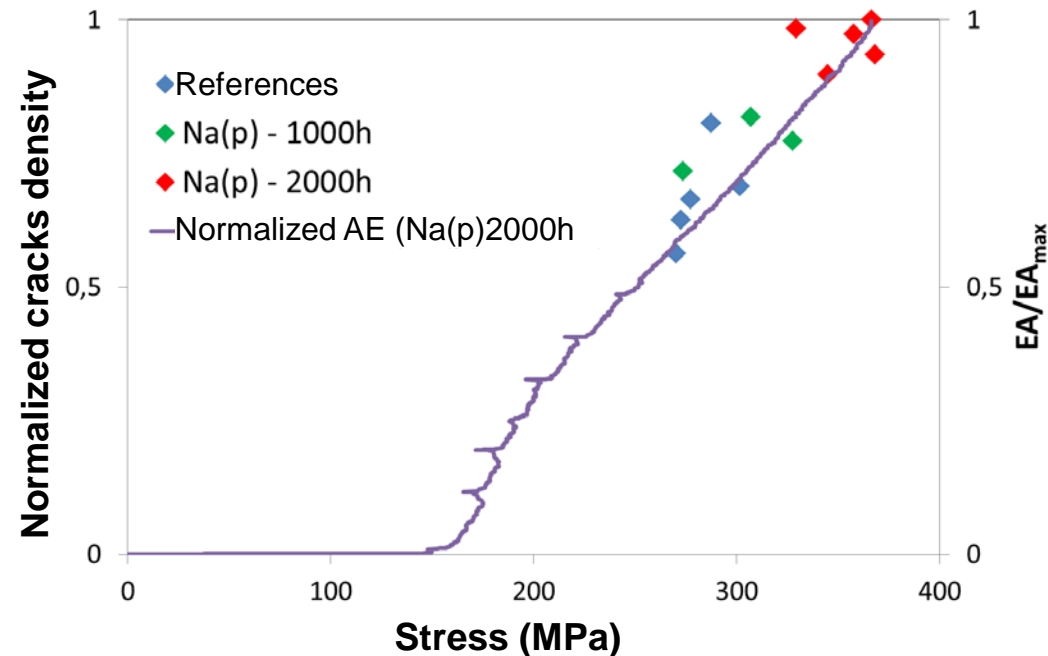
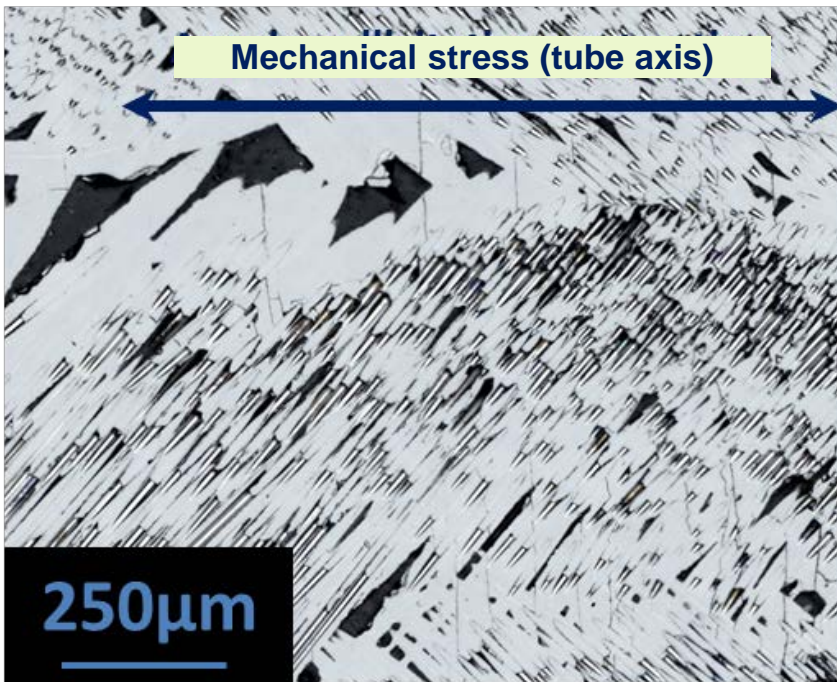
- Increase of the linear elastic range after immersion even if dispersion is noticed
- End of linear elastic range and beginning of acoustic emission are closed
- Phenomenon is more pronounced after longer immersion

Kinetic effect ?

	Deviation from linearity		First Acoustic emission signal	
	ϵ_l (%)	σ_l (Mpa)	ϵ_{EA} (%)	σ_{EA} (Mpa)
Reference	0,012	34	0,053	112
Sodium immersion 2000h	0,041	123	0,046	135

Crack spacing distance:

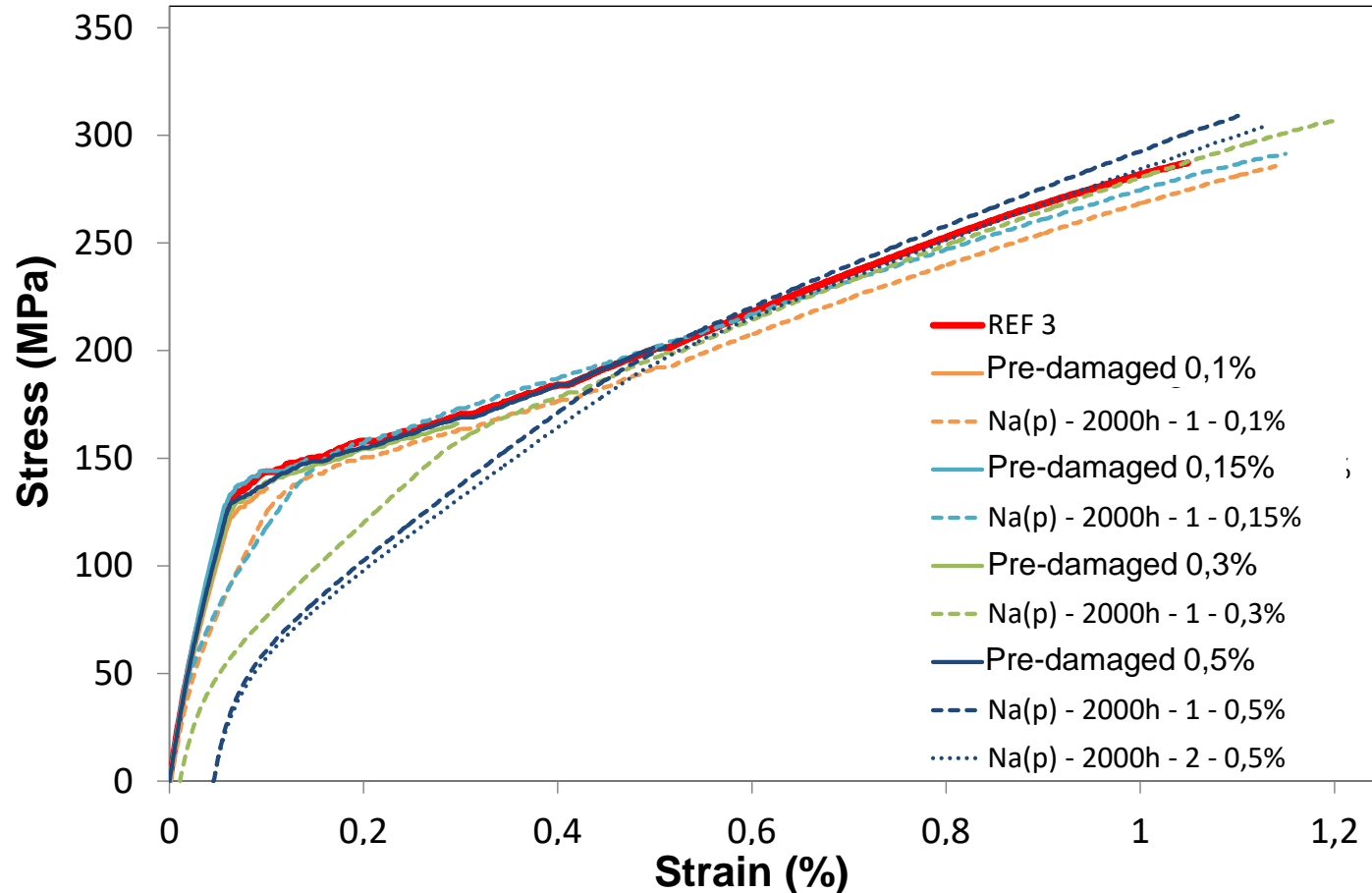
- Bulk crack spacing distance
- Surface crack spacing distance (not representative) :
 - Internal (filament winding)
 - External (2D braiding)



Acoustic emission is a good parameter to follow the evolution of matrix multi-cracking process during mechanical tests

Linear Increase of crack density with stress (no matrix multicracking saturation)

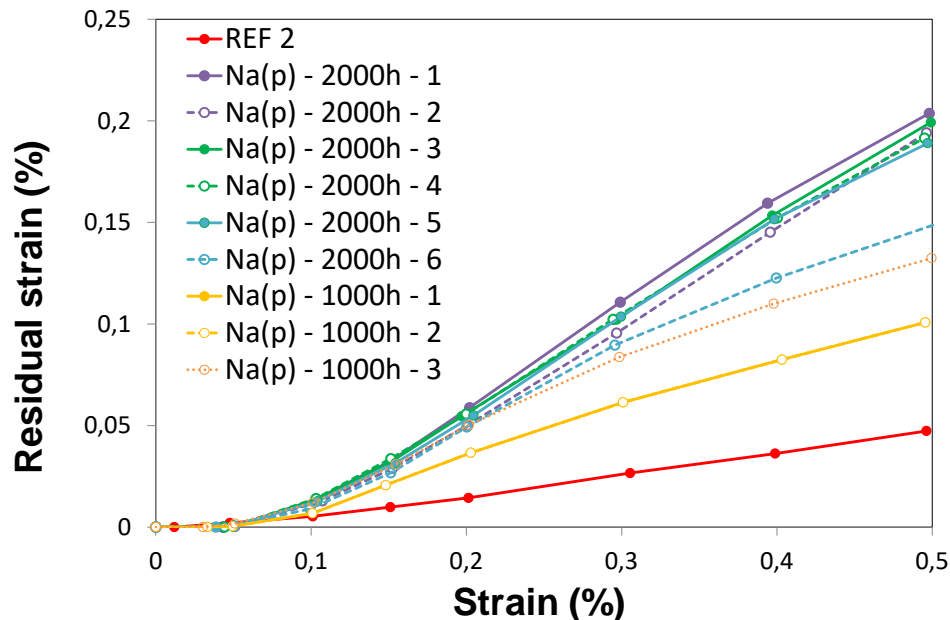
Results of pre-damaged materials



- Same results for Na(O)
- No influence of the pre-damaging on the mechanical properties of composites after immersion in sodium at 550°C up to 2000h.

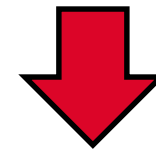
Analysis of loading-unloading cycles during mechanical tensile tests:

- E/E_0 : increase of Young modulus
- $\Delta\varepsilon$ (strain at halfway up) : no evolution \rightarrow fiber/matrix bonding is not modified
- A (area of cycles) and $\Delta W/W$: slight increase
- ε_R (residual strain) : **high increase**



Higher resistance during friction sliding mechanism after immersion

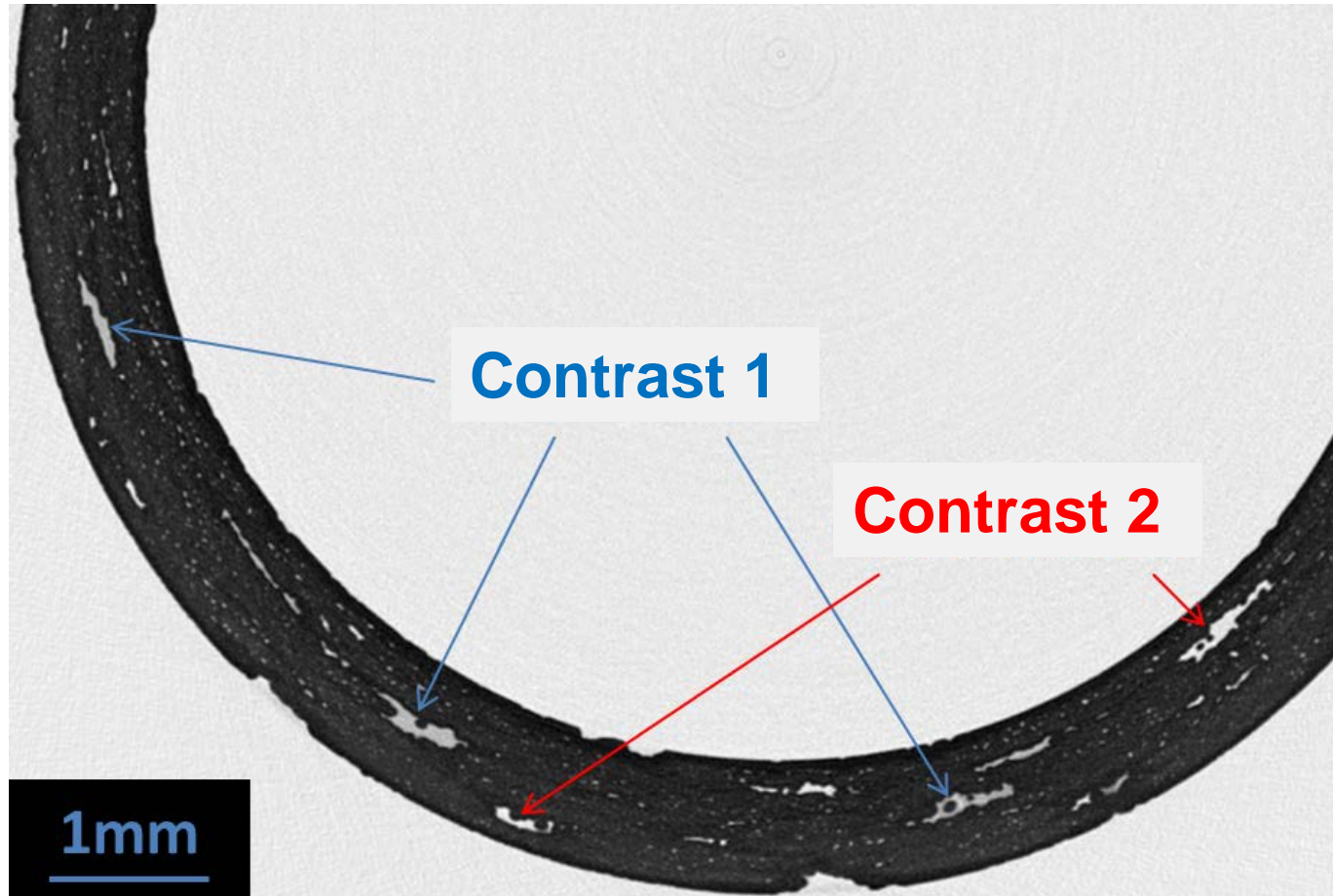
in Na



Reason ?

Tomography experience for a tube section after immersion

- 2 contrasts in porosities of composites: presence of sodium trapped after immersion ?



Video tape during tensile mechanical test after immersion

- Tensile test in air (presence of water vapor and O₂)



- **Off-gassing** → $\text{Na}_{(s)} + \text{H}_2\text{O}_{(g)} = \text{NaOH}_{(s)} + \frac{1}{2} \text{H}_{2(g)}$

- Origin of high residual strains during mechanical unloading after immersion

(presence of reaction products between crack lips that prevents closure of cracks)

■ CVD SiC :

- Slight decrease of Oxide and oxycarbide phases on surface (no weight loss) for Na(p)
- Slight surface oxidation and weight loss for Na(O)

⇒ **SiC is not significantly affected by sodium immersion**

■ SiC/SiC composites :

- **Increase** of stress and strain to rupture for non pre-damaged samples
- No effect of high oxygen concentration in sodium
- No effect of pre-damaging on samples → **Interphase is not affected**
- **Hypothesis : healing of pre-existing cracks by sodium for undamaged samples.**

■ Perspectives :

- Influence of sodium ? (test on SiC/SiC plates)
- Oxidation kinetic of CVD SiC in Na(O)
- Irradiation in BOR60 should give complementary information

SiC/SiC samples in sodium at 550°C and up to 120 dpa neutron irradiation dose!

Questions ?

Commissariat à l'énergie atomique et aux énergies alternatives
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Direction de l'énergie nucléaire

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