# POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

Corso di Laurea Magistrale in Ingegneria dei Materiali

Tesi di Laurea Magistrale

# Selection of Joining Materials for Light Water Reactors



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#### Acronyms

AC: Alternating Current Al: aluminium Ar: argon ATF: Accident Tolerant Fuel B: boron BCC: Body-Centered Cubic **BWR: Boiling Water Reactor** C: carbon CA: Calcia-Alumina CEA: Commissariat à l'énergie atomique et aux énergies alternatives CMC. Ceramic Matrix Composites Cr: chromium CTE: Coefficient of Thermal Expansion Cu: Copper CVD: Chemical Vapour Deposition CVI: Chemical Vapour Infiltration DC: Direct Current dpa: displacement per atom DTA: Differential Thermal Analysis EATF: Enhanced Accident Tolerant Fuel EDF: Électricité de France EDS: Energy Dispersive Spectroscopy EDX: Energy Dispersive X-Rays Fe: iron FE-SEM: Field Emission - Scanning Electron Microscope GHGs: Greenhouse Gases H: hydrogen H<sub>2</sub>O: water HCP: Hexagonal Close Packed

T<sub>m:</sub> Melting Temperature U: uranium UK: United Kingdom UO<sub>2</sub>: uranium dioxide wppm: weight parts per million XRD: X-Rays Diffraction Zr: zirconium ZIRLO: Zirconium Low Oxygen

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## Selezione di materiali di giunzione per reattori ad acqua leggera

Riassunto della tesi di Laurea Magistrale in lingua italiana

#### Introduzione

L'industria energetica si trova di fronte a due sfide impellenti: la necessità di ridurre la quota di energia prodotta da fonti non rinnovabili e quella di incrementare la produzione per soddisfare l'aumento del fabbisogno su scala globale.

L'energia pulita delle fonti rinnovabili dipende fortemente dalle condizioni ambientali. Ciò costituisce un fattore che non agevola la sicurezza energetica fino a quando non saranno disponibili adeguate tecnologie per l'accumulo.

L'energia nucleare permette di ottenere ingenti quantità di energia e garantisce un funzionamento pressoché continuo degli impianti, garantendo l'accesso all'energia prodotta in qualsiasi momento.

Entrambe le tecnologie sono contraddistinte dall'emissione quasi nulla di gas serra, ma l'energia nucleare gode di una pessima immagine nell'opinione pubblica dovuta sia all'elevata percezione del rischio sia alla gestione del combustibile esausto.

L'incidente avvenuto a Fukushima nel 2011 ha riportato alla luce il problema della sicurezza nelle centrali nucleari. La possibilità di un incidente causato da tsunami era stata presa in considerazione nel design della centrale, tuttavia l'altezza massima dell'onda era stata sottostimata. Per questo motivo dopo aver resistito al terremoto, la centrale venne allagata da un'onda di altezza stimata a 14 metri, perdendo l'alimentazione elettrica d'emergenza. Nonostante la reazione a catena all'interno dei rettori fosse stata arrestata nell'istante stesso della perdita dell'alimentazione esterna, causata dal terremoto, il combustibile all'interno dei rettori ha continuato a produrre calore, mentre i sistemi di raffreddamento di emergenza erano fuori uso.

A causa della continua produzione di calore e del fallimento dei sistemi di emergenza, l'acqua venne via via convertita in vapore sino a scoprire le barre di combustibile e limitando sempre più il loro raffreddamento. Tale scenario di incidente è denominato LOCA (Loss Of Coolant Accident).

Le barre di combustibile sono costituite da pellet di urania (UO<sub>2</sub>) contenuti all'interno di tubi in lega di zirconio. Durante il normale funzionamento lo zirconio si ossida gradualmente e in modo controllato secondo la seguente reazione:

 $Zr + 2H_2O \rightarrow ZrO_2 + 4H + calore$ 

In caso di fallimento del sistema di emergenza, il calore si accumula e la temperatura delle barre aumenta. La cinetica della reazione di ossidazione aumenta e la lega di zirconio reagisce rapidamente con l'acqua/vapore producendo grandi quantità di idrogeno e calore. La reazione prosegue nonostante la formazione di zirconia (ZrO<sub>2</sub>) dato che essa ad alta temperatura si comporta come elettrolita solido per l'ossigeno, favorendone la diffusione verso il metallo sottostante dove la reazione di ossidazione prosegue. Inoltre, la formazione di ossido e il progressivo aumento di spessore riducono la conducibilità termica favorendo l'aumento di temperatura delle barre.

L'alta temperatura promuove fenomeni di creep che possono causare fessurazione nelle barre con conseguente esposizione all'ambiente del combustibile e fuga di gas radioattivi. Qualora la temperatura raggiunga livelli critici, il nocciolo del reattore (costituito dall'insieme di barre combustibili) può collassare.

Nel caso di Fukushima i noccioli dei reattori non collassarono, ma le grandi quantità di idrogeno gassoso prodotto dalla reazione di ossidazione dello zirconio furono responsabili delle esplosioni degli edifici di contenimento di quattro reattori con conseguente rilascio di radionuclidi nell'atmosfera.

Il problema legato all'ossidazione delle leghe di zirconio in caso di incidente è noto da tempo. Il trend fino ad oggi è stato quello di implementare maggiormente i sistemi attivi di emergenza per evitare l'incremento di temperatura e le successive conseguenze. Tuttavia, dopo l'incidente di Fukushima l'obiettivo è quello di implementare i sistemi di sicurezza passivi.

A tal fine è necessario modificare le barre di combustibile in modo da limitare i meccanismi di fallimento tipici delle barre realizzate in lega di zirconio.

Lo sforzo del mondo industriale e di quello della ricerca è diretto verso gli Accident Tolerant Fuel (ATF): soluzioni innovative che riguardano sia il combustibile che il rivestimento delle barre combustibile.

Tali sistemi devono garantire rispetto alle leghe di zirconio:

- resistenza all'ossidazione e alla corrosione superiore sia in condizioni operative che in caso di incidente;
- resistenza al creep superiore;
- minore produzione di idrogeno.

Inoltre, al fine di incentivare il loro utilizzo, gli ATF devono essere economicamente convenienti sia per quanto riguarda la loro produzione sia per quanto riguarda l'efficienza neutronica nel reattore.

Tra le soluzioni classificate come a breve termine vi sono quelle basate sul rivestimento delle leghe a base zirconio ad oggi di rilevanza commerciale: M5, Zircaloy-2, Zircaloy-4 e ZIRLO. Tutti i materiali proposti per la realizzazione di rivestimenti sono formatori di ossidi che presentano un comportamento passivante e che possono dunque proteggere il metallo sottostante. Tali ossidi sono: Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> e Cr<sub>2</sub>O<sub>3</sub>.

I candidati principali per rivestire le barre di zirconio sono: cromo, acciai ferritici FeCrAl e fasi MAX (carburi o nitruri ternari). Tra questi, il cromo rappresenta la soluzione industrialmente più rilevante per la realizzazione di rivestimenti nel breve termine. Framatome ha prodotto barre combustibili formate da pellet di UO<sub>2</sub> all'interno di tubi in lega di zirconio M5 rivestita da cromo depositato per Physical Vapour Deposition e attualmente li sta testando in un reattore commerciale.

Soluzioni più a lungo termine prendono in considerazione la sostituzione delle leghe di zirconio con altri materiali. Tra i materiali sostitutivi promettenti oltre alle FeCrAl, c'è il composito SiC/SiC.

La struttura  $\beta$ -SiC ha un'ottima resistenza all'irraggiamento neutronico tra i 150 e 1000°C, ha una maggior resistenza all'ossidazione rispetto alle leghe di zirconio e offre una superiore resistenza meccanica ad alta temperatura. Inoltre, il SiC presenta un basso assorbimento neutronico, proprietà che lo rende molto interessante per l'applicazione.

I compositi SiC/SiC per l'industria nucleare devono essere chimicamente molto puri per evitare differenti risposte all'irraggiamento neutronico da parte delle diverse fasi presenti. La tipica architettura è la seguente:

- Fibre SiC di terza generazione quasi stechiometriche (Hi-Nicalon S o Tyranno SA3). Esse costituiscono la preforma del tubo di SiC/SiC.
- Le fibre sono rivestite via Chemical Vapour Infiltration con carbonio pirolitico oppure con una struttura multistrato di carbonio pirolitico e SiC, al fine di ottenere le proprietà meccaniche richieste al composito.
- La matrice è costituita da SiC depositato sulla preforma tramite Chemical Vapour Infiltration (simile alla CVD), ottenendo una elevata purezza, ma mantenendo elevata la porosità residua (circa 10 %). Un altro approccio è quello di realizzare la matrice tramite sinterizzazione assistita da liquido usando nano polveri di β-SiC e ossidi fondenti come Al<sub>2</sub>O<sub>3</sub> e Y<sub>2</sub>O<sub>3</sub>. Tale processo è brevettato come Nano Infiltration and Transient Eutectic- phase (NITE) process.
- Infine, un rivestimento di CVD-SiC è depositato come barriera.

Le principali criticità legate all'utilizzo di SiC/SiC per realizzare tubi ATF sono:

- la mancanza di dati disponibili;
- l'inesistenza di una tecnica di giunzione affidabile e riproducibile tale da poter essere utilizzata per giuntare tubo e tappo dopo aver caricato il combustibile.

Esistono molteplici tecniche di giunzione utilizzabili per i compositi SiC/SiC, ma poche tra esse sono promettenti per l'utilizzo in campo nucleare. Le proprietà richieste alle giunzioni per poter essere utilizzate in questo tipo di applicazione sono:

- ermeticità;
- resistenza alla corrosione in condizioni operative e durante eventuali incidenti;
- resistenza alla radiazione neutronica.

Uno dei problemi per i trattamenti di giunzione che si basano sulla diffusione allo stato solido è la necessità di applicare pressione e di operare ad alte temperature, alzando i costi di processo e rischiando di danneggiare le fibre.

Tra i processi che non richiedono pressione ci sono quelli basati sull'uso di leghe brasanti o di materiali vetro-ceramici.

Il vantaggio dei materiali vetro-ceramici è quello di permettere di selezionare le proprietà desiderate tramite l'opportuna scelta di ossidi in funzione dell'applicazione. Il sistema vetroso più promettente è il SAY (silice-allumina-ittria) che presenta una buona bagnabilità sul SiC, ha un coefficiente di dilatazione termica vicino a quello del SiC e sino ad oggi ha mostrato buone proprietà sotto irraggiamento. Il vetroceramico CA (calcia-allumina), anch'esso di interesse per applicazioni nucleari, non può essere utilizzato per i reattori ad acqua leggera a causa della sua elevata sensibilità all'umidità.

Una tecnica di giunzione interessante per i compositi SiC/SiC è il processo Mo-Wrap. Tale processo non richiede l'applicazione di pressione e permette di ottenere un materiale di giunzione composito: il MoSi<sub>2</sub>/Si. Un wafer di silicio è inserito all'interno di fogli di molibdeno e trattato termicamente: il silicio fonde e reagisce con il molibdeno, formando particelle di siliciuro, e dando origine alla matrice.

Un aspetto importante è il controllo delle frazioni in peso di molibdeno e silicio al fine di ottenere una giunzione ottimale. La composizione per ottenere una giunzione ottimale prevede:

- 32-35 wt% Mo.
- 65-68 wt %Si.

La possibilità di effettuare il trattamento di giunzione senza applicare pressione, rende questo processo interessante per la giunzione dei tubi SiC/SiC.

#### Attività sperimentale

Il Politecnico di Torino partecipa al progetto europeo Il Trovatore (<u>http://www.iltrovatore-h2020.eu/</u>). Tale progetto ha come obiettivo quello di identificare e ottimizzare alcune delle più promettenti proposte di ATF per i rettori ad acqua leggera.

All'interno del progetto il Politecnico di Torino ha come obiettivi:

- Selezionare possibili metodologie di giunzione.
- Giuntare SiC e compositi SiC/SiC forniti dai partner di progetto.
- Testare meccanicamente le giunzioni.

Questa tesi magistrale copre parzialmente i primi due obiettivi. Di seguito è riportato lo schema di flusso del lavoro sperimentale svolto.



Figura.1: diagramma di flusso della prima parte del lavoro sperimentale

#### Preparazione delle giunzioni di CVD-SiC

Dallo stato dell'arte sono stati selezionati due materiali di giunzione: il vetroceramico SAY e il MoSi<sub>2</sub>/Si prodotto tramite approccio Mo-wrap. Entrambi i materiali sono stati sviluppati all'interno del gruppo di ricerca GLANCE (<u>http://www.composites.polito.it/</u>), presso il dipartimento DISAT del Politecnico di Torino.

I materiali da giuntare utilizzati sono riportati di seguito:

- CVD SiC (10 mm x 10 mm x 5 mm);
- NITE (Nano Infiltration and Transient Eutectic-phase) SiC/SiC, inviato da NITE Corporation (Prof. A. Kohyama). Il NITE SiC è stato fornito in forma di piastrella con dimensioni 58 mm x 58 mm x 3 mm, dalla quale sono state tagliate fette più piccole con l'utilizzo di una troncantrice.
- Tubi CVI (Chemical Vapour Infiltration) SiC/SiC inviati da CEA (Commissariat à l'énergie atomique et aux énergies alternatives). Le dimensioni dei tubi sono le seguenti:
  - o lunghezza: 10 mm;
  - o diametro interno: 8.35 mm;
  - o diametro esterno: 9.56 mm.

Nel primo step sono stati realizzati 7 provini per ciascuna tecnica di giunzione utilizzando esclusivamente il CVD-SiC come substrato. Di questi tre giuntati SAY e tre giuntati con MoSi<sub>2</sub>/Si sono stati rivestiti con 6 µm di cromo, utilizzando Magnetron PVD Sputtering, al fine di valutare la sua efficacia nell'aumentare la resistenza alla corrosione della giunzione.

Tale scelta è stata fatta perché i compositi SiC/SiC di grado nucleare sono molto costosi e dunque è risultato più conveniente fare le prime valutazione sul CVD SiC, che è il materiale di rivestimento per i compositi.

Per realizzare la giunzione mediante il processo Mo-wrap sono stati utilizzati:

- fogli di molibdeno 99,95% con spessore 0.025 mm (Alfa Aesar);
- wafer di silicio di spessore 584 μm (MEMC Electronic Materials).

Il wafer di silicio è stato tagliato e inserito all'interno di due fogli di molibdeno. Secondo lo schema in fig.2. Wafer e fogli sono stati pesati in modo tale da mantenere le proporzioni in peso al 32-35wt% di Mo e 65-68wt% di Si.



Figura 2: schema del Mo-wrap

L'involucro così ottenuto è stato interposto tra i due pezzi di SiC ed è stato sottoposto a trattamento termico:

- Rampa termica: 16.6 °C/min.
- Temperatura di trattamento: 1450°C.
- Tempo di trattamento: 5 minuti.
- Atmosfera inerte (flussaggio di argon).

Il vetro SAY è stato ottenuto partendo da polveri di ossidi secondo la composizione in peso riportata in tabella 1:

SiO <sub>2</sub> (silice)	Y <sub>2</sub> O <sub>3</sub> (ittria)	$Al_2O_3$
54 wt%	27.93 wt%	18.07 wt%

Tabella 1: composizione del SAY

Le polveri sono state trattate termicamente all'interno di un crogiolo platino-rodio per 5 ore a 1700°C, in aria, e colate su un piatto di ottone. Il vetro è stato poi macinato in 3 granulometrie distinte: >75  $\mu$ m, 38-75  $\mu$ m e <38  $\mu$ m.

Un altro lotto di SAY è stato prodotto seguendo la stessa metodologia, fatta eccezione per quanto concerne la fusione delle polveri condotta a 1750°C per 1 ora in aria. Questo secondo lotto è stato caratterizzato tramite diffrattometria ai raggi X e tramite analisi termica differenziale (DTA) per valutarne le proprietà. La caratterizzazione ha permesso di appurare che il vetro ottenuto era totalmente amorfo e che le temperature caratteristiche sono in linea con quelle osservate per SAY ottenuto dopo 5h a 1700°C, permettendo di utilizzare lo stesso trattamento di giunzione.

La polvere di vetro SAY utilizzata per le giunzioni era di granulometria 38-75 µm. Con la polvere è stato realizzato uno slurry a base etanolo che è stato distribuito sulla superficie del SiC, prima di sovrapporre la controparte.

Il trattamento di giunzione per il SAY è il seguente:

- Rampa termica: 16.6 °C/min
- 20 min a 1375 °C.
- 1 h a 1235 °C.
- Atmosfera inerte: flussaggio di argon.

La caratterizzazione delle giunzioni è stata condotta con le seguenti tecniche:

- Microscopia SEM (Scanning Electron Microscopy) + Analisi EDX (Energy Dispersive X-ray Analysis).
- Micro Computed Tomography scan, condotta dal gruppo del professor James Marrow alla Oxford University.
- Diffrattometria ai raggi X.

La fig. 3 mostra la microstruttura del materiale di giunzione MoSi<sub>2</sub>/Si dopo il trattamento di giunzione. Le particelle bianche sono MoSi<sub>2</sub>, si trovano uniformemente disperse all'interno della matrice di silicio. Nessuna cricca è osservabile nella giunzione. La buona bagnabilità del silicio sul SiC garantisce una buona interfaccia, priva di difetti.



Figura 3: microstruttura del materiale di giunzione MoSi2/Si ottenuto con processo Mo-wrap

La microstruttura del MoSi<sub>2</sub>/Si è coerente con quella identificata nella tesi di dottorato di Gianchandani P. K.

Il SAY permette di ottenere un'interfaccia continua e priva di difetti (fig. 4). Tuttavia, vi sono zone in cui compaiono vuoti apprezzabili dovuti alla tecnica di deposizione. Vuoti di piccola taglia possono invece essere imputabili al ritiro del vetroceramico durante il trattamento di devetrificazione. L'assenza di cricche è un buon indice di compatibilità tra il coefficiente di dilatazione termica del vetroceramico e quello del SiC. La microstruttura del SAY è coerente con quanto riportato negli articoli di riferimento.



Figura 4: microstruttura della giunzione con SAY

#### Test in autoclave (SCK-CEN)

Il test in autoclave statica ha avuto l'obiettivo di fornire prime indicazioni sulla resistenza alla corrosione dei materiali proposti in condizioni vicine a quelle operative. Il test è stato condotto al SCK-CEN (Centre d'étude de l'énergie nucléaire) in Belgio.

Le condizioni simulate erano quelle tipiche di un rettore ad acqua leggera pressurizzata (PWR):

- Composizione dell'acqua: boro (1000 ppm), litio (2ppm).
- 330°C.

Il test è stato condotto per 14 giorni sui seguenti campioni:

- SiC giuntato con SAY.
- SiC giuntato con SAY con rivestimento di cromo.
- SiC giuntato con Mo-wrap.
- SiC giuntato con Mo-wrap con rivestimento di cromo.
- MoSi<sub>2</sub>/Si (pastiglia).

Sono stati inoltre testati dei materiali come riferimento:

- Wafer di silicio
- Wafer di silicio rivestito con cromo
- Segmento di tubo in Zircaloy-4 (fornito da SCK-CEN, Belgio).

Di interesse è la variazione in peso dei campioni misurata dopo il test che è indice della loro resistenza alla corrosione, riportata in fig. 5.



Figura 5: risultati del test in autoclave statica (SCK-CEN, Belgio)

Il SiC giuntato con SAY ha mostrato una migliore resistenza alla corrosione confrontato con il SiC giuntato con Mo-wrap, riportando una variazione in peso prossima allo zero (-0,35% contro -1,46%).

Il silicio non rivestito è stato del tutto dissolto in autoclave. In merito alle cause della dissoluzione nelle condizioni di autoclave non è stata trovata letteratura.

La pastiglia di  $MoSi_2/Si$  ha perso circa il 35% in peso. Tale risultato è coerente con la dissoluzione del silicio.

L'effetto positivo del rivestimento di cromo è apprezzabile considerando il wafer di silicio: quello privo di rivestimento è stato dissolto, mentre quello rivestito ha esibito una perdita in peso del 17,6%.

I provini di SiC giuntato con SAY e di SiC giuntato con Mo-wrap rivestiti con cromo (6  $\mu$ m), hanno perso il rivestimento e dunque non è stato possibile verificare se esso permettesse di migliorare la resistenza alla corrosione anche nel caso delle giunzioni proposte.

I risultati del test in autoclave, hanno suggerito che la soluzione Mo-wrap priva di rivestimento non è adatta all'applicazione a causa della dissoluzione subita dalla matrice, costituita da silicio, nelle condizioni ambientali del reattore.

Dopo il test in autoclave, i campioni testati sono stati caratterizzati per studiare la microstruttura e l'eventuale trasformazione di fasi.

#### Caratterizzazione delle giunzioni dopo l'autoclave

Il SAY dopo autoclave si presenta danneggiato in superficie (fig. 6). Il danneggiamento motiva la perdita in peso riscontrata dopo il test in autoclave. Il SiC giuntato con SAY dopo lucidatura presenta una microstruttura non modificata (fig. 7) con interfaccia continua e priva di difetti.

La diffrattometria ai raggi X sulla giunzione non lucidata (fig. VI) conferma la presenza delle fasi cristalline tipiche per questo vetro ceramico: keyvite (Y<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>), cristobalite (SiO<sub>2</sub>), mullite (Al<sub>4.95</sub>Si<sub>1.05</sub>O<sub>9.52</sub>). La presenza del SiC è dovuta al substrato.



Figura 6: SiC giuntato con SAY dopo autoclave



Figura 7: SiC giuntato con SAY lucidato dopo autoclave



Figura 8: diffrattometria ai raggi X sul SiC giuntato con SAY dopo autoclave

La caratterizzazione del SiC giuntato con Mo-Wrap ha invece confermato la perdita della matrice, spiegando la perdita in peso rilevata (fig. VIII). L'analisi EDX condotta sulla giunzione ha evidenziato che la matrice è ancora presente in alcune zone della giunzione e che nelle sferette è riscontrabile una elevata presenza di ossigeno a discapito del silicio, suggerendo ossidazione dei siliciuri.



Figura 9: micrografia della giunzione con Mo-wrap dopo autoclave

L'ossidazione ha trovato riscontro con la diffrattometria ai raggi X: nello spettro sono identificabili solo il MoO<sub>2</sub> e il silicio, non c'è traccia di MoSi<sub>2</sub> (fig. 10).



Figura 10: diffrattometria ai raggi X MoSi2/Si dopo autoclave

L'ossidazione del MoSi2 richiede ulteriori analisi per essere confermata.

Alla luce dei risultati ottenuti dal test in autoclave e della successiva caratterizzazione eseguita sui campioni testati, si è scelto di escludere il  $MoSi_2$  come materiale da giunzione e di utilizzare esclusivamente il SAY per giuntare i compositi SiC/SiC.

#### Giunzione dei compositi SiC/SiC

La seconda fase della parte sperimentale è incentrata sulla giunzione dei compositi proposti per la realizzazione delle barre di combustibile: CVD SiC/SiC (*CEA*, Francia) e NITE SiC/SiC (*NITE Corporation*, Giappone).

I tubi CEA sono stati giuntati testa a testa attraverso l'utilizzo di un porta-campioni appositamente costruito per mantenere l'allineamento dei tubi. Il vetro SAY è stato depositato in forma di slurry e successivamente il sistema è stato sottoposto al trattamento di giunzione. In fig. 11 sono mostrati due tubi CEA giuntati.



Figura 11: tubi CEA giuntati con SAY

La zona di giunzione è stata studiata con la micro CT-Scan (eseguita dal gruppo del prof. James Marrow, Oxford University, UK) e il SEM. Le analisi hanno evidenziato che la maggior parte dell'area di giunzione è priva di vetro-ceramico, presumibilmente a causa della fuoriuscita della polvere durante l'impilaggio dei tubi. In fig.12 è mostrata una sezione della zona di giunzione ottenuta con la micro CT-scan. All'interno della zona di giunzione non vi è quasi traccia di vetro-ceramico, che si trova quasi totalmente sulla faccia esterna e in misura minore sulla faccia interna.

Tali risultati suggeriscono una bassa resistenza meccanica della giunzione, pur non avendo condotto prove meccaniche. Pertanto, la giunzione testa a testa per spessori di parete così sottili non sembra essere la soluzione ottimale. È necessario studiare nuovi tipi di configurazione per le giunzioni di tubi.

Le giunzioni di NITE SiC/SiC sono tuttora in fase di caratterizzazione.



Figura 12: Sezione dell'area di giunzione di tubi CEA ottenuta mediante micro CT-scan (gruppo di ricerca del prof. J. Marrow, Oxford University, Regno Unito)

#### Test sul comportamento del vetro-ceramico SAY ad alta temperatura

Dal momento che il SAY ha come obiettivo quello di giuntare barre classificate come ATF, è importante valutare il suo comportamento ad alte temperature. Per anticipare futuri test e ottenere delle prime valutazioni si è scelto di studiare il materiale al microscopio riscaldante e di effettuare delle prove di creep.

Al microscopio riscaldante è stata studiato del SAY (<38  $\mu$ m) sottoposto al trattamento di giunzione. L'altezza del campione non ha subito alcuna modifica sino alla temperatura di 1362°C e dopodiché ha esibito una decrescita con tratto quasi verticale fino a 1391°C (fig. 13). Le temperature caratteristiche identificate dalla microscopia riscaldante sono in accordo con la letteratura riguardante il SAY che individua la temperatura di fusione a 1377°C per il sistema silice-allumina-itrria proposto.

La maggior parte dei test in cui viene simulato uno scenario di incidente con perdita di refrigerante è condotto intorno ai 1200°C in aria o in vapor d'acqua. Il SAY non mostrando deformazioni sotto il proprio peso- durante la prova- sino ai 1362°C ha dato risultati incoraggianti.

Altra informazione utile è che l'andamento ottenuto al microscopio riscaldante indica che non è presente fase vetrosa residua dopo il trattamento, confermando quanto evidenziato in studi precedenti.



Figura 13: risultati miscroscopia riscaldante (in colore blu è riportato l'andamento dell'altezza del campione)

Le due prove di creep sono state condotte sulla medesima pastiglia di SAY nelle seguenti condizioni:

- Prima prova: 1200°C, 1 h, 9,3 kPa.
- Seconda prova: 1250°C, 1 h, 26 kPa.

I risultati del test sono riportati in tab. 2.

Materiale	Peso applicato (g)	Pressione di carico (kPa)	Diametro iniziale (mm)	Diametro finale (mm)	Altezza iniziale (mm)	Altezza finale (mm)
SAY	59	9,3	8,87-8,92	8,87-8,92	8,40-	8,40-
					8,43	8,43
SAY	166	26	8,87-8,92	8,89-8,92	8,40-	8,40-
					8,43	8,46

Tabella 2: prove di creep condotte sul SAY

Nessuna variazione dimensionale è stata evidenziata.

#### Autoclave dinamica (SCK-CEN)

Il SAY massivo e due campioni di SiC giuntato con SAY non rivestiti sono stati testati al SCK-CEN per 30 giorni in autoclave dinamica.

- Composizione dell'acqua: simile a quella di rettore ad acqua pressurizzata
- 330°C

Rispetto alla prova in autoclave statica in questo caso il profilo di pressione non è costante, ma varia durante la prova.

I campioni SiC giuntato con SAY non hanno superato il test mostrando un netto distacco all'interfaccia SAY/SiC (fig. 14).



Figura.14: Giunzioni SiC/SAY dopo autoclave dinamica

Tale risultato rimette in discussione il SAY come materiale di giunzione, senza rivestimento, per l'applicazione. Future analisi serviranno a capire le motivazioni del distacco.

#### Conclusioni

Tra i due materiali proposti per la giunzione di SiC/SiC solo il vetro-ceramico SAY è stato selezionato come promettente per l'applicazione.

Dopo il test in autoclave statica, il SAY ha riportato una perdita in peso trascurabile. La successiva caratterizzazione ha mostrato che la microstruttura e le fasi presenti sono rimaste invariate.

Il MoSi<sub>2</sub>/Si è risultato inadatto per l'applicazione. La matrice di silicio del MoSi<sub>2</sub>/Si è stata quasi del tutto dissolta in autoclave e i siliciuri sono stati ossidati (risultato che richiede ulteriori conferme).

L'approccio Mo-Wrap è stato pertanto scartato, mentre il SAY è stato utilizzato per giuntare i compositi SiC/SiC.

I tubi CEA SiC/SiC sono stati giuntati testa a testa, ma è stato osservato che questo tipo di design non permette di ottenere una buona distribuzione del vetro-ceramico all'interno dell'area di giunzione. Per questo motivo è indispensabile utilizzare nuove configurazioni al fine di incrementare l'area della giunzione. Le future giunzioni non saranno più effettuate tra tubi, ma direttamente tra tappo e tubo, nell'ottica dell'applicazione finale.

La caratterizzazione delle giunzioni NITE SiC/SiC con SAY è ancora in corso.

Il microscopio riscaldante ha evidenziato una buona stabilità termica del SAY sino a 1265°C, risultato che, insieme alle prove di creep effettuate, è incoraggiante per l'applicazione di questo materiale nella giunzione di barre ATF.

Il distacco all'interfaccia riscontrato dopo autoclave dinamica ha rimesso in discussione l'effettiva possibilità di utilizzare il SAY come materiale di giunzione. È necessario comprendere le motivazioni del fallimento della giunzione per validare o meno il SAY come materiale di giunzione.

È importante studiare le soluzioni di rivestimento. Occorre comprendere le ragioni del fallimento del rivestimento durante il test in autoclave in modo tale da valutare l'efficacia del cromo come protezione. Nuovi test verranno effettuati variando le condizioni di deposizione del cromo e variando lo spessore dello strato depositato. Eventuali modifiche superficiali del substrato verranno prese in considerazione.

Un altro potenziale candidato come materiale di rivestimento è il CVD-SiC, che ha il vantaggio di essere il medesimo utilizzato per il rivestimento dei tubi SiC/SiC di CEA. Le giunzioni di tubi realizzate con SAY verranno rivestite in CVD-SiC da CEA e saranno poi testate.

Futuri test necessari per valutare l'efficacia del SAY per l'applicazione sono:

- Test di ossidazione a 1200°C in vapore per 1 h per simulare la perdita di refrigerante.
- Test di irraggiamento neutronico.

Per quanto concerne le giunzioni dei tubi è importante ottimizzare il design per agevolare la deposizione e incrementare l'area di giunzione tra tappo e tubo. Le nuove giunzioni dovranno poi essere testate meccanicamente per valutare la resistenza a taglio della giunzione.

Ad oggi, non va escluso l'uso del SAY come materiale da giunzione, nonostante gli esiti del test in autoclave dinamica. Nel caso in cui non fosse possibile utilizzarlo tale e quale, l'uso di rivestimenti potrebbe ridurre drasticamente la corrosione del materiale e quindi permetterne l'utilizzo permettendo di sfruttare la buona stabilità termica e il processo di giunzione offerti da questo vetroceramico.

## Introduction

### 1 Why are new materials required for Light Water Reactors?

The 2030 Agenda for Sustainable Goals [1] is a commitment signed by all members of the United Nations, whose aim is to pursue a sustainable development for the entire planet.

In this context, energy has an important role because it is involved in the achievement of several goals, from climate change mitigation to social inclusion.

Access to energy is crucial to guarantee a sustainable development all over the world. An increase in the energy production is needed to enable a rapid economic growth in poorer countries. The implementation of the global power production must be pursued without harming human health and the environment. For this reason, a progressive reduction of fossil fuels in global production is required to reduce issues related to greenhouse gases emissions and the formation of harmful products as PM (Particulate Matter) 2.5- particulates under 2,5  $\mu$ m.

Reducing the impact of energy on the environment while increasing power capacity can bring to a massive electrification. This would lead to lower greenhouse gases (GHGs) emissions produced by transport sector.

Implementing the sustainability of the power sector requires to reduce the use of fossil fuels by substituting them with renewable energies, nuclear power and investing on carbon dioxide capture technologies[2].

Advantages provided by nuclear power are high security of energy supply and low GHGs emission, but there are many arguments against its use. Risk perception linked to this technology is high in the population, there are risks of nuclear weapon proliferations and there are issues about the management of spent fuel. It is necessary to find solutions to enhance the likability of nuclear power to propose it as a solution for energy transition [3].

With the aim to increase their energy security and to substitute fossil fuels, about 30 countries in the world are planning to start their own nuclear program. Currently in the world there are 407 operating nuclear reactors and 59 are under construction. Among them, Light Water Reactors (LWRs) are the 83% of the operating reactors and they constitutes the 90% of those under construction (fig. 1.1) [4].

So, according to IAEA (International Atomic Energy Agency) data, LWRs are the most common nuclear reactor type. They can be categorized in Boiling Water Reactors (BWRs) and Pressurised Water Reactor (PWRs). Both of them work using natural water as coolant and as neutron moderator. However, they exhibit a main difference: in BWRs water is directly converted in steam inside the reactor, while in PWRs this does not occur.



Figure 1.1: Types of nuclear reactors currently in the world (on the left) and those under construction (on the right). Blue colour indicates Pressurised Water Reactors, red colour Boiling Water Reactors [4].

An overview on PWRs and BWRs is provided.



#### 1.1 Pressurised Water Reactor

Figure 1.2: Scheme of PWR [5]

A PWR plant consists of different systems[6]:

Pressure vessel

Pressure vessel hosts the reactor core. The core is composed of fuel rods groped in square assemblies, whose number depends on the size of the vessel. Each 4 metres long fuel rod consists of fuel -uranium dioxide- enveloped in a cladding tube made of zirconium alloys.

The core is where fission reaction occurs. Control on reactivity is achieved selecting a proper water chemistry – borated water is used- and inserting in the core the desired number of control rods. Control rods are made of a silver-indium-cadmium alloy (80wt% Ag, 15wt%In-5wt%Cd) which has excellent neutron absorption properties[7]. Control rods are positioned in the upper part of the vessel and they are lowered in the core from the top. In the event of accident, chain nuclear fission reaction must be immediately stopped, so all the control rods are lowered to shut down the reactor.

Material selected for the vessel is steel. Nozzles are disposed symmetrically around the cylindric vessel and they connect it to the primary loop.

#### <u>Coolant system</u>

The coolant system connects the pressure vessel to the steam generators. Its main task is to remove heat from the core using it for energy production. Coolant fluid is water, it enters in the pressure vessel at approximately 290°C and exit, after the heat exchange with the fuel rods, at about 325 °C. Keeping water liquid in these conditions require pressurisation. Pressure is about 15 MPa.

Pressure must be controlled inside the reactor to avoid local boiling. This is possible using a pressuriser, a surge tank partially filled with steam and partially with water. When a change of pressure occurs in the primary loop, pressurizer resets pressure to the desired value by changing the equilibrium conditions between the two phases. This is possible using heaters and sprays inside the pressuriser. Sprays allow to condense steam bringing to a decrease in pressure inside the primary circuit. Heaters do the opposite evaporating water. There are also relief valves which are a passive safety system to prevent over-pressurisation.

When water exits from the pressure vessel, it reaches the steam generators. Here it exchanges heat with a secondary circuit evaporating low-pressurised water. Steam is dried and then reaches turbine where electricity is produced.

If the reactor is tripped, decay heat is removed first by steam generators and then another system comes into operation cooling water by heat exchange with another loop. This safety system is the Reactor Heat Removal System (RHRS) and it becomes operational when coolant temperature is lower than 180°C and the pressure lower than 3.2 MPa.

#### <u>Containment</u>

The coolant system and the pressure vessel must be surrounded by a containment building which can have different designs. Its main task is the insulation of the reactor to prevent

interactions with the environment, protecting against the release of radionuclides in accident scenarios.



#### **1.2 Boiling Water Reactor**

Figure 1.3:Scheme of BWR [5]

As can be observed in figure 1.3, the BWR provides a single loop for water. No steam generation is required, because steam is directly produced inside the primary loop. Heat transfer is more effective because the thermo-vector fluid can absorb more heat thanks to the evaporation latent heat. The higher effectiveness of heat transfer enables to pump water in the vessel at a lower rate compared to PWRs. Water enters in the core from the bottom, pumped via circulation pumps. It passes through the core and boils. At the top of the reactor the steam exits and reaches the turbines generating electricity and after that it is condensed and repumped into the core.

Steam is radioactive, so containment is not only required for pressure vessel and the primary loop, but also for the turbine building.

Vessel must stand lower pressure, about 7 MPa. So, typically BWR vessels have thinner walls compared to PWR one. Fuel rods design is quite identical to that used in PWR and they are disposed in configuration close to that observable in PWR. A major difference is that for BWR

is not possible to locate the control rods on the top of the core because of steam, so they entered in the core from the bottom.

#### 1.3 Zirconium alloys

Zirconium alloys are the standard choice as fuel cladding for LWRs. In table 1.1 are reported the most important commercial alloys[8].

Reactor type	Zr alloy composition	Thermomechanical treatment
BWR	Zircaloy-2 (1.5% Sn-0.15% Fe-0.1% Cr-0.05% Ni)	Recrystallized
PWR	Zircaloy-4 (1.5% Sn-0.2% Fe-0.1% Cr)	Cold-worked and stress relief anneal
PWR	ZIRLO (1-2% Nb-1% Sn-0.1% Fe)	Quench and temper/stress relief anneal
PWR	M5 (1% Nb)	Recrystallized

Table 1.1: Common commercial alloys for LWRs

Zirconium was first proposed as fuel cladding in 1949 during the development of the United States nuclear propulsion program for submarines. The first nuclear submarine, the Nautilus, was driven by a PWR reactor containing fuel rods made of Zircaloy-2[9].

Zirconium is a metal, with a melting point of 1852°C[10]. It can be extracted from zircon (Zr,Hf-SiO<sub>4</sub>) and from complex silicates and oxides which can be found in nature. All these minerals contain also Hafnium in a small amount and this constitute an issue for nuclear application, due to the high neutron cross-section of this element which is detrimental for neutron economy. Hafnium finds application as material for control rods and it must be removed to get nuclear grade zirconium.

In table 1.2 are reported neutron absorption cross section for different elements. As can be noticed zirconium exhibits a quite low value. Beryllium is the metal that provides the lower value of neutron absorption cross section, but it cannot be used to realise fuel cladding tubes because it is very sensitive to radiation induced embrittlement[11]. Aluminium and magnesium can provide comparable neutron absorption with zirconium, but they are not suitable due to their low melting point. First reactors used stainless steel as cladding material, but as can be seen in the table, iron exhibits a quite high cross-section, causing a remarkable reduction in neutron utilisation compared to that achievable using zirconium alloys[12].

Elements	Neutron absorption cross section (Barns)
Ве	0.009
С	0.004
Mg	0.063
Si	0.16
Zr	0.185
Al	0.231
Mo	2.48
Cr	3.05
Nb	1.15
Fe	2.55
Ni	4.43
V	5.04
Sn	0.63

Table 1.32: neutron absorption cross section of different elements [11]

Low neutron absorption cross section is an important property for nuclear applications, but pure zirconium does not exhibit enough corrosion resistance and mechanical properties. To improve these properties, zirconium alloys are used. They provide remarkable features for the application:

- Resistance to corrosion in an aqueous environment and in steam at reactor working temperature.
- Good thermal conductivity.
- Good mechanical strength at the reactor operating temperature.

Pure zirconium at room temperature exhibits an anisotropic hexagonal crystal structure. Near 800 °C transformation from HCP (alpha phase) to BCC (beta phase) starts and it is completed at around 980°C[13]. It is important to avoid a phase transformation during the operations and LWRs operate at temperatures plenty lower in normal conditions.

Zirconium alloys are used since the beginning of the civil use of nuclear power. Over the years different alloys have been developed to enhance performances in LWRs. Fig. 1.4 shows the most used zirconium alloys from the 1950s until today.

1940	1950	1960	1970	1980	1990	2000	2010	2020	Remarks
Stainle	ass steel								Obsolete
				Zircaloy-2 ar	nd Zircaloy-4				
					E110,	E125, E635			in
					1	ZIRLO			commercial use
						N	15		
							OP	TZIRLO	in
							[	X5A	phase

Figure 1.4: Timetable for cladding materials [13]

First remarkable commercial zirconium alloys are Zircaloy-2 (for BWR) and Zircaloy-4 (for PWR), which have been used in reactors since 1950s. Their compositions [9] are reported in table 1.3.

Table 1.3: compositions of Zircaloy-2 and Zircaloy-4

Element	Zircaloy-2 (wt%)	Zircaloy-4 (wt%)
Sn	1.5	1.5
Fe	0.1	0.2
Cr	0.1	0.1
Ni	0.1	-
Oxygen	1400 ppm max.	1400 ppm

Alloying elements in these alloys are tin, iron, chromium and nickel.

Tin is an  $\alpha$ -Zr stabilizer. It was initially used to enhance corrosion resistance by contrasting the effects of nitrogen, deleterious when it overcomes about 0.07wt%. Today it is possible to control better the intake of nitrogen by optimising the manufacturing process and this enables reduction in tin weight percentage. Furthermore, tin can modify mechanical properties increasing the yield strength[11]. Although tin is effective in reducing the detrimental effect of N on corrosion, high amount of Sn decreases corrosion resistance as well.

Iron, nickel and chromium are  $\beta$ -stabilizer; they enhance the corrosion resistance, the creep resistance and the strength of the Zircaloy. Chromium and iron have a limited solubility in zirconium, so during the transformation from cubic to hexagonal structure, they tend to form intermetallic compounds providing strengthening. Furthermore, Cr and Fe reduce the hydrogen pick-up. Nickel must be limited because it increases the amount of hydrogen pick-up.

Zirconium tubes are manufactured by hot working. When zirconium alloy is cooled, depending on cooling rate it can undergo through a martensitic or a bainitic transformation. The manufacturing process exploits the cell anisotropy to tailor the grain texture: c-axis is oriented in thickness and a-axes and b-axes are oriented parallel to the tube length.[14]. Zirconium-based cladding microstructure after recrystallisation and after rolling are provided in fig. 1.5.



Figure 1.5: On the left zirconium alloys after recrystallisation, on the right the same alloys after rolling along (011) direction [14]

New zirconium alloys have been developed to increase their performance in corrosion resistance and mechanical properties. Zirconium low oxygen (ZIRLO) alloys was developed to increase the corrosion resistance of fuel cladding in PWR environment and to enable higher burn-up. For this series of alloys nickel is replaced by niobium.

Niobium exhibits high solubility in cubic zirconium and it is mildly soluble in its hexagonal structure. Nb improves mechanical properties and it prevents detrimental effects induced by impurities like nitrogen. The amount of Sn is reduced, but to keep satisfying mechanical properties can be further lowered.

A further development of ZIRLO series is the optimised ZIRLO alloy (OPT-ZIRLO) which contains lower amount of tin. It provides higher creep resistance and corrosion resistance compared to Zircaloys and previous ZIRLO alloys[11].

AREVA developed a new zirconium alloy named M5 in the end of 1990s which is currently used in PWRs. Sn is removed from the alloy. M5 is a Zr-Nb system with the controlled presence of O, Fe and Cr. Composition is reported in table 1.4.

Nb (%wt)	O (ppm)	Fe (ppm)	Cr (ppm)	Zr
1	1450	370	41	Bal

Table 1.4: M5	alloy com	position [15]
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Typical microstructure for M5 alloy consists of  $\beta$ -Nb precipitates uniformly dispersed within the recrystallized  $\alpha$ -Zr matrix. It enhances the creep resistance of the alloys.

M5 compared to Zircaloy-4 offers better resistance against thermal creep and corrosion, and it reduces the size of hydrogen pickup[11].

The corrosion performances for ZIRLO and M5 in autoclave at 360°C are reported in figure 1.6. They are compared with Zircaloy-4 (Zr-4). The weight gain indicates the growth of the

oxide layer. The improvement due to the new alloys is remarkable observing the lower slopes of their curves (fig. 1.6). M5 alloy exhibit the lower weight gain rate among the described alloys under autoclave conditions (fig.1.6).



*Figure 1.6: Autoclave test at 360°C. On the left ZIRLO weight gain compared with different types of alloys of the Zr-4 series. On the right M5 weight gain compared with Zr-4[16].* 

#### 1.4 Fukushima Daichii Accident

Fukushima Daichii plant includes six BWR reactors. Fig. 1.7 provides the scheme of the plant showing the height of different buildings. After 2002, the design basis tsunami height for the plant was set at 5.7 metres[17]. Reactors from 1 to 4 are located at 10 metres above the sea, while reactors 5-6 are at 13 metres.



Figure 1.7: Scheme of Fukushima plant [18]

On March 11<sup>th</sup>, 2011 at Fukushima Daiichi plant, reactors 1, 2 and 3 were operating. Reactor 4, 5 and 6 were shut down for maintenance and refuelling. At 14:46, the Great East Japan Earthquake occurred, cutting off the plant from the power grid. Control rods felt down immediately to shut down the operating reactors. No damages were detected after the earthquake.

45 minutes after the earthquake, a 4-meters high tsunami wave hit the coast, followed by a 13meters high one which flooded the plant and damaged the emergency diesel generators. Only one generator, which provided power to unit 6, resisted to water coverage and derived damages. Reactors from 1 to 5 lost their AC power supply[19], [20]. Water level in the plant after tsunami is shown in fig.1.8.

Loss of electricity made it impossible to cool the reactor, and staff could not control the situation because indicators and signals in control room were not available anymore. The plant regained access to external power only after ten days when a temporary system was installed on  $20^{\text{th}}$  March.

Nothing occurred to reactor 5 and 6, but the others experienced meltdown and explosions. Investigation of the dynamics of the accident is complex and it is not the aim of this paragraph. The focus is on how fuel rods behave in the accident scenarios.

After scram (emergency shutdown of the reactor), the chain neutron reaction was stopped, but the fuel continued to decay generating heat. The cooling system did not work due to the loss

of electricity and so the heat extraction was achieved only by the water remaining inside the reactors. The coolant water was consumed and converted in steam, its level dropped exposing the fuel rods.



Figure 1.8: Section of the plant reporting the height of the flooding water [18]

When fuel rods are left uncovered, no more heat is extracted by coolant and the temperature rises. This is an event of accident identified as Loss Of Coolant Accident (LOCA). The scheme below (fig.1.9) summarises the possible issues related to fuel rods during accident scenarios. During LOCA the fuel bars can fail due to two different mechanism which are related to the increase in temperature: creep and corrosion.



Figure 1.9: Failure mechanisms of zirconium fuel tubes under accident scenarios [13]

#### 1.5 Oxidation reaction of zirconium

The corrosion of zirconium is due to the transformation of metal into its native oxide, according to the exothermic reaction:

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 + heat$$

Under normal conditions the oxide growth is slow and uniform. The corrosion rate of the fuel cladding tubes depends on conditions inside the reactor and it determines the lifetime of rods. Fig. 1.10 summarises the formation of the oxide film during normal operation.



Figure 1.10: Oxidation of zirconium alloys during normal operation [13]

In the event of accident, temperature raises up due to the overheating causes by decay heat. When temperatures raise up, the oxidation rate increases enhancing the corrosion of fuel cladding tubes. In fig 1.11 the behaviour of two zirconium alloys is shown, exposed to steam at two different temperatures: 700°C and 1200°C.

At 1200°C the size of corrosion is higher compared to that observed at 700°C. ZIRLO exhibit a lower slope compared to Zircaloy-4, but its corrosion resistance in those conditions is not acceptable. Observing the curves related to oxygen absorption, it can be noticed that the amount of absorbed oxygen increases with time; because  $ZrO_2$  behaves as solid electrolyte at high temperature, so the growing oxide layer conducts the oxidising species instead of acting as protective layer. Furthermore, it can be noticed that the slope of the curves decreases with time. This behaviour can be explained suggesting that the thickening of the oxide layer causes a slowdown of the oxygen .... Conduction of oxygen ions within the zirconia layer is the ratelimiting factor for the process.

The higher the temperature, the higher the conductivity within zirconia and this explains why oxidation occurs faster at higher temperatures[16].


Figure 1.11: Oxidation test conducted in steam at 700°C (left) and 1200°C(right) for Zircaloy-4 and ZIRLO alloys [21]

The oxidation reaction of zirconium is self-enhancing because it is exothermic. The heat generated by oxide formation is added to that derived from decay, raising the temperature of the rods. In addition, the thick grown oxide layer reduces the heat conductivity, enhancing the temperature rise. The temperature increases making the cladding more sensitive to creep, oxidation and interaction with fuel. The contribute to the total heat provided by oxidation can be visualised in fig 1.12.



Figure 1.12: Heat produced by decay heat and zirconium oxidation during short-time blackout [22]

Under normal conditions hydrogen and oxygen are produced at the interface water-tube due to water molecule splitting induced by the harsh conditions of the core environment. During LOCA the oxidation of zirconium produces a large amount of hydrogen, which is responsible for zirconium embrittlement. When hydrogen content excesses the solubility in zirconium,

which can be  $\alpha$  or  $\beta$  depending on the temperature of the system, it precipitates as hydrides. Hydrogen produces two types of precipitates in zirconium matrix: ZrH (orthogonal) and ZrH<sub>2</sub> (tetragonal). Zirconium instead exhibits hexagonal and cubic structures, so hydrides are incoherent precipitates which generates stress increasing brittleness[14]. Fig. 1.13 shows the microstructure of cladding after the hydridation.



Figure 1.13: Hydrides layers in zirconium-based clad [14]

Hydrogen fraction which does not diffuse in zirconium, accumulates rising pressure inside the vessel. The large amount of hydrogen gas, produced inside the vessel by oxidation reaction of cladding, was responsible for explosions documented in Fukushima accident.

Fig. 1.14 summarises what the cladding experiences because of LOCA conditions focusing on the waterside and not considering possible reactions with fuel. The oxide layer is thick, cracked and unprotective. Due to high temperature zirconium transforms from  $\alpha$  phase to  $\beta$  phase, causing dimensional changes that provide additional mechanical stresses. Hydrogen and oxygen diffuse through the zirconia layer reaching the underlying metal. Oxygen dissolves into zirconium matrix stabilising the  $\alpha$ -phase, which can be detected immediately under the oxide layer. Hydrogen dissolves into zirconium matrix up to solubility limit and then precipitates forming hydrides which cause deterioration of mechanical properties.

The behaviour of zirconium alloys when emergency cooling system is not available is not acceptable because it rapidly exposes the reactor to risks of core meltdown (due to the rapid temperature increase and mechanical properties deterioration) and to explosions due to hydrogen pressure.

It is important to find new materials that can increase the coping time in the event of accident and can provide better creep resistance and lower oxidation rates.



Figure 1.14: Section of zirconium cladding after LOCA event [13]

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## 2 Accident Tolerant Fuels (ATFs): state of the art

Fukushima accident has pushed the nuclear industry in the direction of improving plant safety. The loss of electricity both from external grid both from emergency system exposes nuclear plants to large LOCA accidents and so one of the trends in safety implementation is the development of new passive safety systems.

Zirconium alloy claddings were not able to withstand the temperature rise occurred during the black-out time in Fukushima. As seen in the previous chapter zirconium cladding experiences rapid oxidation at high temperatures, generating a large amount of hydrogen and heat. A change in materials used for cladding and fuel is considered a key to improve safety inside the reactor, so universities and industries are collaborating to find new solutions.

The aim of this global effort is to realise the so-called Accident Tolerant Fuels (ATFs). This term is used to indicate a new generation of materials and/or designs -both for cladding both for fuel- which would improve safety inside the reactor by providing a better behaviour during normal operations and in the event of accident.

Fuel pellets must retain as much as possible volatile fission products to prevent their release in accident scenarios like Fukushima Daichii; to maintain their integrity they require a better thermal conductivity to reduce the stored energy[1]. Short-term solutions are based on uranium dioxide, which is the current fuel for LWRs, while new candidates are uranium silicides ( $U_3Si_2$ ,  $U_3Si_5$ ) and composites like UN- $U_3Si_2$  UN-  $U_3Si_5$ . The use of  $U_3Si_2$  would provide higher uranium density and this would mitigate the neutron penalty due to some ATF cladding materials like FeCrAl alloys, which exhibits a higher thermal neutron cross section compared to zirconium alloys[2].

In table 2.1 are listed some requirements for new ATF cladding compared to the current standard[3].

Performances	Standard Zr alloy	Target ATF Cladding
Melting temperature	1843 °C	>2000°C
Maximum operating	650°C	>650°C
temperature		
Creep (both	Zircaloy-4 at 25°C	Lower than Zircaloy
irradiational both	creep strain: 0.66%	
thermal)		
Clad Peak	1200°C	>1200°C
Temperature Limit		
Swelling	Swelling occurs	Lower swelling than
		Zircaloy
Unirradiated thermal	17.41 W/m K	>17.41 W/m K
conductivity at 300 °C		
Hermeticity	Yes	Yes
Coping Time	10 hours – depending	Longer time
	on specific nuclear	
	plant	

 Table 2.1: desired properties for ATF compared with standard cladding properties [3]

Safety improvement cannot be the only benefit, so other requirements for ATF cladding are economical: they have to enhance the uranium utilization by allowing an increase of heavy metal loading, to extend operational time providing a reduction of operational costs, to be able to guarantee large scale production like zirconium rod. [3].

A material which can be used as ATF cladding should provide the following features:

- Low thermal neutron cross-section to guarantee a neutron efficiency comparable to that achievable using zirconium alloys.
- High melting temperature to reduce creep phenomena and to increase time to melting.
- Radiation stability.
- Hermeticity to prevent leakage of fission products and to protect fuels from water.
- Good manufacturability.
- Enough thermal conductivity to dissipate decay heat.
- Chemical compatibility with fuel and coolant.
- Minimization of hydrogen production at high temperature to prevent explosions.
- Reduce heat generation due to oxidation reaction in the event of accident.

Areas for improvement for ATFs are summarised in figure 2.1, which shows also the typical failure mechanism experienced by a traditional zirconium alloy rod under LOCA.



Figure 2.1: Typical failure mechanisms for zirconium fuel rods during LOCA and areas of improvement for new ATF clads [4].

## 2.1 EU project "IL TROVATORE" (\*)

The research for new solutions to improve safety inspires IL TROVATORE, a European project - funded by Horizon 2020 program (<u>http://www.iltrovatore-h2020.eu/</u>). Its goals are the identification of the most promising ATF cladding materials for Light Water Reactors of II and III generation and their validation by testing them in operative-like conditions. The project partners are 30 and among them there are academic institutions, national laboratories and industries, split in 14 work-packages with different tasks [5].

The project aims to select some cladding materials classifying them as short-term solutions or mid-term solutions. Mid-term solutions are SiC/SiC composite and oxide-dispersed strengthened FeCrAl alloys, while short- term solutions are coated zirconium alloys. Coatings under investigations within the project are MAX phases, nanocrystalline oxides and thin oxide scales obtained by GESA process[6].

Using the material-based solutions proposed by Il Trovatore as starting point, the following paragraphs offer an overview on the most promising ATF cladding technologies from coating of zirconium alloys to complete material substitution.

(\*) The IL TROVATORE project receives funding from the Euratom research and training programme 2014-2018 under grant agreement N°740415.

#### 2.2 Zirconium alloy surface modification

Zirconium has valuable properties as cladding material and the related technology is well consolidated. Mitigation of its oxidation rate in event of loss of coolant accident could be obtain through coating solutions. Native oxide,  $ZrO_2$ , exhibits high stability in steam and it adheres well on zirconium also when temperature excesses 1100°C, but it is not suitable as protective layer because it behaves as solid electrolyte at high temperatures allowing diffusion of oxygen towards the underlying metal and propagating the oxidation reaction[7].

Otherwise, oxides like alumina, chromia and silica are efficient as barrier against diffusion of oxidizing species. Coatings to provide protection of zirconium cladding should contain at least one oxide-forming element among chromium, aluminium and silicon. However, chromia is the only oxide which is stable both in steam both during normal operation conditions; alumina and silica are stable in steam but they experience dissolution in sub-critical water of PWR[7].

Chromium coating is the choice of main nuclear industrial players for short-term ATF technology and different coating deposition methods are currently under investigation. In addition to the considerations for a protective-oxide former, chromium exhibits a body-centred cubic metal structure and so irradiation stability at operating temperatures is expected[7].

#### 2.2.1 Chromium 3D Laser Coating

3D Laser coating technology allows to get a Cr-coated Zircaloy-4 (fig 2.2) and it is the solution proposed by Korea Atomic Energy Research Institute (KAERI - South Korea). Chromium powders are spread on tube surface while a laser beam melts them forming a rough coating surface, which can be smoothed using SiC papers. The mean thickness obtained in the study is 80 µm and through an optimisation of the process it is possible to limit the heat affected zone[8]. Creep deformation for ATF should be limited to 1% in hood direction under normal conditions, the obtained coatings does not exhibit spalling and peeling during ring tensile and compressive tests showing an increase in mechanical properties of tubes both under hood compression both under hood traction[9]. No cracks are formed up to 4 % strain as can be noticed in fig 2.3.



Figure 2.2: cross-section of Cr-coated zirconium alloy manufactured by 3D Laser beam deposition and associated hardness profile [8].

Cr-coated layer				
	Cr-coated layer			
2% strain		Cr-coated layer	1	7
	4% strain			
		6% strain		<b>100 μm</b>

Figure 2.3: cross-sections of Cr-coated Zircaloy-4 by 3D Laser Coating at different strains [9].

Behaviour of Cr-coated Zircaloy-4 in LOCA conditions was investigated exposing the sample to steam at 1200°C for 2000 seconds and then it was compared with uncoated Zircaloy-4(fig 2.4). Coated sample does not show spallation and oxidation is limited only to 4  $\mu$ m of oxide

thickness, a low value compared to the 113  $\mu$ m measured in Zircaloy-4 sample, exhibiting a remarkable improvement in oxidation resistance[8].

The absence of  $\alpha$ -Zr(O) phase in the coated sample is a prove of the effectiveness of chromia as barrier against oxygen diffusion.



Figure 2.4: cross-section of Cr-coated Zircaloy-4 tube by 3D Laser coating compared with a standard Zircaloy-4 tube. They were exposed for 2000 s at 1200°C in steam environment [8]

#### 2.2.2 Cold Spray Chromium Coating

Another technique under investigation is cold spray process (fig.2.5). Cold spray is a process which uses metallic or ceramic particles as feedstock. Powder particles are accelerated using high-temperature gases under pressure and they hit the surface of the substrate at high speed[10].



Figure 2.5: scheme of cold spray process [11]

At impact the dissipation of kinetic energy binds particles on the substrate surface due to localized plastic deformation in the particle and at the interface. A peculiarity of this process is that particles are in solid state for the duration of the entire process.

Two different stages are involved in the process: firstly bonding between particles and substrate and then deposition on sprayed coating layers. For each step different velocities are required.

Cold spray coatings are denser and without evidence of oxidation making the process suitable for operating in atmosphere. Low process temperature prevents diffusion between coating and substrate, allowing deposition of reactive materials[12].

In this study the presence of chromium provides an effective oxidation protection at high temperature  $-1200^{\circ}$ C in air for 20 minutes (fig 2.6) [11].



Figure 2.6: On the left, cross-sectional SEM images of the Cr-coated Zr-alloy tube by cold spray process, after being tested at 1200°C in air for 20 minutes. On the right, the EDX scan path along the tube thickness is shown [11].

### 2.2.3 Physical Vapour Deposition chromium coating

Another relevant technology for chromium deposition is Physical Vapour Deposition which has been selected by Framatome – in collaboration with EDF (Électricité de France) and CEA (Commissariat à l'énergie atomique et aux énergies alternatives) - for industrialization of short-term EATF (Enhanced Accident Tolerant Fuel). Chromium-coated M5 alloy tubes with chromia-doped urania pellets are going to be tested in a commercial reactor this year to test their behaviour in real operating in-pile conditions.

Via PVD they deposited 15  $\mu$ m thick chromium dense coatings. No porosity was observed at the interface between chromium layer and substrate (fig 2.7).

Tubes are manufactured using the traditional process and then they are coated using a property process inside a special PVD reactor which can work on full size tubes. Tubes are welded using a resistance welding technology which showed to be compatible with chromium deposition and it can guarantee the same level of hermeticity of current M5 tubes.

During normal condition in a static autoclave, with the same PWR water chemistry, coated samples exhibited an excellent behaviour. No spalling or dissolution of coating were observed. Hence, it was important to test coated samples in a degraded water chemistry containing 70 ppm of lithium, simulating a possible accident condition.



Figure 2.7: SEM cross-sectional micrography of Cr-coated M5 alloys by AREVA NP [13]



Figure 2.8: corrosion behaviour of coated and uncoated M5 tube in water containing 70 ppm Li [13]

Compared to uncoated M5, chromium coated tube exhibits no evident corrosion also after 160 day while the former shows a dramatic increase of oxidation rate after 140 days (fig 2.8). Furthermore, wear resistance increases in coated sample helping to prevent accidental damage

during occasional contact with harder materials which can occur during handling and placement.

An issue for Cr-coated zirconium alloys is the eutectic of the Cr-Zr system at about 1330°C. It was therefore crucial to test the EATF claddings at this temperature to investigate how they behave. Temperature was raised following a ramp of 25°C/s up to 1500°C in argon atmosphere. No changes in geometry were observed and sample did not exhibit evident damages suggesting that no severe degradation occurs in those conditions. A later analysis showed diffusion of chromium forming eutectic-like microstructure for 100  $\mu$ m under the surface. This result shows that the selected thickness of coating allows to prevent a significative degradation due to an increase of temperature over eutectic transformation[13].

High temperature oxidation test performed on Cr-coated Zircaloy-4 showed a behaviour like that observed for coated samples obtained by laser coating technique and cold spray process. Coated samples were tested in steam at 1200°C and then quenched in water. Cr-coated Zircaloy-4 exhibited a remarkable reduction in oxide growth compared to the uncoated Zircaloy-4 (fig 2.9) [14].



Figure 2.9: steam oxidation behaviour of Cr-coated and uncoated Zircaloy-4 tested in steam environment at 1200°C. Cross-section of the two sample after 300s at 1200°C [14]

Presence of cracks in coating or ballooning during LOCA accidents results in incomplete protection of the underlying zirconium alloys. In fig. 2.10 is shown an example of SEM fractography for a Cr coated-Zircaloy-4 with pre-cracks in the chromium layer after steam oxidation at 1200°C for 5 minutes and following water quenching. As can be observed, near the pre-crack zirconium alloy is locally exposed to steam and this cause the formation of a small region of zirconium oxide. Under  $ZrO_2$  spot can be observed  $\alpha$ -Zr(O) stabilised by diffusion of oxygen through the native oxide layer. Presence of  $\beta$ -Zr is due to the temperature rise which bring to phase transformation from beta to alpha. Where cracks are absent Cr-Coated sample behave as expected.



Figure 2.10: SEM micrography of the cross section of unperfect Cr-coated Zircaloy-4 sheet after 300s at 1200°C [15]

Results of irradiation in-pile test performed in commercial reactors and in facilities of research laboratories will be useful to evaluate how chromium coated fuel road behave under neutronic radiation.

#### 2.3 Ferritic alloys

FeCrAl are a family of ferritic alloys which exhibit high corrosion resistance and they are considered a viable short-term solution as ATF claddings both to substitute zirconium alloys both as protective coating for current material. Metallurgically, they exhibit a fully ferritic phase which does not transform in austenite at higher temperature before melting point due to the stabilizing effect provided by chromium and aluminium[16].

One of the major concern during LOCA conditions is cladding burst which is due to short-term creep resistance and the increase of pressure difference between the internal volume and the external environment which experience depressurisation. In this scenario advanced steels showed a better behaviour than zirconium alloys despite their lower melting point[17].



Figure 2.11: creep rupture stress vs temperature graph for different alloys [17]

As can be observed in fig. 2.11 both austenitic steels -310SS- both ferritic steels- PM2000, APMT, APM- exhibit higher creep rupture stress than Zircaloy-4 and Zircaloy-2. The creep resistance strength of zirconium alloys is even lower if hydrogen uptake occurs during high temperature exposure.

Steels under examination exhibit a higher elastic modulus compared to zirconium alloys, as can be notice in fig. 2.12.



Figure 2.12: elastic modulus vs temperature diagram for different alloys [17]

The main advantage of using FeCrAl alloys is the enhanced corrosion resistance during normal operation and during accident conditions. Formation of an alumina scale during high temperature steam oxidation allows to protect the cladding from several degradation. Alumina forms when temperature exceeds 600°C and this is important because it would not be stable in supercritical water conditions where it undergoes dissolution.



Figure 2.13: weight gain constant vs temperature for different materials. Zirconium alloys and 304 SS were tested in pure steam, while 310 SS and APMT in a mixture 50% argon- 50% steam. All tests were conducted at atmospheric pressure [17]

In steam the oxidation rate of FeCrAl (APMT, in figure 2.13) is more than 2 order of magnitude lower than zirconium alloys and almost an order lower than traditional stainless steels[17].

In another study [18] Kanthal APM (22 wt% Cr - 5 wt% Al- Bal Fe) was tested in two different conditions (fig. 2.14): steam exposure at  $1200^{\circ}$ C and corrosion test performed in a static autoclave simulating PWR operating conditions.



Figure 2.14: on the left, the oxidation behaviours at 1200°C in steam of Zircaloy-4 and a selected FeCrAl are compared. On the right, the corrosion test results in static autoclave for Zircaloy-4, the same FeCrAl alloy and ZIRLO alloy are reported [18].

During steam oxidation FeCrAl exhibits a lower weight gain compared to Zircaloy-4. When exposed to steam at 1200°C a slow growing  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is formed providing protection, TEM (Transmission Electron Microscope) analysis measured an average thickness of the oxide of approximately 480 nm after the test.

In autoclave, behaviour is very different: FeCrAl exhibited a small increase in weight in the first days, then starting from the 150<sup>th</sup> day it lost weight until a minimum near the 250<sup>th</sup> day and then another little increase in weight is observable before reaching a plateau.

In static autoclave conditions iron oxides grow on steel surface with a prevalence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Under the oxide scale pores are formed and this contributes to scale spallation which explain weight loss. Pores formation is imputed to Kirkendall Effect because outward diffusion of iron is not compensated by inward oxygen diffusion which is lower. [18] Under irradiation this material experiences some property changes like radiation-induced hardening and embrittlement. Yield strength modification offers a measure of the phenomena: for austenitic steels it can raises up to four time the initial value while for ferritic ones it can double using as reference the same steels at 300°C. Main mechanisms of radiation-induced hardening for ferritic steels are formation of dislocation loops and precipitation.

Ferritic steels containing chromium over 9 wt% exhibit a peculiar mechanism known as 475°C embrittlement. At that temperature a spinodal decomposition of ferrite in two phases  $\alpha$  and  $\alpha$ ' occurs: the first phase is rich in iron and the latter in chromium[19]. At lower temperatures there is not enough energy to enable mobility for the decomposition, while higher temperatures increase chromium solubility preventing the 475°C embrittlement. Under irradiation, diffusion is enhanced and this can produce an embrittlement also operating at temperatures lower than 475°C, like those of LWR which are in the range of 300-400°C. The presence of aluminium does not provide any effect on preventing this phenomenon. The best compromise between radiation-induced embrittlement and corrosion resistance lies in the choice of alloys with a chromium content of approximately 9 wt%.

Due to hardening, fracture toughness is reduced in ferritic steels, but it was observed that at least 50 MPa $\sqrt{m}$  is retained. In contrast, zirconium-based claddings exhibit fracture toughness in the range of 20-50 MPa $\sqrt{m}$ , but, if concentration of hydrogen overcomes 1000 wt ppm, this value is expected to decrease to 12-15 MPa $\sqrt{m}$  [17].

A great challenge for FeCrAl cladding is tritium retention. Tritium can be produced via fission or via neutron absorption by boron - in BWRs there is not soluble B and so there is only contribution by fuel. One of the main tasks of the fuel cladding is to avoid release of fission products, but steels are not good in contrasting hydrogen permeation and hence tritium permeation. Comparing a standard Zircaloy with 304SS the release fraction of tritium is 1% against 50% and a higher hydrogen permeability is expected for ferritic alloys because they exhibit a bcc cell[17]. This issue could be solved by adding a barrier to prevent hydrogen diffusion[20].

Iron-based claddings would have a higher neutron absorption cross section compared to zirconium alloys (table 2.2) and this increase is a drawback because it affects the neutron economy of LWR. The incremental for the proposed FeCrAl alloys is higher than 12 times.

Table 2.2: composition of Zircaloy-4, 310SS and a promising FeCrAl alloy and their neutron absorption cross-
sections [17]

			_							
Alloy	Fe	Cr	Al	Zr	Ni	Sn	Mn	Мо	Si	$\sigma_a^a$ (barns)
FeCrAl 310SS Zircaloy-4	75 52.5 0.15	20 25.2 0.10	5 0 0	0 0 98.75	0 19.5 0	0 0 1.50	0 1.9 0	0 0.13 0	0 0.7 0	2,43 3,21 0,20

Composition in mass fraction (wt%) of evaluated cladding materials.

<sup>a</sup> Average thermal neutron absorption cross section for the alloy.

Three solution are proposed for getting over the reduced neutron economy:

- Minimization of cladding thickness.
- Incremental of fuel mass.
- Increase of enrichment degree of fuel.

Reducing the thickness of tubes is a challenge and it requires an increase of strength of FeCrAl alloys at temperature higher than 600°C, which can be achieved by oxide dispersion strengthening achievable by powder metallurgy. This solution, joined with the development of low chromium alloy, to prevent the radiation embrittlement, can provide the future ATF FeCrAl claddings.[21]

Substitution of zirconium-based cladding is not the only possible application for FeCrAl, they are also investigated as coating material to reduce oxidation issues during LOCA scenarios. This solution allows to get over the issue related to neutron economy and tritium release taking advantage on the corrosion resistance properties of FeCrAl alloys.

However, there are two concerns: diffusivity between iron and zirconium and low temperature eutectic (928°C) of Fe and Zr system (fig. 2.15).



Figure 2.15: Fe-Zr phase diagram [22]

Exposure in steam of a tube with one FeCrAl-coated surface for 20 minutes at  $1200^{\circ}$ C shows a large region with evidence of diffusion of iron in zirconium and formation of eutectic ZrFe<sub>2</sub>/Zr structure (fig 2.16). Cracks visible in eutectic zone can be due to shrinkage during solidification of the intermixed phase[23].



Figure 2.16: (a) cross-section of FeCrAl coated Zircaloy-4 tube (one side), after 20 minutes at 1200°C in steam. (b) Details of the eutectic structure [23]

A barrier is needed to prevent diffusion of Fe and Cr in zirconium and avoid the formation of low melting point eutectic. A candidate material is molybdenum which exhibits high melting point (2632°C), high temperature creep resistance and its eutectics with iron and zirconium present high melting points too. Diffusion activation energy of Fe and Cr in molybdenum is three times larger than that in  $\beta$ -Zr at high temperatures. Furthermore, inter-diffusion of Mo and Zr is very limited. The only potential issue for this concept is the radiation-induced embrittlement of Mo alloys under 700°C.

Cold spray process can be used to deposit both the molybdenum diffusion barrier and both the FeCrAl protective coating by selecting the proper parameters. Exposing the obtained system to air at 1200°C for 20 minutes, it can be observed that the presence of the molybdenum enhances performances. SEM micrographs after exposure are provided in fig. 2.17.

A thin alumina oxide layer (approximately 700nm) is formed on FeCrAl surface. At the interface between Mo and FeCrAl is visible, at high magnification, an interdiffusion layer of about 1.4  $\mu$ m in thickness and at the interface Mo-Zr the interdiffusion layer is limited to about 1  $\mu$ m. Molybdenum layer remains continuous and unreacted guaranteeing further diffusion protection and allowing the suitability of FeCrAl coated zirconium alloys tube.



Figure 2.17 SEM micrographs of the cross-section of cold spray FeCrAl coated zirconium alloy with cold spray deposited Mo diffusion barrier: (c) focus on alumina oxide layer, (d) focus on reaction layers [23].

#### 2.4 MAX phases

MAX phases are ternary compounds which satisfy the following formula:  $M_{n+1}AX_n$ , where n can be 1, 2 or 3. Depending on the value of n, MAX phases are classified as 211, 312 and 413.

- M indicates a transition metal of groups 3, 4, 5, 6;
- A represents an element belonging to groups 11,12, 13, 14, 15, 16.
- X indicates carbon for ternary carbides and nitrogen for ternary nitrides.



Figure 2.18: MAX phases former elements [24]

Unit cell for MAX phases is made up with MX<sub>6</sub> octahedra separated by A elements layers. The difference between 211, 312 and 413 lies in the number of layers of MX present between A layers: 2, 3 and 4 respectively (fig 2.19) [25].



Figure 2.19: possible MAX phases structures [25]

MAX phases are peculiar materials because they exhibit a mixture between properties typical of metals and ceramics. These layered carbides/nitrides exhibit ductility due to their structure which enables basal slip, also at low temperatures like 77 K, making them machinable. Dislocations can move only on basal planes and this means that work hardening is not possible for this class of materials. Generally, they present a quite high elastic modulus together with a low hardness value for ceramics. Some MAX phases- although ceramics- provide toughness even at room temperature because of their energy absorption mechanisms like delamination, crack deflection and microcracking. Creep resistance is comparable to those found for metallic alloys for high temperatures. They exhibit also a good thermal shock resistance. As electrical conductors they behave better than titanium and this property makes them also good thermal conductors. Oxidation resistance is linked to their chemistry and it's provided by oxide formation[24].

The documented features of MAX phases make them interesting for accident-tolerant fuel applications as coatings- and eventually as substitute for zirconium. The most promising candidates among MAX phases are alumina-forming and silica forming ones.

Concerning accident-tolerant performance, particularly in case of LOCA scenarios, interesting MAX phases for coatings are those containing aluminium which can form a protective scale in presence of steam at high temperatures. For a  $Ti_2AlC$  coating in oxidizing environment – exposure in a mixture of steam and argon at 1005°C for 20 minutes - the formation of a protective oxide scale was observed (fig 2.20). The absence of  $ZrO_2$  under the coating is an indication of the protection provided [26].



Figure 2.20: SEM micrograph of the cross-section of cold spray Ti2AlC-coated Zircaloy-4, tested at 1005°C for 20 min in steam-argon mixture and then quenched in boiling water. EDS line is placed on the SEM micrography [26].

In addition to high temperature oxidation resistance it is crucial to verify corrosion resistance of MAX phases in hydrothermal conditions of the reactor environment.

A study [27] compared the behaviour of four different MAX phases inside an autoclave which simulates the LWR environment. The tested materials were  $Ti_3SiC_2$ ,  $Ti_3AlC_2$ ,  $Ti_2AlC$  and  $Cr_2AlC$ . Among them,  $Cr_2AlC$  exhibits the best behaviour because the formation of a chromia layer prevents further oxidation. Max phases containing Si or Al does not form protective oxide during the autoclave test at 300° C, making them unsuitable for this application.

MAX phases can be deposited on zirconium alloy substrate using several techniques, but it is important to select those which operate at temperature lower than the range of 800-1000°C, due to issue related to zirconium behaviour at high temperature.  $Cr_2AlC$  can be deposited by magnetron sputtering maintaining the substrate at 650°C obtaining a high quality pure-phase coating. Under the pure  $Cr_2AlC$  coat, a buffer layer is formed. Inside the interfacial layer concentration of Cr, Al and C decrease while the amount of Zr increases, under this area there is pure zirconium alloy (fig 2.21).



Figure 2.21: TEM micrograph of the cross-section of Cr2AlC-coated Zircaloy-4 [28]

Tests conducted in argon at 1000 °C for 5 minutes showed a consumption of the  $Cr_2AlC$  due to a reaction with the substrate which bring to coating degradation. Similar results were observed for  $Ti_3SiC_2$  and  $Ti_2AlC$  for temperatures between 1100°C and 1300 °C, suggesting an outward diffusion of Al and Si which brings to the formation of intermetallic compounds with zirconium alloys. This result suggests the need for a diffusion barrier to make MAX phases suitable candidates for coatings [28].

An interesting feature of some MAX phases is the self-healing intrinsic behaviour exhibited in oxidative environment at high temperatures. In such scenario the oxidation, which occurs on crack surfaces, provide a volume expansion able to repair induced damages. This is possible for MAX phases such as Ti<sub>2</sub>AlC, Ti<sub>3</sub>AlC<sub>2</sub> and Cr<sub>2</sub>AlC which exhibit the formation of a stable oxide and a high diffusivity of the A element.[29].

A coating thickness under 25  $\mu$ m is suggested to prevent a detrimental effect on neutron economy of LWRs together with the selection of a proper chemistry.[27]

#### 2.5 SiC composites

A ceramic material which is investigated as accident-tolerant fuel cladding is silicon carbide. It exhibits high thermal, mechanical and chemical stability, making it an ideal candidate for high thermal applications in harsh environments like LWRs. Theoretical thermal conductivity is estimated to be 490 W/mK for SiC. However, bulk SiC cannot be used for safety applications due to its brittle behaviour, so the research is going towards SiC-based composites [30].

A specific class of SiC/SiC composites are considered suitable for nuclear environments from LWRs to IV generation reactors. The most stable SiC phase under irradiation is the  $\beta$  phase which has a cubic cell, so one of the features of nuclear grade SiC/SiC composites is the presence of this phase. Nuclear grade SiC/SiC composites consist of near-stoichiometric SiC fibers braided into 3D-tubes coated by pyrolytic carbon deposited via Chemical Vapour Deposition, then SiC matrix is deposited via Chemical Vapour Infiltration or it is added via NITE sintering via hot pressing. Coatings can be used for inner and outer surfaces of tube[31].

#### 2.5.1 Nuclear grade architecture

Fibers used for nuclear grade application are the commercial Hi-Nicalon Type S and Tyranno SA3, which are third generation SiC fibers. In table 2.3 different fibers are compared, made of pure  $\beta$ -SiC obtained by CVD.

Trade name	CG-Nicalon NL-202	Hi-Nicalon	Hi-Nicalon Type S	Tyranno SA3	Sylramic	Pure β-SiC
Manufacturer	NCK <sup>a</sup>	NCK	NCK	Ube <sup>b</sup>	COI <sup>c</sup>	(CVD SiC)
SiC fiber generation	I	II	III	III	III	
C/Si atomic ratio Oxygen mass concentration (%) Other additives SiC grain size (nm)	1.31 11.7 ~2	1.39 0.5 ~10	1.05 0.2 ~50	1.07 <1 Al ~200	1.00 0.8 B, N, Ti ~100	1.00 0
Young's modulus, RT (GPa)	220	270	420	380	380	$^{+50}_{-0.4^{d}}_{-0.1^{d}}$
Tensile strength, RT (GPa)	3.0	2.8	2.6	2.8	3.2	
Elongation (%)	1.4	1.0	0.6	0.7	0.8	
Density (g/cm <sup>3</sup> )	2.55	2.74	3.10	3.10	3.0-3.1	3.21
CTE (ppm/K), to 500 °C	3.2	3.5	5.1	4.5 <sup>e</sup>	5.4 <sup>e</sup>	3.9, 4.5 <sup>e</sup>
Thermal cond., RT (W/m K)	3.0	7.8	18.4	65	46	~400 <sup>f</sup>

 Table 2.3: properties of different SiC fibers [32]

Properties of commercially available near-stoichiometric SiC fibers and comparison with representative non-stoichiometric SiC-based fibers.

<sup>a</sup> Nippon Carbon (Tokyo, Japan).

<sup>b</sup> Ube Industry (Ube, Japan).

<sup>c</sup> COI Ceramics (San Diego, CA).

<sup>d</sup> Strength and elongation of monolithic SiC widely vary depending on effective surface and machining.

e To 1000 °C.

<sup>f</sup> Thermal conductivity of SiC varies significantly depending on purity and grain size.

First generation fibers are a low-cost solution, but they contain a too high content of silica and carbon which makes them unsuitable for operating under irradiation. Indeed, they exhibit an important loss of strength due to debonding caused by volumetric radiation-induced swelling

of fibers. Furthermore, the high content of oxygen causes degradation due to formation of CO when temperature exceeds 1200°C[33]. First generation of Nicalon SiC-based fibers are obtained by melt-spinning of polycarbosilane, a polymeric SiC-precursor. After spinning, the obtained fibers are cured by exposing them at high temperature in oxygen atmosphere and then they undergo pyrolysis in inert atmosphere at 1300°C to obtain the ceramic fibers.

Nicalon second generation- known as Hi-Nicalon- exhibits lower oxygen content by curing green fibers using electron beam irradiation in helium environment. They still exhibit high Carbon content which results in SiC micro-crystals and amorphous carbon. As reported in table 3.2, this generation, compared with the previous one, shows greater grain size , higher modulus, a lower tensile strenght and a density which is the 85 % of theoritical SiC. They still present an important reduction in strenght after irradiation due to fiber shrinkage and debonding, making them unsuitable for nuclear industry[34].



Figure 2.22: production routes for I and II generation of Nicalon fibers [33]

Hi-Nicalon Type S belongs to third generation, a class of SiC fibers which share common properties if compared with second generation:

- larger grain size
- near-stoichiometric composition
- higher Young modulus
- CTE closer to CVD β-SiC
- higher thermal conductivity

A critical consideration when composites are chosen for an application lies on fiber architecture. Fibers exhibit different properties in longitudinal direction and transversal direction and so it is important to select the proper fibers orientation to obtain the desired mechanical properties. Some examples of fiber architecture proposed for CVI SiC/SiC tubes are shown in fig. 2.23.



Figure 2.23: proposed fibers architecture for fuel cladding tubes [31]

Interphase is needed to provide toughness to composite allowing an adequate load transfer between fibers and matrix, debonding and then pull-out. Common interphases for SiC<sub>f</sub>/SiC are pyrolytic carbon and boron nitride, the latter cannot be used in nuclear applications due to the rapid transmutation <sup>10</sup>B, when neutron irradiated. Interphase can be monolayer PyC or multilayer PyC/SiC (fig. 2.24) which can guarantee a better behaviour in oxidizing atmosphere.



Figure 2.24: SEM micrography for PyC monolayer (left) and PyC-SiC multilayer (right) [32].

Pyrolytic carbon is deposited on fibers by CVD before matrix densification. When It is subjected to irradiation, shows contraction after low doses followed by swelling and possible amorphization. Despite irradiation instability of pyrolithic carbon, when it is used as interphase for SiC composites satisfactory mechanical properties are provided also after exposure to high neutron doses. Common thickness for interphase is 50-200 nm, higher values are considered a potential issue for radiation stability. Deposition conditions influence pyrolytic carbon microstructure which can vary from an oriented graphite to near-isotropic carbon. The most used interphase layer for nuclear grade SiC/SiC is turbostratic graphite.

Matrix must be high-purity  $\beta$ -SiC to provide radiation stability, without second phases which can be detrimental due to differential radiation swelling. A technique able to provide this result is Chemical Vapour Infiltration (CVI), so CVI SiC/SiC is the standard technology for densification of nuclear grade composites.

CVI is a CVD performed onto fiber preform at 1000-1200°C, allowing to minimise damages to fibers and residual stresses. CVI process continues until matrix reaches a satisfying density. Typical microstructure for CVI SiC/SiC is shown in fig. 2.25.



Figure 2.25: TEM micrography of the interfaces fiber/interlayers and interlayers/matrix [32]

The CVI process does not allow to reach a high densification: a final porosity of 10-20% is expected for composites obtained using this technique. In fig. 2.26 are reported different type of pores classified by their positions. The most detrimental among the showed pores, affecting thermal and mechanical properties, are considered the interlaminar ones. Porosity is dependent on deposition rate: the higher the deposition rates the more porous the composite will result. However, also optimising the deposition parameters, it is very hard to reach a porosity lower than 5% and this avoid obtaining hermeticity against fission product gases.



Figure 2.26: different types of pores. Intra-bundle pores, indicated by letter A (right). On the left: (B) interbundles pores, (C) inter-layer pores and (D) pores alignes along fiber directions [32]

An alternative to CVI process is the NITE (Nano Infiltration and Transient Eutectic-phase) process which can allow to obtain a matrix near to theoretical density. A SiC fiber preform coated with an interphase material is infiltrated with a slurry containing nanoparticles of  $\beta$ -SiC with sintering additives like alumina and yttria, which are needed to obtain the liquid phase. The system undergoes sintering at temperatures in the range of 1700-1800°C under pressure (15-20 MPa). Oxides melt and they promote densification[35]. Typical aspect of NITE SiC/SiC composite is shown in fig.2.27.



# (b) NITE-SiC/SiC composite

Figure 2.27: SEM micrography on NITE composite cross-section [36]. White areas are the sintering aid oxides.

After densification SiC grains are larger up to 10<sup>3</sup> times compared to initial powders and sintering aid oxides are secluded in islands at the triple junction or they form thin layers at grain boundaries as shown in fig 2.28. Irradiation test on NITE-SiC with content of oxides lower than 10 wt% was performed at 400°C and at 700°C up to 10 dpa (displacement per atom). The result suggests a good irradiation stability for a matrix obtained using this technique. Compared to CVI process, NITE, provide higher density, is cheaper and less time-consuming.[37].



Figure 2.28: preferential locations for oxides in NITE composites [37]

To improve hermeticity of the cladding an outer coating of bulk CVD-SiC can be used as impermeable barrier to protect the fuel and the primary circuit reciprocally.

#### 2.5.2 SiC/SiC as substitute for zirconium alloys

The improvements SiC/SiC could bring as substitute of zirconium alloys are the following[30]:

- Improvement in creep resistance sublimation temperature for SiC is 2730°C.
- The high temperature strength of SiC-composites prevents ballooning and bursting during typical accident conditions. Using composites, no catastrophic failure is expected.
- SiC is the only ATF clad candidate material which exhibits a neutron thermal crosssection even lower than zirconium alloys (table 2.4), allowing a reduction in fuel enrichment levels.

Material	Melting	Absorption cross section	Thermal conductivity
	point [°C]	for thermal neutrons [barn]	[W/(m•K)]
SiC	~2800	$\begin{array}{c} 0.019\\ 2.6\\ \sim 0.19\\ \sim 0.18 \end{array}$	~20 ÷ 350
Mo	2623		138
Zr alloy	~1800		22
ZrO <sub>2</sub>	2715		2-3

Table 2.4: absorption cross section for thermal neutrons of different materials [38]

- Lower oxidation rate compared to zirconium.
- No interaction with fuel pellets below 1200°C
- Irradiation stability to high fluences.

An initial volume swelling is experienced by SiC, but it saturates within 1 dpa, after this point no further swelling is observed. Volume swelling is more intense at lower temperature. The graphs in fig 2.29 refer to CVD-SiC, which exhibits isotropic volume swelling. Saturation for CVD  $\beta$ -SiC is reached within 1 dpa in the range of temperature of 150-1000°C.



Figure 2.29: volume swelling vs dpa at different temperatures for CVD-SiC (left). Volume swelling vs temperature at different dpa for CVD SiC (right) [39].

For SiC/SiC composites the presence of two phases does not seem to be an issue because transversal and longitudinal swelling are comparable[39].

SiC provides high oxidation resistance in steam at high temperature but it is susceptible to aqueous dissolution in the LWR conditions due to the instability of silica protective passivation layer. Especially SiC/SiC composites exhibit a low corrosion resistance under boiling water reactor normal water chemistry. The graph in fig. 2.30 shows the behaviour of different materials in conditions: 288°C water with 2 wppm (weight parts per million) dissolved oxygen[40]. The best performances are provided by CVD SiC which exhibits negligible weight loss also after 400 h, out-performing also chromium which has been presented before as promising coating material for ATF application. CMC-T indicates a composite realised with Tyranno-SA3 fibers infiltrated by CVI process, while CMC-N is realised with second generation fibers. CMC-T behaves better than CMC-N, but the weight loss observed is unacceptable for the application. These results suggest the need for protective coatings able to enhance corrosion resistance of SiC/SiC composite in normal operating conditions. A coating which is already used for nuclear grade material is monolithic CVD-SiC which as observed in the presented test, behave well in these conditions.



Figure 2.30: comparison of oxidation behaviour of different materials in water (2 ppm Li) at 288°C [40]

Main challenges for the utilisation of SiC/SiC as ATF cladding are[3]:

- Development of a reliable and reproducible joining technique, which proves to be hermetic and resistant in light water environment.
- Lack of data on behaviour of SiC/SiC composite in LWR-simulating conditions like those inherent in-pile tests.
- Need for an economic analysis of the potential substitution of zirconium alloys with these materials.

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# 3 Nuclear grade joints: state of the art

A main challenge for the utilisation of ATF SiC/SiC cladding is the reliability of a joining technology to join an end cap seal after fuel load. In fig. 3.1 is shown the sketch of the terminal part of a hypothetical SiC/SiC tube[1]. The end-cap is a plug needed to seal the system after the load of fuel pellets inside the rod.



Figure 3.1: sketch of the terminal part of a SiC/SiC fuel rod [1]

Joining techniques for SiC composites are well-established for common applications, but few processes can provide joint able to satisfy the strict requirements imposed by LWR environment. The geometry of the end cap is also under investigation because geometry of the parts to be joined are important to provide enough joining area to obtain enough strength and joining material retention when brazing or glass-ceramic approach is used. The end tube should be realised using monolithic  $\beta$ -SiC and it should be inserted inside the tube to avoid modification of the dimensions of actual LWR fuel rods. Some proposed designs are shown in the fig 3.2. Among them, the most promising ones are scarf and butted scarf concept because they exhibit the better performance both in strength both in gas retention. [2]



Figure 3.2: proposals for end-cap designs [2].

The imposed requirements to ATF joints are the same imposed to the cladding:

- Hermeticity: fission products must be kept inside the cladding.
- Resistance to hydrothermal corrosion.
- Radiation resistance.

• Resistance to high temperature oxidation which can occurs during a LOCA.

The following paragraphs want to provide an overview on the most promising joining techniques proposed for ATF application.

# 3.1 Solid State Diffusion Bonding

Obtaining a joint by self-diffusion bonding for SiC/SiC would be the ideal solution because it would provide structural and chemical continuity, which is important to show a better behaviour under irradiation, and it would avoid the utilisation of a joining material which does not exhibit the same outstanding properties of SiC for nuclear applications. The main limitation to self-diffusion bonding of SiC is the need of high temperature and high pressure, factors which make this technique unsuitable for large production of tubes.

A study conducted by Moore, on joining SiC to SiC with commercial  $\alpha$ -SiC using hot isostatic pressing at 1950°C for 2 h applying 138 MPa, failed to provide a joint, suggesting the need of sintering aids, which could be detrimental during work conditions.

However, interesting results were obtained using Spark Plasma Sintering (SPS) on polished CVD-SiC blocks applying enough pressure to induce deformation by creep, enhancing the contact between the parts to be joined. Direct joint by SPS can be performed at 1900-2000°C for 5 minutes applying a pressure of 60 MPa (relatively low, compared to that required for diffusion bonding process) and adequate surface polishing. As can be noticed in fig. 3.3, it is difficult to identify the joining line, only few aligned nanopores pointed up by arrows indicate its presence. 4-point bending test performed on SPS joined sample exhibit failure outside the joined area evidencing a good joint quality[3]. Fig. 3.4 shows the interface for direct joint by SPS with inadequate application of pressure and surface polishing.



Figure 3.3: SEM micrograph of the interface of two pieces of CVD SiC joined using SPS (1900°C, 60MPa, 5 min). White narrows indicate the nanopores aligned along the interface [4].



Figure 3.4: SPS joined CVD SiC interface for SPS bonding performed without polishing and pressure application [4].

Diffusion bonding process is utilised to join SiC-based composites using refractory metal (molybdenum, tantalum and tungsten) foils or powders which tends to form carbides thermodynamically more stable than silicon carbide. Another common solution is the choice of titanium as interlayer material. Three parameters are crucial to obtain a sound joint utilizing diffusion bonding technique: metal layer thickness, pressure, temperature and time.

Molybdenum and titanium are good candidates to produce joint suitable for nuclear environment due to their relatively low CTE and their relatively low neutron capture cross-section. Hot pressing was performed in vacuum under pressure (about 7 MPa) at 1400°C on SiC plates with a Mo/Ti foil obtaining a joint[4].

Titanium is converted to reaction products due to silicon and carbon diffusion: at the interface there is a single phase which consists of  $Ti_3SiC_2$ , while in the inner part of joint can be detected two phases:  $Ti_3SiC_2$  and  $TiSi_2$ . The SEM micrograph (fig. 3.5) suggests a successful junction without cracks.

Diffusion in molybdenum foil is limited to less than 10  $\mu$ m, so pure metal is still present in the core of the joint (fig 3.5). At the interface Mo/SiC, Mo<sub>5</sub>Si<sub>3</sub>C is formed by chemical reactions.



Figure 3.5: SEM micrograph cross sections for molybdenum joints (left) and titanium joints (right), manufactured by hot pressing process [5]

In fig 3.6 is shown a graph which compare the different shear stress measured using 4-point bending test for the two different joints.



Figure 3.6: variations in shear strength for Ti-joint and for Mo-joint [5]

### 3.2 Metallic alloy brazing

Brazing technology is interesting because it does not require pressure application and it is a well-known technique. However, the selection of a proper brazing alloy is challenging due to radiation and accident-tolerant requirements demanded for LWR application. Few papers describing SiC brazing alloys are available, many systems are based on BraSiC<sup>TM</sup>, a brazing alloy formulated by CEA. It is a metal-silicon alloy processed without pressure at temperatures from 1200°C to 1800°C. Shear strength at 800°C is in the range of 80-100 MPa depending on the brazing alloy composition. The main drawback for nuclear application lies in the presence of residual silicon which can reduce the strength due to irradiation swelling[1].

The choice of the filler metal is crucial to guarantee suitable properties for nuclear environment. Silver-based brazing alloys cannot be used due to activation issues, while other metals like nickel and cobalt are not good choices due to their high thermal neutron absorption cross sections.

For reactive brazing alloy a zirconium-copper alloy was investigated for nuclear application. Copper is the melting element, while zirconium produces carbides and silicides thermodynamically more stable than SiC at the interface with the composite. SiC is a stable compound but it becomes unstable when in contact with reactive metal at high temperature. When the reactive brazing alloy is in contact with SiC surface, SiC decomposes into Si and C which are now available to react with the reactive metal, similarly to what observed for the solid state diffusion bonding.

> $SiC \rightarrow [Si] + [C]$   $Zr + [C] \rightarrow ZrC$  $2 Zr + [Si] \rightarrow Zr_2Si$

Brazing process conducted on a 80 wt% Zr- 20 wt% Cu alloy at 1200°C – identified as the temperature which provided the highest shear strength (57 MPa)- for 4 minutes forms the microstructure presented in fig 3.7, where four different regions can be detected [5].



Table 3 EDS analysis of the brazed joint at 1200 °C (at%)

Phase region	Zr	Cu	Si	С	Possible phase
a	75.59	24.08	0.13	0.20	$CuZr_2 + Zr$
b	70.48	27.94	0.50	1.08	Eutectic alloy
c	63.58	9.80	19.39	7.23	Zr <sub>2</sub> Si
d	58.90	1.45	23,24	16.41	$ZrC + Zr_2Si$

Figure 3.7: SEM cross section for SiC joined using Zr-Cu alloy. EDS analysis for different regions is reported in the table [7].

The different phases can help to relieve thermal stresses due to the formation of a gradient transition of CTE from the SiC CTE (4.8 x  $10^{-6}$  K<sup>-1</sup>) to Zr-Cu one (7 .4x  $10^{-6}$  K<sup>-1</sup>) by the presence of ZrC and Zr<sub>2</sub>Si.

Edison Welding Institute developed a technology for brazing SiC destinated to nuclear application. SEM micrography of the cross section of joined SiC by Si-Al brazing alloy is provided in fig. 3.8. The proposed alloy consist of a hypereutectic mixture of silicon and aluminum, with addition of some alloying elements. A microstructure formed by silicon plates and aluminum-rich silicon areas is obtained by treating the system to be joined at a temperature higher than melting point of aluminum and lower than silicon melting point. The samples were heated in air 25 times up to 350°C and then they underwent a cycle at 1200°C with no evidence of modification of joint structure. Also water quench was performed on one assembly heated at 750°C with the formation of cracks which did not prevent joint integrity due to the crack-deflecting properties of the two-phase structure.



Figure 3.8: SEM micrograph of SiC joined using Si-Al brazing alloy [8]

Also irradiation testing was performed without joint failure, but further investigation on modification of microstructure must be conducted. Hydrothermal corrosion typical of LWR must be evaluated[6].

An interesting pressure-less joining method for SiC/SiC has been developed, but it has never been tested for nuclear applications. This joining process will be presented in next paragraph because it is investigated in this final project.

## 3.3 Mo-Wrap joining

The joining material obtained by Mo-Wrap process[7] is a composite with a matrix made of silicon with spherical  $MoSi_2$  particles embedded. The peculiarity of this process is the formation of the composite in situ, with well dispersed particles, by operating at temperature slightly higher than silicon melting point for a short time and without the application of pressure. The total CTE of the joining composite can be tailored by selecting the proper proportion between silicon (2.6 x  $10^{-6}$  K<sup>-1</sup> – in the range of 20-1000 °C) and MoSi<sub>2</sub> (8 x  $10^{-6}$  K<sup>-1</sup> – in the range of 20-1000 °C).

The joining preparation is shown in fig. 3.9. A silicon wafer is interposed between two foils of molybdenum. Special attention is paid to the weight percentage of each component, because it is the way for controlling the proportion between particles and matrix for obtaining the desired silicides. This structure has the purpose to contain molten silicon (rephrase this)-which exhibits low viscosity near its melting point- in the joining area.



Figure 3.9: Mo-wrap sketch [7]

Three high temperature molybdenum silicides are possible, but among them only  $MoSi_2$  (melting point: 2020°C) exhibits a self-passivating behaviour which makes it suitable for oxidation resistant applications. Optimal composition for joining process is 32-35 wt% Mo and 65-68 wt% Si, to provide enough liquid phase to get a good joint without applying pressure. Mo-Si phase diagram[7] is provided in fig. 3.10.



Figure 3.10: Mo-Si phase diagram with suggested weight proportions for the process [7]

No molybdenum is detectable in the matrix, pointing out a complete reaction of molybdenum foils with silicon to provide silicides operating with the proposed temperature and weight percentages. No Mo<sub>2</sub>C is detected, this can occur because Si diffuses faster in Mo than C and molybdenum tends to react preferentially with molten silicon during the process.

The Mo-wrap technique allows to join both coated and uncoated composites because the presence of molybdenum foils which envelope the Si wafer prevent a detrimental infiltration of

silicon in the composite pores, depleting silicon from the joining area. In the fig 3.11 are presented different joints realised with this technique for CVD-SiC coated C/SiC, uncoated SiC/SiC and coated SiC/SiC. As can be observed the particles are uniformly distributed in the silicon matrix and they exhibit a spherical shape. The joint presents a well-defined interface and a uniform thickness along the SiC interface suggesting an excellent wettability of SiC by Si. Apparent lap shear stress is found to be in the range of 7-10 MPa, comparable with interlaminar shear strength of SiC/SiC composites.

The fracture surface (fig. 3.12) obtained after lap shear test of SiC/SiC composites joined using Mo-wrap technique exhibit a mixture of cohesive and adhesive nature of the failure. The presence of particles can increase toughness of the joint due to crack-deflection mechanism, they are resistant to oxidation and they increase the creep resistance of the joint – pure silicon is not suitable over 1000°C due to important creep deformation. The silicon matrix could provide oxidation resistance after the formation of a passivation layer made of silica.



Figure 3.11: SEM micrographs for different composites joined Mo-wrap [7]



Figure 3.12: fracture surface for SiC/SiC joined Mo-wrap after lap test [7]

## 3.4 Glass-ceramic joining

What makes a glass-ceramic joining material interesting for nuclear application is the possibility to avoid the application of pressure and high temperatures during joining process. Selecting the starting glass, it is possible to tailor CTE, microstructure and radiation response of the final glass-ceramic.

The proposed candidate is a silica-yttria-alumina glass which exhibits a low induced radioactivity in neutronic environment, a CTE close to SiC and good wettability on SiC. The composition is 54 wt% SiO<sub>2</sub> – 18.07 wt% Al<sub>2</sub>O<sub>3</sub> – 14.77 wt% Y<sub>2</sub>O<sub>3</sub> with glass-transition temperature at 910°C, crystallization temperature at 1235 °C and melting at 1375°C [8]. Thermal treatment is tailored on the information obtained by Differential Thermal Analysis (DTA) curve, represented in fig 3.13.



Figure 3.13: Differential Thermal Analysis (DTA) curve for SAY glass [9]

Glass powder is deposited onto the substrate by a slurry deposition technique and then the counterpart is added. The assembly is thermal treated at 1375°C for 20 minutes and then at 1235°C for 60 minutes to promote crystallization, heating rate is 1000°C/h and the atmosphere

is inert. After the treatment three crystalline phases can be detected: keiivite (yttrium disilicate), cristobalite and mullite. The XRD pattern (fig 3.15) does not show any amorphous halo suggesting the absence of glassy phase.



Figure 3.14: X-rays Diffraction spectrum for SAY glass-ceramic [9]

DTA analysis after thermal treatment does not detect glass-transition temperature ( $T_g$ ) confirming the absence of glassy phase and it identifies melting temperature at 1377 °C[9].

Interface between SAY glass-ceramic and nuclear grade SiC/SiC (fig 3.15) is well-defined, homogeneous and without cracks. The absence of glassy phase can be beneficial in enhancing irradiation resistance, but it avoids the possibility of self-healing behaviour.



Figure 3.15: SEM micrography for SiC joined SAY [9]

Investigation on neutron effects on SAY joint reports a good resistance for SAY joined SiC/SiC. Porosity and microstructure do not seem to be affected by irradiation and bending test does not exhibit difference in strength for irradiated and unirradiated joints [10]. The joining strength is strongly influenced by the joint configuration as can be observed in fig 3.16, where best results in strength retention after irradiation are achieved by the type-2 configuration.

	Before irradiation	After irradiation (HFR-Petten, NL)		
	Bending strength [MPa]	550 °C 9-11 10 <sup>24</sup> n/m <sup>2</sup>	600 °C 16-22 10 <sup>24</sup> n/m <sup>2</sup>	820 °C 31-32 10 <sup>24</sup> n/m <sup>2</sup>
As received, not joined SiC/SiC	418 ± 45	304	113 ± 14 (*)	59 ± 17 (*)
Not joined SiC/SiC (1420 °C, 30 min; 1240 °C 1h, Ar)	283 ± 8	-	-	-
SAY Joined SiC/SiC type2	122 ± 10	-	118	89±17
SAY Joined SiC/SiC type3	149	-	65	-

Figure 3.16: bending strength of SiC joined SAY before and after irradiation [11]

Another glass-ceramic proposed for nuclear applications is based on CaO-Al<sub>2</sub>O<sub>3</sub> system. Similarly to SAY glass-ceramic, after joining treatment the material is fully crystalline without glassy phase. Phases detected are 12CaO·7Al<sub>2</sub>O<sub>3</sub>, 3CaO·Al<sub>2</sub>O<sub>3</sub> and at the interface CA/SiC, 3CaO·SiO<sub>2</sub> is formed as reaction product. CA joint exhibit a good irradiation resistance and enough shear strength to make them suitable for operating in fusion environment, but its sensitivity to water does not allow its utilisation for LWRs[11].

# 3.5 Hybrid polymer/Chemical vapour infiltration joining

This technique allows to realise a  $\beta$ -SiC joint having the same composition of the SiC/SiC tubes and this is an advantage because it should provide the same thermo-mechanical properties and good radiation stability typical of the substrate, suggesting that this joint can be considered nuclear grade.

A slurry containing the preceramic polymer and SiC whiskers is infiltrated between the SiC/SiC parts to be joined. Once the slurry is well distributed a curing step is performed to increase its viscosity obtaining a green state. Then it is subjected to a pyrolyzing process until the formation of polymer-derived SiC, with dispersed SiC whiskers[12]. Amount of  $\beta$ -SiC in the joint can be estimated in the range of 99wt%-99.7wt%. The obtained joint cannot provide hermeticity and so a CVI process is performed on the polymer-derived framework. Pyrolysis is usually performed at temperatures from 850°C to 1300°C for polycarbosilane, providing an amorphous structure with possible nanocrystals, which is not acceptable. A post treatment is performed heating at more than 1500°C to obtain a grain size similar to third generation SiC fibers, which exhibit nuclear grade properties. joined composite Fibers can be damaged by thermal treatment when temperature exceeds 1400°C, so it is important to consider this limitation during joining process[13].

In fig 3.17 is shown the microstructure obtained by this method. As can be noticed the outer areas of joint are denser than inner ones due to the most effective deposition. After the densification provided by CVI the remaining porosity is estimated to be less than 5%. Joining thin wall composites can be an advantage because it limits the presence of density gradient along the joint thickness.



Figure 3.17: SEM micrography of SiC joined by polymer precursor/CVI hybrid process(a). SEM micrographs of inner (b) and outer (c) regions of the joint [14]

Radiation stability was studied evaluating hourglass-type specimens (fig. 3.18), tested in torsion before and after neutron irradiation of 4.5 x  $10^{25}$  n/m<sup>2</sup> at 730°C. The measured apparent shear strength was 77.7 MPa for unirradiated joint and it was 81,3 MPa for the irradiated one [14].



Figure 3.18: SiC joined hourglass specimen manufactured by hybrid method [14]

No phase degradation was observed by XRD after irradiation test, detecting the presence of only  $\beta$ -SiC prior and after neutron dose.

Cohesive fracture can be observed in almost the total area of fracture surface, although in the outer regions also substrate fracture occurs due to higher density reached by CVI (fig 3.19).



Figure 3.19: fracture surface after torsion test [14]

## 3.6 NITE-based joining

NITE process can be used not only to produce SiC matrix, but also as joining process. It can be performed pressure-less for low cost production, but only with pressure it is possible to increase silicon carbide volume fraction reducing to minimum percentage the sintering aids. Sintering aids are the same used for matrix densification: silica, alumina and rare-earth oxides which constitute the eutectic phase to help densification. If the selected nuclear grade SiC is realised by NITE process, this joining technique has the advantage of providing no discontinuity between matrix and joined area; and simultaneously a good radiation resistance of the joint is expected due to previous study on NITE SiC-composites. Best results are expected using pressure between 5 and 20 MPa at about  $1800^{\circ}$ C [1]. It is possible to utilise both powders both green tapes consisting of SiC nanophase powder, Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>.

# 3.7 Laser joining technology

SPS allows to obtain a rapid joining process compared to traditional diffusion bonding, but it exhibits size limitations both for diameter and both for length which is imposed by the electrical resistivity of the material to be joined. Laser-based technology can be used to overcome size limitation. The laser beam provides localised heating which depends on absorptivity of the material and on the specific heat and thermal conductivity. SiC has high absorptivity under several wavelengths and this means that different types of laser are available for SiC joining.



Figure 3.20: example of laser joining setup (left) and the joined tube (right) [15]

Composites exhibit some complications compared to bulk SiC, fibers and matrix do not provide the same absorption of laser beam and also thermal conductivity is different. The porosity typical of composites brings to an important decrease of thermal conductivity.

This class of processes allows an efficient local heating and consequently short processing time, dimension flexibility of components and types of processing atmospheres –inert atmosphere is

often required during joining process in furnace. If a glass-ceramic SAY-based material is used as filler, its low viscosity causes loss of material in the joining area due to infiltration in composite pores. This issue can be solved avoiding infiltration, applying a coating on the composite with a protective layer made up of CVD SiC [14].

The interface, when CVD-SiC is used as protective layer, is free of defects, suggesting an optimal wettability of silicon carbide by glass-ceramic material (fig 3.21).



Figure 3.21: example of laser joined SiC composite (left) and SEM micrograph of its joining interface (right) [16]

Joining materials suitable for laser-based joining process must melt due to rapid heating provide by laser beam and so other candidates as well as glass-ceramics are metal interlayers. After treatment the joints are comparable to those obtained by traditional furnace process. In perspective of producing a large number of SiC/SiC tubes for nuclear industry, this technology should be energy-efficient and provide a cost reduction.

#### 3.8 MAX phases joining

As presented in last chapter MAX phases are investigated as ATF clad, suggesting that they could be suitable as accident-tolerant joining technology. Among the MAX phases studied for nuclear applications, the most promising one as joining material is  $Ti_3SiC_2$ , which has a CTE higher than that of SiC (~9.1 X 10<sup>-6</sup> K<sup>-1</sup> vs 4.5 X 10<sup>-6</sup> K<sup>-1</sup>), but, as already written, has a mixture of metal and ceramic properties which can help to mitigate thermal stresses.

This approach uses pressing and sintering starting from pre-synthesized  $Ti_3SiC_2$ . Treatment is performed by heating the assembly in inert atmosphere (Ar) up to 1600°C under 40 MPa for 30 minutes, following the scheme reported in fig 3.22[15]. The obtained joint, after being subjected to a bend strength test, with configuration presented in fig. 3.22, provides a maximum value of 110.4 MPa joining strength.



*Figure 3.22: pressing and sintering setup for MAX phases joining (left). Bending test scheme for the joint (right)*[17]

The joint thickness is uniform along the interface (fig. 3.23). The bonding appears good due to the plasticity typical of MAX phases which offsets the CTE mismatch between the two materials and due to chemical reactions occurring.



Figure 3.23: SEM micrography of the joinining area for Ti3SiC2 joint manufactured by pressing and sintering [17]

Pressing and Sintering approach exhibits a drawback because to reach higher strength values it is necessary to operate at high temperature, but this causes a decrease in the amount of available Ti<sub>3</sub>SiC<sub>2</sub> in favour of TiC and TiSi<sub>2</sub> because of chemical reactions. No reactions were observed between the joining material and the substrate at temperature lower than 1300°C.

An alternative process proposed for MAX phases joining is Spark Plasma Sintering (fig. 3.24). Instead of pre-synthesized powders, a pre-sintered  $Ti_3SiC_2$  foil is used. Process parameters optimised to avoid decomposition and obtain a sound joint are: 1300°C, 50 MPa, 5 minutes[16].



Figure 3.24: sketch for Ti3SiC2 SPS joining [18]

The pre-sintered  $Ti_3SiC_2$  foil is moulded easily to the CVD-SiC coated surface under the applied pressure infiltrating the surface cracks and increasing the effectiveness of the bonding process. Final joint thickness depends of the initial foil thickness. The shear strength of joined SiC/SiC composites is in the range 35-50 MPa, the reported values of apparent shear strength of joined coated SiC/SiC are lower:  $18.3 \pm 5.8$  MPa. This result suggests that the SPS conditions could be too harsh for SiC fibers, that at 1300°C under 50 MPa experience accelerated degradation.

## 3.9 Reaction bonding

Reaction between carbon and silicon is a quite common method to join SiC parts and it is generally performed mixing powder of Si and C. The mixture is heated up to a temperature a little higher than silicon melting point and the reaction continue until all the carbonaceous agent is fully consumed leaving a microstructure characterised by crystalline stoichiometric SiC and remaining silicon. This joint is not indicated for nuclear applications due to differential swelling of the two phases which is more intense if the content of unreacted silicon is high. The only way to reduce this effect is to obtain a microstructure with all the silicon confined in tiny grains embedded in SiC matrix[1]. Performing the joining process in air, an additional phase, silica, is formed which participates to differential swelling under irradiation.

## 3.10 Mechanical testing of joined samples

An additional challenge lies in the absence of standard test to evaluate the joint shear strength, which represents the most relevant mechanical property to assess joint reliability, for complex geometry joint before and after irradiation. For fusion applications, which inspire several joining techniques then proposed for ATFs, an effort towards standardisation is performed by the community for the development of a reliable joint shear strength test.

The focus is on the achievement of a standard torsion test of hourglass-shaped ceramic joints because it is considered the best solution to get uniform stress application and to be performed on small specimen which are needed for irradiation test.

The proposed test is effective when the joining material is brittle and fracture occurs in the joint area, if this condition is not achieved, it is necessary the utilization of theoretical models to get the true joint shear strength[17]. Fig 3.25 shows the tests available to evaluate the joint shear strength.



Figure 3.25: available shear test configuration [18]

Among them single lap test (SL), single lap offset test (SLO), double lap offset test (DLO) and double-notch test (DN) can only find the apparent shear strength [18].

Hourglass-specimen torsion test was performed on different SiC joints to provide information on joint strength before and after irradiation[6]. Joints tested are reported in table 3.1 and the test results are visible in figure 3.26. the Highest shear strength values are obtained using a NITE-like joining process (indicated as TEP in the graph) with the best result showed using powders (TEP-. Titanium diffusion bonded joint does not exhibit variation in strength after irradiation. CA/SiC experiences a 21% reduction in shear strength after irradiation both after 3 dpa at 500°C and both after 5 dpa at 800°C. TSC/CVD SiC shows a decrease in strength after irradiation of 5 dpa at 800°C, but it retained about the 84% of initial strength. The relevant increase observed for TEPs/CVD after irradiation is suspected to be an artefact.



Figure 3.26:: shear strength before and after irradiation for different joints [6]

Designator	Method of joining	Base material joined	Phases present in joint layer
Ti/CVD TEPs/CVD	Ti diffusion bonding TEP/NITE SIC slurry	CVD SiC <sup>1</sup> CVD SiC	Ti <sub>3</sub> SiC <sub>2</sub> , Ti <sub>5</sub> Si <sub>3</sub> SiC, YAG, Al <sub>2</sub> O <sub>3</sub>
TEPs/NLS TEPs/NITE		NITE-like sintered SiC <sup>2</sup> NITE SiC/SiC <sup>3</sup>	
TEPt/CVD TEPt/NLS	TEP/NITE SIC tape	CVD SiC NITE-like sintered SiC	SiC, YAG, Al <sub>2</sub> O <sub>3</sub>
CA/CVD TiSiC/CVD	CA glass ceramic Ti–Si–C MAX-phase	CVD SIC CVD SIC	12CaO·7Al <sub>2</sub> O <sub>3</sub> , 3CaO·Al <sub>2</sub> O <sub>3</sub> Ti <sub>3</sub> SiC <sub>2,</sub> SiC

Table 3.1: Joints tested by torsion before and after neutron irradiation (Katoh et al.) [6]

Hydrothermal corrosion for different water chemistry of LWRs was investigated for four types of joints: Mo diffusion, Ti diffusion, Ti-Si-C reaction sintering and NITE-like. The test conditions were those reported in table 3.1. The tests were performed in autoclave for 5 weeks without irradiation[19].

Table 3.2: autoclave test environments [19]

Summary of environments of autoclave corrosion tests.

Autoclave environment	Chemistry	Temperature [°C]	рН	Pressure [MPa]
PWR	3.57 ppm H <sub>2</sub>	330	7.2	15
BWR-HWC	0.3 ppm H <sub>2</sub>	290	5.6	7
BWR-NWC	1.0 ppm O <sub>2</sub>	290	5.6	7

Appearance of the specimens after the tests are provided in figure 3.27, while evolution of joint thickness is reported in table 3.3.

Joint	nt As received		toclave environments	
Materials	As-received	PWR	BWR-HWC	BWR-NWC
Mo diffusion bond	•	٠	0	•
Ti diffusion bond	0	•	•	The joint failed.
Ti-Si-C reaction sintered joint	•	•		•
SiC nanopowder sintered joint		Not available		

Figure 3.27: specimens before and after autoclave test [19]

Material	PWR	BWR-HWC	BWR-NWC
SiC substrate	-0.20	0.05	-0.25
Mo diffusion bond	-110	95	-235
Ti diffusion bond	0	0	>-750
Ti—Si—C reaction sintered joint	0	0	+35
SiC nanopowder sintered joint	No data	0	-5

Table 3.3: changes in thickness of the tested joints for the different environments [19]

The poorest performances for each environment are provided by Mo diffusion bond which exhibits a remarkable corrosion for all testing conditions, suggesting that this type of joint is not suitable for LWR applications. Titanium bonding with single Ti<sub>3</sub>SiC<sub>2</sub> phase exhibits good behaviour in PWR and BWR-HWC chemistry but the joint failed due to an extreme corrosion when tested in BWR-NWC conditions. For Ti-Si-C reaction sintered joint the performances are very good in PWR and BWR-HWC chemistry, while weight gain is observed in BWR-NWC oxidizing water chemistry. The NITE-like joint is the only one which exhibit a limited corrosion in BWR-NWC autoclave suggesting the best behaviour both in oxidizing conditions both in reducing conditions.

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# 4 Experimental activity

Experimental work has been performed as part of the activities of Workpackage 3 within Il Trovatore project. Politecnico di Torino is involved in this project within the following tasks:

- Selection of joining approaches for SiC/SiC composites.
- Joining of SiC and SiC/SiC composites.
- Mechanical testing of joints.

The experimental work carried out in this thesis regards the first two activities.

Two joining materials were selected as suitable for LWRs SiC/SiC fuel clads: SAY glassceramic and MoSi<sub>2</sub>/Si composite. Both of them, already described in chapter 3 and developed within the research group GLANCE (<u>http://www.composites.polito.it/</u>) at Politecnico di Torino, DISAT, have the peculiarity to be processed pressure-less. As discussed in chapter 3, using pressure-less approaches can be beneficial for reducing damages on fibres of SiC/SiC tubes and the complexity of the joining process.

The aim of the experimental part was the assessment of joining feasibility of both materials for the application, by investigating their behaviour under relevant conditions.

According to the process parameters reported in literature [1]–[3], SiC joints have been manufactured first. The joined SiC were then tested in static autoclave as go/no go test, then they were characterised to understand what occurred during the test. Finally, the best material was selected to be used in the second part of the experimental work, focused on SiC/SiC joints. Figure 4.1 shows the flow chart for the first experimental part.



*Figure 4.1: flow chart for experimental activity, first part, on SiC* 

Nuclear grade SiC/SiC composites are quite expensive, and it was important to get more information about their joining before starting the experimental activity on them. Since nuclear grade SiC/SiC are coated with CVD-SiC, joining of bulk CVD-SiC provided valuable information to select the joining materials before starting joining of composites.

SAY was selected as the most suitable joining material for nuclear grade SiC/SiC: several characterisations of these joints were carried out to investigate the feasibility of the proposed method for joining nuclear grade SiC/SiC tubes.

# 4.1 Materials and methods

### 4.1.1 SiC and SiC/SiC

Joints for autoclave test were manufactured using CVD-SiC as substrate. CVD SiC slices were square-shaped with a section of about 10 mm x 10 mm and a thickness of about 5 mm.

The second part of the experimental activity was conducted using SiC/SiC composites as materials to be joined, provided by different suppliers. All materials are classified as nuclear grade.

NITE SiC/SiC was provided by *NITE Corporation* (Prof. A. Kohyama, Japan) in form of one tile 58×58×3 mm<sup>3</sup>. Nominal properties are reported in table 4.1. Several smaller slices were cut from the original tile.

Property	Value	
SiC fiber content (vol.%)	40-50	
Residual porosity (%)	< 3%	
Tensile strength (MPa)	UD: 250-400 / XP:150-250	
Flexural strength (MPa)	UD: 550-650 / XP:200-300	
E-modulus (GPa)	300-350	
Strain-to-failure (%)	0.1	
Thermal conductivity (W/m·K)	20-50	
Thermal expansion (10 <sup>-6</sup> C <sup>-1</sup> )	5-10	

Table 4.1: Nominal properties for NITE SiC/SiC by NITE Corporation [4]

CVI SiC/SiC tubes with standard nuclear fuel geometry were provided by CEA (Commissariat à l'énergie atomique et aux énergies alternatives, France). Nominal properties are shown in table 4.2.

Property	Value	Remark
SiC fiber content (unit)	$0.40 < \alpha < 0.45$	Hi-Nicalon <sup>™</sup> type S SiC fibers;
Sic fiber content (unit)	$0.40 < \alpha_{\rm f} < 0.45$	multilayered filament winding
Density	2.95 ± 0.02	Bulk density
Residual porosity (%)	7%	-
Tensile strength (MPa)	278 ± 22	
Yield strength (MPa)	98 ± 8	Uniovial tancila loading
Strain at failure (%)	0.94 ± 0.08	
E-modulus (GPa)	260 ± 10	
Roughness Ra	1 – 3 µm	-
Thermal conductivity (W/m-K)	28 - 32	Room temperature

Table 4.2: CEA tubes nominal properties[4]

CEA tube dimensions:

- Length: 10 mm
- Inner diameter: 8.35 mm
- Outer diameter: 9.56 mm

### 4.1.2 Mo-wrap joining

The joining material is a composite MoSi<sub>2</sub>/Si obtained following the original paper[1]. Materials used are:

- Alfa Aesar Molybdenum foil 0.025mm thick, 99.95%.
- MEMC Electronic Materials Si wafer 584 µm thick.
- Alfa Aesar Molybdenum foil 0.050 mm thick, 99.95%.

The silicon wafer was cut to the size of SiC substrate and then it was enveloped between two molybdenum foils following the sketch in figure 4.2. During the procedure Mo foils and Si wafer were weighted to respect the proportion: 32-35 wt% Mo and 65-68 wt% Si. Respecting this weight proportion was achieved by using 0.025 mm thick molybdenum foil.





The wrapped silicon wafer was interposed between two slices of SiC. The obtained assembly was subjected to the described thermal treatment in a Carbolite STF 16/180 tubular furnace:

- Heating rate: 16.6 °C/min
- Dwell temperature: 1450° C
- Dwell time: 5 minutes
- Inert atmosphere (argon flow)

Sample holder was made of graphite. To maintain the contact, between the wrap and the SiC slices, and to avoid misalignment, a tungsten weight (44.85 g) was used. To prevent oxidation, titanium sponges were utilised as an oxygen getter.

A batch of 7 SiC joined Mo-wrap specimens were manufactured:

- 2 samples for static autoclave test
- 2 samples for loop autoclave test
- 2 samples for high temperature steam exposure test.
- 1 sample as reference.

### 4.1.3 SAY glass-ceramic joining

SAY glass was produced by melting alumina, silica and yttria powders (as reported in table 4.3) in a platinum-rhodium crucible at 1700°C for 5 h in air, then, it was casted on a brass plate, as reported in [2].

SAY glass was machined by ball-milling and it was sieved in three different batches: >78  $\mu$ m, 38-75  $\mu$ m and <38  $\mu$ m. Only the powder fraction between 38 and 75  $\mu$ m has been used to produce the joints, according to previous [2].

	Ĩ	
SiO <sub>2</sub>	Y <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
54 wt%	27.93 wt%	18.07 wt%

Table 4.3: SAY composition

A second batch of SAY glass was produced following the previous indications but varying the thermal treatment. Oxide powders were heated in a platinum-rhodium crucible for 1h at 1750°C in air and then the glass was casted on a brass plate.

A slurry was prepared dispersing SAY powders (38-75  $\mu$ m) in ethanol, then it was deposited on the lower CVD-SiC slice. The upper SiC slice was then put over the lower one to form the sandwich to be joined, which was placed in a graphite sample holder.

Joining thermal treatment was performed in Carbolite STF 16/180 tubular furnace respecting the conditions indicated in the previous work [2]. Titanium sponges are used to prevent oxidation. The joining treatment conditions are reported below:

- Heating rate: 16.6 °C/min
- 1<sup>st</sup> Dwell Temperature: 1375°C
- 1<sup>st</sup> Dwell Time: 20 minutes
- 2<sup>nd</sup> Dwell Temperature: 1235°C
- 2<sup>nd</sup> Dwell Time: 1 hour.
- Inert atmosphere (argon flow)

A batch of 7 SiC joined SAY specimens were manufactured:

• 2 samples for static autoclave test

- 2 samples for loop autoclave test
- 2 samples for high temperature steam exposure test.
- 1 sample as reference.

All joints were manufactured using the first batch of SAY glass produced accordingly with the previous works[2][3].

The joining of CEA tubes was performed using a specific sample holder which was developed within the final project. SAY joined tubes were butt joints, so the sample holder must satisfy two requirements: to keep the tubes aligned and to maintain the tubes in contact during the joining treatment.

The sample holder was designed using Solidworks and it was realised in graphite. Figure 4.3 shows the parts of the sample holder, fig. 4.4 reports the dimensions of the main body while fig. 4.5 shows those of the hollow cylinders. All the values are expressed in millimetres.



Figure 4.3: sketch of the sample holder designed to join tubes



Figure 4.4: size of the main body



Figure 4.5: Sizes of the hollow cylinders

### 4.1.4 Coating deposition

Half of the joined CVD-SiC samples were coated by PVD sputtering using a chromium target. The system used to coat the joined specimens is a Kenosistec<sup>TM</sup> magnetron confocal target co-sputtering.

The magnetron sputtering is a variant of the typical PVD sputtering which exploits a magnetic field to optimise the deposition. Under the magnetic field the efficiency of plasma is enhanced enabling higher sputtering yield.

The sketch of the PVD Magnetron sputtering process is shown in fig. 4.6.

Sputtering settings for the deposition were:

- Power: 200 W (0,530 A; 370 V) DC (Direct Current).
- Vacuum pressure: 2 x 10<sup>-6</sup> mbar (0,2 MPa).
- Working pressure: 6,3 µbar (6,3 dPa)
- Gas flow: 25 sccm.
- Atmosphere: argon.
- Deposition time: 2 h.

The thickness of the deposited chromium layer was estimated about 6  $\mu$ m, based on the choice of settings.



Figure 4.6: sketch of DC magnetron sputtering process [5]

## 4.1.5 Testing

### 4.1.5.1 Static Autoclave test

Static autoclave test was performed at SCK-CEN (Centre d'Étude de l'énergie Nucléaire - Belgium) as go/no go test, simulating PWR water chemistry.

The conditions were[4]:

- Water chemistry: boron (1000 ppm) and lithium (2ppm).
- Temperature: 330°C.
- Time: 14 days

Fig. 4.7 provides the profiles of temperature and pressure inside the autoclave during the test.



Figure 4.7: pressure and temperature profiles vs exposure time for the static autoclave test [4]

Below is reported the list of tested samples:

- SAY joined SiC.
- Cr-coated SAY joined SiC.
- Mo-Wrap joined SiC.
- Cr-coated Mo-Wrap joined SiC.
- Bulk MoSi<sub>2</sub>/Si.

As reference materials in the autoclave were tested:

- Si wafer.
- Cr-coated Si wafer.
- Zircaloy-4 tube segment, supplied by SCK-CEN.

Weighting of samples was performed prior and after autoclave test at SCK-CEN in the reported conditions:

- 26°C
- 1013 bar
- Hygrometry: 46%

### 4.1.5.2 Hot stage microscopy

Hot Stage Microscopy was performed using an Expert System Solutions heating microscope (maximum temperature 1500°C) The SAY glass-ceramic was prepared with the same conditions of joining process. Heating rate was set at 5°C/min until melting temperature. The analysis was performed on a glass pellet (diameter of 3 mm and height of 3 mm) prepared pressing a slurry powder-ethanol. Then the pellet was placed in the heating microscope for the analysis.

### 4.1.5.3 Loop Autoclave test

Loop autoclave test was performed at SCK-CEN as go/no go test, simulating PWR water chemistry.

Samples tested were:

- SAY bulk
- 2 SAY joined SiC specimens.

The conditions (courtesy of Konstantza Lambrinou, SCK-CEN, Belgium) were:

- Water chemistry: boron (1000 ppm), lithium (2ppm)
- Temperature: 330°C.
- Time: 30 days.
- -

# 4.1.5.4 Creep tests

Two creep tests were conducted on SAY glass pellet. Test temperatures were chosen according to those used for oxidation tests conducted on ATF. Those tests, described in chapter 2, aim to simulate a LOCA scenario and they are conducted at 1200°C for 20-60 min at 1200°C in steam environment or in air. [6], [7]. During LOCA, creep is a mechanism of failure for zirconium alloys, so the temperatures used for oxidation tests were selected as relevant to investigate the mechanical behaviour of SAY at high temperature.

The furnace used to run the test was a CARBOLITE CWF1300 (maximum temperature: 1300°C).

The SAY pellet was realised using powders with granulometry in the range of 38-75  $\mu$ m from the batch 2. Then the pellet underwent the joining thermal process (1375°C for 20 min, 1235°C for 1 h in argon atmosphere).

The dimensions of the cylindrical pellets were:

- Height: about 8,42 mm
- Diameter: about 8,9 mm.

First test was conducted in air applying a weight of alumina on the top of the pellet with a mass of 59 g. The contact area was calculated to be approximately 62 mm<sup>2</sup>.

The resultant stress on the sample was calculated using equation 4.1. P indicates the resultant stress, m is the mass of the weight, g is the gravity acceleration and A is the contact area between the specimens and the weight

$$P = \frac{mg}{A}$$

The applied stress for the first creep test was 9,3 KPa.

The set program on the furnace for the test was the following:

- Heating rate of 10°C/min up to 900°C.
- Heating rate of 5°C/min up to 1200°C
- Dwell at 1200°C for 1 h.
- Cooling rate of 10°C/min.

Second creep test was performed on the same SAY glass-ceramic pellet. The alumina weight used was 166 g.

The applied stress was calculated to be 26 kPa.

The set program on the furnace for the second test was:

- Heating rate of 10°C/min up to 900°C.
- Heating rate of 5°C/min up to 1200°C
- Dwell at 1250°C for 1 h.
- Cooling rate of 10°C/min.

Variations on the size of the pellet before and after the creep test was measured using a digital caliper.

### 4.1.6 Characterization

### 4.1.6.1 X-rays Diffraction (XRD)

XRD analysis was performed to get information about crystalline phases of SAY joined SiC and MoSi<sub>2</sub>/Si bulk after the autoclave test. The facility used for the analysis was an X'Pert Philips diffractometer with hot stage. XRD analysis was performed also on SAY glass powder with granulometry below 38  $\mu$ m from the second batch of SAY glass. The software used to investigate the spectra was X'Pert Highscore. MoSi<sub>2</sub>/Si was powdered to conduct the analysis.
## 4.1.6.2 Field Emission- Scanning Electron Microscopy (FE-SEM)

To prepare the samples for FE-SEM analysis it was necessary to polish them using a Struers grinding equipment to get a mirror-like surface. SiC grinding foils used were P 600, P 800, P 1000 and P 2500. Rotational speed was set to 150 rpm.

Samples were chromium or gold coated before the analysis to make them conductive.

FE-SEM used for the characterization was Field Emission Scanning Electron Microscopy (FESEM- ZEISS Supra 40) with an Energy Dispersive Spectroscopy (EDS- SW9100 EDAX) detector.

FE-SEM was used to investigate the morphology of the joint using secondary electrons and backscattered electrons, prior and after autoclave test. Energy Dispersive X-Rays (EDX) analysis was conducted to evaluate composition of the joining materials and at interfaces between them and joined substrates.

#### 4.1.6.3 Micro Computed Tomography scan (micro CT-scan)

To get more information on tested samples, micro CT-scan was performed on specimens after static autoclave. The analysis was performed by Prof. J. Marrow's group, Oxford University, UK.

One SAY joined SiC specimen was manufactured with size about 2 mm x 2 mm and sent to Prof. J. Marrow group to be analysed at micro CT-scan prior and after autoclave test. Size was selected to allow the evaluation of the entire volume of SAY/SiC interface and to investigate the where corrosion starts.

## 4.1.6.4 Differential Thermal Analysis (DTA)

DTA was performed on  $<38 \ \mu m$  SAY glass powder from the second batch. The analysis was performed to detect the characteristic temperatures for the glass and to compare them with those reported for SAY in previous studies.

The equipment used for the analysis was a DTA Netsch (max temp. 1500°C).

## 4.2 Results and discussion

## 4.2.1 Characterisation of SAY glass (1750°C, 1h)

The second batch of SAY glass (casted at 1750°C after 1h) was characterised before its use to check its properties in comparison with the first batch casted after 5 h at 1700°C.

The spectrum obtained by XRD analysis of the SAY glass after casting showed only the typical glassy halo without any peak related to crystal phases. So, no crystallisation occurred during casting of this glass. The DTA analysis provided the characteristic temperatures for the glass, which are the same found for the SAY glass treated at 1700°C for 5 h. DTA curves of the two batches of SAY glass are shown in fig. 4.8.

The DTA analysis on the SAY glass revealing a glass transition temperature (Tg) at 911°C, a crystallization temperature at 1233°C and the melting point at1390°C, according to [2].



*Figure 4.8: DTA curves: green for second batch SAY glass (casted 1750°C, 1h) and red for first batch SAY glass (1700°C, 5h)* 

DTA found negligible differences between the characteristic temperatures of SAY from batch 2 and that casted after 5 hours at 1700°C.

## 4.2.2 Joints before autoclave test

After joining treatment, SAY joined SiC specimens looked sound from visual inspection (fig 4.9). Some glass-ceramic can be observed outside the joining area due the slurry squeezed between the two SiC parts.

Before applying the slurry, the two slices of CVD-SiC were overlapped and their overall thickness was measured using a digital caliper. The same measurement was performed after the joining treatment. Thickness of the joint was obtained as difference between the final value and the initial one. Thickness of the joint was in the range of 150-250  $\mu$ m.



Figure 4.9: SAY joined SiC after joining treatment

Subsequent analysis performed at FE-SEM showed that SAY-joined CVD SiC samples exhibited a well-defined continuous interface free of defects (fig. 4.10). Some large voids are visible in the joining area and they can be attributed to the manufacturing method which does not guarantee a homogenous distribution of the slurry. Smaller voids can be attributed to the shrinkage experienced by SAY glass during the crystallization process. Where the large pores are not present, the structure looks quite dense and this is important to satisfy the requirement of hermeticity.

No evidence of cracks was found in the joint, suggesting limited thermal stresses due to the low mismatch between SiC (4 x  $10^{-6}$  K<sup>-1</sup>) and SAY glass-ceramic (5,49 x  $10^{-6}$  K<sup>-1</sup>, between 400 and 700°C [3]) CTE.

Two different phases can be evidenced in the joining area: one is dark grey and the other is white. In the previous works [2][3] EDX analysis on the grey zone detected silicon, yttrium and oxygen, while the same analysis on the white regions identified aluminium, silicon and oxygen. The same peculiar microstructure was observable in the analyzed SAY joined SiC specimen.



Figure 4.10: Back-scattered SEM micrograph of the outer face of a polished SAY joined SiC sample

Micro CT-SCAN (fig. 4.11) performed on the 2 mm x 2 mm SiC joined SAY sample confirmed the observation made after the SEM analysis. Interface appears continuous and without defects. There is no evidence of cracks, but large voids are still visible. The presence of several remarkable voids is indicative of a poor slurry deposition during the manufacturing process.

The microstructure detected is what expected and already observed for SAY glass-ceramic after joining.



Figure 4.11: Micro CT-Scan on a 2mmx2mm SiC joined SAY specimen (Prof. J. Marrow group, Oxford University, UK)

An image at CT-Scan was taken at higher magnification on a white region free of voids of the 2 mm x 2 mm specimen. The image is reported in fig. 4.10. Pores can be detected in the selected area.



Figure 4.12: CT-Scan at higher magnification on the 2mmx2mm SiC joined SAY specimen (Prof. J. Marrow's group, Oxford University, UK)

The fig 4.13 shows the SEM micrograph of MoSi<sub>2</sub>/Si joining material before the autoclave test. The microstructure consists of MoSi<sub>2</sub> spherical particles (white) well-distributed within the silicon matrix (grey). No cracks can be detected in the joining area, as already reported in [1].

Typical joint appearance for Mo-Wrap joined SiC was investigated in the PhD Thesis of Gianchandani P. K. [8], two micrographs are provided in fig.4.14 .The joining material is identical to that provided in fig. 4.13. It is easy to distinguish the MoSi<sub>2</sub> particles within the silicon matrix. Silicon exhibits a good wettability on SiC and this explains the well-defined, continuous and defect-free interface between MoSi<sub>2</sub>/Si and SiC.



Figure 4.13: Back-scattered SEM micrograph of MoSi<sub>2</sub>/Si joining material



Figure 4.14: microstructure of Mo-Wrap joined SiC [8]

## 4.2.3 Tests in autoclave (SCK-CEN, Belgium)

The main requirement for joints for LWR environment is to resist under normal operation conditions. These preliminary autoclave tests were done as first assessment on the materials' resistance against water corrosion at normal conditions.

In table 4.4 the weight modification observed on samples after the static autoclave test is listed. The weight loss of the tested materials is an important information, because weight modification is an important indicator for corrosion resistance.

Important data to assess during the simulation of normal operation conditions include:

- outer surface visual inspection.
- evaluation of microstructural changes in joining and bulk materials and at the interfaces.
- weight change measurement (the increase indicates growth of oxides on the sample while the decrease spots dissolution).

Table 4.5 provides the weight modification for silicon, Cr-coated silicon and zircaloy-4 tube segment.

Silicon wafer, tested as reference material, underwent complete dissolution in autoclave water, suggesting unacceptable corrosion resistance. To the best of my knowledge, no literature is available on this subject.

Mo-Wrap joined SiC exhibited a higher weight loss percentage (1,46 %) compared to SAY joints (0,35%). To understand the different weight loss between the two specimens is useful to comment the results for the bulk MoSi<sub>2</sub>/Si.

Bulk MoSi<sub>2</sub>/Si lost 35.6% of its initial mass. This result is consistent with the dissolution of silicon, which is the matrix for this joining material.

The choice to coat some joined specimens with chromium was motivated by the good results in term of corrosion resistance observed for Cr-coated zirconium alloys[9]. The aim was to explore the effectiveness of chromium in enhancing the corrosion resistance of the joints, by comparing the weight loss achieved by coated and uncoated samples in autoclave.

The Cr-coated Si was not dissolved, its weight loss was of 17,6% compared to the initial value. This result suggests a positive effect provided by chromium in enhancing the corrosion resistance.

Cr-coated samples provided similar results compared to uncoated ones due to the detachment of the coating during the autoclave test. The failure of the coating does not allow to make considerations on the effectiveness of the chromium layer in enhancing corrosion resistance of joints.

Zircaloy-4, the standard material for PWR fuel cladding, exhibited the best corrosion resistance (increase of 0,01% due to oxidation reaction), but the weight loss experienced by SAY joined SiC was low enough (near to zero) to confirm this material as promising.

Bulk MoSi<sub>2</sub>/Si gave important information about the behaviour of the material under autoclave conditions.

The weight losses associated with Mo-Wrap joined SiC and SAY joined SiC provided important data to assess the feasibility of the joints and the subsequent characterization was conducted to understand what occurred during the test.

Specimen	Weight before	Weight after Weight		Relative
	autoclave test (g)	autoclave test (g)	difference (g)	weight
				change
				percentage
SAY joined SiC	2,9652	2,9547	-0,0105	-0.35 %
Cr coated- SAY	1,9832	1,9760	-0,0072	-0,36%
joined SiC				
Mo-Wrap joined	3,4756	3,4248	-0.0508	-1,46%
SiC				
Cr coated Mo-	1,1281	1,1133	-0,0148	-1,31%
Wrap joined SiC				
MoSi <sub>2</sub> /Si bulk	0,6378	0,4106	-0,2272	-35,6%

Table 4.4: weights before and after static autoclave test (SCK-CEN, Belgium)

Table 4.5: reference materials weights before and after static autoclave (SCK-CEN, Belgium)

Specimen	Weight before	Weight after	Weight	Relative weight
	autoclave test	autoclave test	difference (g)	change
	(g)	(g)		percentage
Si	0,2064	-	-	-
Cr-coated Si	0,2064	0,1700	-0,0364	-17,6%
Zircaloy-4	0,9843	0,9844	+0,0001	0,01%

## 4.2.4 Post-autoclave characterization

SEM backscattered micrograph on SAY joined SiC after autoclave (fig. 4. 15) shows damages on the joining material which looks carved. This result is coherent with the weight loss experienced by SAY joined SiC because of the static autoclave test.

The SAY joined SiC was then polished. The SEM backscattered micrograph of the polished specimen (fig.4. 16) suggests that the glass-ceramic microstructure inside the joint is unmodified after autoclave exposure. The glass-ceramic/SiC interface is still continuous and no cracks are visible in the joint. Corrosion due to autoclave interested only the surface of SAY.

Micro CT-Scan- performed at Oxford University by prof. James Marrow's group- on the postautoclave SAY joined SiC (fig 4.17) showed that the joining material presented voids distributed randomly within the area. The absence of interconnected pores seems to guarantee the hermeticity of the joint. The voids could be attributed once again to the manufacturing process and to the shrinkage caused by the recrystallization treatment.



Figure 4.15: SEM backscattered micrograph on SAY joined SiC after autoclave. The cross-section is unpolished.



Figure 4.16: backscattered micrograph on polished SAY joined SiC after autoclave



Figure 4.17: CT-Scan on SAY joined SiC after autoclave (Prof. J. Marrow's group, Oxford University, UK)

SEM performed on chromium-coated SiC joined SAY sample post autoclave (fig 4.18, fig. 4.19) showed few areas in which the deposited coating was still observable. Where detected, the coating layer seems dense, but most of it was detached during the test. The microstructure is the same one observed for the un-coated SAY.



Figure 4.18:back-scattered micrographs of Cr-coated SAY joined SiC after autoclave test: most of SAY is uncoated. This cross section is unpolished.



Figure 4.19: back-scattered micrograph of Cr-coated SAY joined SiC after autoclave test: most of SAY is uncoated. This cross section is unpolished.

SEM analysis performed on Mo-wrap joined SiC sample (fig 4.20 and fig.4.21) confirmed that the matrix was dissolved under autoclave conditions. As it can be observed no matrix can be found in the outer face of the joint, whose integrity is only guaranteed by the network of particles. This result explains why the weight loss was higher for the Mo-wrap joined SiC specimen than for SAY joined SiC, which in contrast appears to be unmodified.

Matrix is responsible not only for holding together the silicides particles, but also for the formation of a continuous interface with SiC. In absence of the silicon phase, no interface is observable. The joint is held together by few contact points provided by the framework of particles.

The loss of the matrix makes the joint unsuitable for operating in the nuclear environment. Joint strength was not measured, but it would probably be classified as insufficient after the autoclave test due to absence of the interface. Furthermore, a similar microstructure cannot guarantee hermeticity because the network of particles fills only a small portion of the initial joint thickness allowing the release of fission gases.



Figure 4.20: back-scattered SEM micrograph on unpolished Mo-wrap joined SiC after autoclave

EDX analysis provided compositional information about the joints. The elements found in two selected areas, indicated by orange and blue rectangles on fig. 4.20, on MoSi<sub>2</sub>/Si joint after autoclave are reported in the figures 4.21 and 4.22 respectively.

It is interesting to notice the abundant presence of oxygen at the expense of silicon, which could indicate oxidation of silicides under autoclave conditions (fig 4.22, area corresponding to orange rectangle in fig. 4.21). In the other investigated area (blue rectangle in fig 4.21) 100% silicon was detected, indicating that matrix is still present in some regions (fig 4.23).



Figure 4.21:back-scattered SEM micrograph on unpolished Mo-wrap joined SiC after autoclave at higher magnification. The orange and blue rectangles indicate where EDX analysis was conducted.



Element	Weight%	Atomic%	
ОК	31.46	71.98	
Si K	2.02	2.63	
Mo L	66.53	25.39	
Totals	100.00		

Figure 4.22: EDX analysis on Mo-wrap joined SiC after autoclave (within the area indicated by orange rectangle in fig. 4.21)



Element	Weight%	Atomic%	
Si K	100.00	100.00	
Totals	100.00		

Figure 4.23: EDX analysis on Mo-wrap joined SiC after autoclave (area indicated by blue rectangle in fig 4.21).

Cr-coated Mo-wrap joined SiC (fig 4.24) exhibited results similar to that provided by Cr-coated SAY joined SiC. Cracks detectable in the coating suggest that the coating could be removed by spallation mechanism during the test.

The Cr-coating deposited on the specimens was 6  $\mu$ m-thick. Its detachment under the autoclave test could be caused by a poor adhesion on the substrate due to deposition parameters or by a too small thickness. The thickness of several coatings proposed for zirconium alloys is thicker, for example the KAERI (Korea Atomic Energy Research Institute) solution [10], presented in chapter 2, shows an average thickness of 80  $\mu$ m. Compared to this value the coating realised in this work was thinner. However, the coating proposed by AREVA NP (Framatome), deposited using PVD sputtering, has a thickness of about 5  $\mu$ m (fig. 4.25) and it was not affected by autoclave test with 70 ppm Li[11].

AREVA NP coating, deposited by PVD, is the most akin to the coating proposed in this project. This could suggest that the main concern for the tested Cr-coated specimens could have been a not optimised deposition. Future evaluation will be needed on chromium coatings deposited with different thicknesses, different deposition conditions. Also surface modification of the substrate should be investigated.



Figure 4.24: back-scattered SEM micrograph of unpolished Cr-coated Mo-Wrap joined SiC after autoclave



Figure 4.25: PVD Cr-coated M5 zirconium alloys by AREVA NP [11]

The appearance of  $MoSi_2/Si$  in the Cr-coated Mo-wrap joined SiC sample after the autoclave test is the same observed in Mo-wrap joined SiC one.

SEM analysis provided information about the morphology of the joints. EDX analysis suggested the oxidation of MoSi<sub>2</sub> during the autoclave test.

To confirm the hypothesis of oxidation, XRD analysis was conducted on MoSi<sub>2</sub>/Si bulk.

The spectrum obtained (fig 4.26) seems to confirm the oxidation of the reinforcement particles: no peaks related to MoSi<sub>2</sub> was found, the only phases detected were silicon and molybdenum oxide (MoO<sub>2</sub>). No reference pattern was found for the peaks which are not labelled. So, in addition to matrix dissolution, the MoSi<sub>2</sub>/Si could experience oxidation of the reinforcement particles under autoclave conditions. MoSi<sub>2</sub> is expected to show a high oxidation resistance up to high temperatures [1], but eventually the aggressive environment of the autoclave could have promoted the oxidation reaction. Further analysis on MoSi<sub>2</sub> after static autoclave are needed to confirm the suspected oxidation of silicides.



Figure 4.26:MoSi2/Si XRD spectrum after autoclave

SAY microstructure observed at SEM after autoclave test (fig. 4.15, fig 4.16) looked the same as before and the crystalline phases were still the same as before autoclave.

XRD analysis, conducted on the unpolished SAY joined SiC after autoclave, confirmed that no phase change occurred under autoclave conditions. The resultant spectrum (fig. 4.27) contains all the three crystalline phases expected for the SAY glass-ceramic system: keivyite ( $Y_2SiO_2$ ), mullite (Al<sub>4.95</sub>Si<sub>1.05</sub>O<sub>9.52</sub>) and cristobalite (SiO<sub>2</sub>), according to [2]. Peaks related to the SiC substrate are also visible in the pattern.

The pattern is without any amorphous halo, thus suggesting that the original glass-ceramic is fully crystalline after joining process.

Phase stability, absence of microstructural changes and a low weight loss associated to autoclave test confirm the SAY as a potential candidate for this application.



Figure 4.27: XRD spectrum of SAY joined SiC after autoclave

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## 4.2.5 Joining of nuclear grade composites

The results of autoclave test and those provided by subsequent characterization suggested that MoSi<sub>2</sub>/Si is not suitable for the LWR environment, at least if uncoated. Instead, SAY showed a lower weight loss compared to Mo-Wrap joints in autoclave test and its microstructure did not change. The second part of the experimental work was conducted using SAY as joining material.

Several SiC/SiC CEA tubes were joined using SAY glass-ceramic (fig 4.28). The main challenge was the deposition of the slurry containing the glass powders on the thin-wall of the tube due to its small thickness. The average thickness of the wall was calculated as difference between the external and the internal tube radius and it was found to be about 600  $\mu$ m.

Preliminary joints were manufactured using plates with a square section 10 mm x 10 mm and this made the deposition easier. However, the slurry deposition was proved to be suitable also to deposit the slurry on the thin walls of CEA tubes.

The use of the sample holder, designed for this scope allowed to keep the tubes aligned, which was a strict requirement for the joining success.

Visual inspection after the joining treatment suggested the achievement of a sound joint.



Figure 4.28 : SAY joined SiC/SiC CEA tubes

Tubes seemed soundly joined at visual inspection, but CT-Scan (Prof. J. Marrow's group, Oxford University, UK) evidenced that the joining material was not completely covering the joining area. When the tubes were overlapped to realise the joint, it was possible that the joining material got squeezed outside. This would explain why, in the CT-scan cross-section of the joint (fig. 4.29), the joining material can be detected on the inner and outer sides of the tube walls; the lack of material in the joining area would result in poor joint strength.



Figure 4.29: Micro CT-Scan section of the joining area of joined tubes (Prof. J. Marrow's group, Oxford University, UK)

FE-SEM analysis on cut joined tubes provided similar results (fig. 4.30). Within the joining area few SAY glass-ceramic can be found, but unfortunately the presence of joining material is not enough to provide a good joint strength. Some SAY glass-ceramic is detected on the walls of the tube.

The other side of the cut joined tubes (fig. 4.31) does not show SAY in the joining areas. The detectable SAY is all located on the external wall.



Figure 4.30: cross-section of SAY joined SiC/SiC CEA tubes



Figure 4.31: cross-section of SAY joined SiC/SiC CEA tubes

Thin-walled tubes are very difficult to be joined using butt joining, as observed in the micrograph from CT-scan and SEM, so to get successful joint new design should be explored to maximise the uniformity of the SAY deposition.

A good result is that, where SAY was detected, it provided a good interface. This was expected because tubes are coated with CVD SiC, which was the substrate used for the manufacturing of the tested joint. The need is to find different joint geometry to join the tube with the end cap.

Some NITE SiC joined SAY were realised, but characterisation is still on going.

## 4.2.6 Hot Stage Microscopy

A main concern for ATF claddings is the behaviour in the event of LOCA, when temperatures can reach values far higher than 1000°C. As described in chapter 2, main issues related to the temperature increases are creep phenomena and severe degradation of the material due to redox reaction.

SAY glass-ceramic is proposed as joining material for ATF cladding and so it should withstand high temperatures.

A first evaluation of SAY glass-ceramic behaviour at high temperature was conducted using Hot Stage Microscopy. Fig. 4.32 shows the variation on the sample height at different temperatures. The aim of the test was to evaluate how SAY behaves over 1200° in air– typical temperature chosen to evaluate oxidation response of ATF cladding under LOCA conditions. The analysis identified the softening temperature at 1362°C. Up to this temperature the glassceramic did not experience deformation, suggesting high temperature resistance. Characteristic temperatures detected by the analysis are reported below:

- Softening temperature (DT): 1362 °C.
- Spherical temperature (ST): 1387 °C.
- Hemispherical temperature (HT): 1388°C
- Flow temperature (FT): 1391 °C

It is interesting to notice that when the sample reaches softening temperature its mechanical behaviour deteriorates in a small range of temperatures, reaching flow temperature at 1391°C, typical behaviour of a crystalline materials.

In literature [3] a melting temperature of 1377 °C was found, according to the phase diagram of the system SiO2–Al2O3– Y2O3 ; the hot stage microscopy analysis detected characteristic temperatures in agreement with previous experimental investigations.

Images provided by heating microscope for the indicated characteristic temperatures are provided in fig. 4.33.



Figure 4.32: hot stage microscopy conducted on SAY glass-ceramic





Figure 4.33: images taken at characteristic temperatures during hot stage microscopy

## 4.2.7 Creep test results

One of the requirements for ATF is to provide an enhanced oxidation and creep resistance at accident scenarios.

The hot stage microscopy provided important information about the behaviour of the SAY glass-ceramic at high temperature, but it did not allow to apply any pressure on the sample. In real conditions the joint would be stressed by the fission gases released inside the tubes and by water/steam pressure imposed in the vessel.

In chapter 2 was observed that many tests which simulate accident scenarios where conducted at  $1200^{\circ}$ C. This was the motivation for the selection of the test temperatures of  $1200^{\circ}$ C and  $1250^{\circ}$ .

Table 4.5 reported the size of pellet before and after the test. Sizes of diameter and height are reported as range of values provided by the digital caliper.

			Creep test			
Material	Applied Weight (g)	Applied load (kPa)	Initial diameter (mm)	Final diameter (mm)	Initial height (mm)	Final height (mm)
SAY	59	9,3	8,87-8,92	8,87-8,92	8,40-8,43	8,40-8,43
SAY	166	26	8,87-8,92	8,89-8,92	8,40-8,43	8,40-8,46

#### Table 4.6: results for creep tests

After the application of 9,3 kPa on the pellet at 1200°C for 1h there was no evidence of deformation. Repeating the test on the same pellet at higher temperature (1250°C) for 1 h and applying a higher stress (26 kPa), no size variations were measured.

Although the creep tests were not conducted taking in account the real stresses which the fuel rod must withstand, they are important as a first evaluation of its creep behaviour.

## 4.2.8 Loop autoclave test results

Loop autoclave test results are provided in fig. 4.34 (courtesy of Konstantza Lambrinou, SCK-CEN, Belgium).

SAY bulk and two SAY joined SiC specimens were tested for 30 days. The SAY bulk exhibited a relative weight change of -0,005 during the test, which was more aggressive compared to static autoclave test due to the pressure loop: the SAY joined SiC specimen failed during the test, as shown in fig. 4.35. The failure occurred at the SAY/SiC interfaces. The visual inspection

identifies a complete detachment of the joining material from the SiC substrates, whose surfaces appears bare.



SiC/SiC CORTELINI loop test (30 days)

Figure 4.34: Loop autoclave test results (Koba Van Loo, KU Leuven, Belgium)

The weight loss experienced by SAY is not high and it can be compared to the weight variations of some composites proposed for these applications. Micrographs on SAY joined SiC before and after static autoclave evidenced a good interface, so the complete detachment of the joining material during the loop autoclave test was not predictable.

These results could suggest that interface is the weakest area of SAY joined SiC and that water corrosion can occur preferentially at the interface. Further investigations are needed to understand what occurred to the joints.

To date, the feasibility of SAY as joining material, at least uncoated, is called into questions because of the loop autoclave test, which was intended as a go/no go test.



Figure 4.35: SAY joined SiC after loop autoclave test ((Koba Van Loo, KU Leuven, Belgium)

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# **5** Conclusions

The aim of this Master final project was to assess the suitability of two joining materials for their utilisation in Light Water Reactor environment.

The two joining materials were MoSi<sub>2</sub>/Si manufactured by Mo-wrap process and SAY (silicaalumina-yttria) glass-ceramic.

Both materials have been already studied in previous works, but they had never been tested before for this use.

Their most relevant advantage is that they can be used as pressure-less joining materials, thus limiting possible damages when applied to SiC/SiC composites.

Both Mo-wrap joined SiC and SAY joined SiC were investigated before and after static autoclave simulating Pressurised Water Reactor water chemistry (1000 ppm B and 2 ppm Li dissolved, at 330°C). at SCK-CEN for 14 days.

 $MoSi_2/Si$  was found unsuitable under autoclave conditions because of the two following mechanisms:

- Dissolution in autoclave water of silicon matrix confirmed by complete dissolution of reference silicon wafer during autoclave test and subsequent SEM analysis on joint post autoclave.
- Oxidation of MoSi<sub>2</sub> as observed at EDX and XRD analysis. MoSi<sub>2</sub> is considered to be resistant to oxidation, so this result needs further confirmation.

The SAY joint exhibited a negligible weight loss after the autoclave test and no changes in microstructure and phases were found during joints characterisation.

These results justified the choice of SAY as better joining material than  $MoSi_2/Si$ , but a coating of the joint is to be considered.

The second part of the experimental activity focused on the joining of nuclear grade SiC/SiC composite materials, such as:

- NITE SiC/SiC plates (provided by *CEA*, France)
- CEA SiC/SiC tubes (provided by Prof. A. Kohyama, *NITE Corporation*, Japan).

Joining material used was SAY applied by slurry deposition. Tubes joining was performed using a sample holder developed within this final project to guarantee alignment of tubes and to keep them in contact during the joining process.

Joined CEA tubes appeared successful at visual inspection, but further characterization using Micro CT-Scan (Prof. J. Marrow group, Oxford University, UK) showed that few joining material was retained within the joining area, due to its squeezing outside the joined region during joining process. SEM performed on the cross-section of two joined tubes showed the same result. To overcome this issue, the joint design should be modified.

Characterisation of NITE SiC/SiC joined SAY is still underway.

Hot stage microscopy was performed on SAY glass-ceramic to investigate its behaviour at high temperature and it evidenced that it can withstand temperatures up to 1265°C before deforming

under its own weight. Furthermore, the analysis confirms that SAY glass-ceramic is fully crystalline.

Investigation on the high temperature behaviour of SAY was conducted with creep tests:

- 1 h at 1200°C under 9,3 kPa.
- 1h at 1250°C under 26 kPa.

No deformation was observed, thus providing hope in the outcome of future tests on creep behaviour with relevant conditions for the application.

Loop autoclave test (30 days, 330°C, PWR-like water chemistry) was conducted at SCK-CEN on SAY joined SiC and on SAY bulk. The two SAY joined SiC specimens failed at the interface. This result calls into questions the suitability of SAY glass-ceramic as joining material for the application.

Reasons for the failure must be investigated before continuing the assessment of SAY. Further tests to investigate SAY joints would be:

- Steam oxidation test at 1200°C for 1 h, performed by Karlsruhe Technology Institute (KIT) – as simulation of LOCA event.
- Irradiation test.

It is important to find why SAY joined SiC after static autoclave maintained a good interface and it looked unmodified and why it exhibited failure at the interface when tested in loop autoclave.

If the SAY joined SiC would not be confirmed as potential joining material, the solution could be the selection of a coating which could provide protection against the environment.

The evaluation of coating solutions for SAY glass-ceramic joint is on-going. It would be important to assess the effectiveness of chromium as coating layer under static and loop autoclave conditions. The coating failure observed, after static autoclave test, could be caused by a non optimal deposition or by a too thin coating. Future works will be focused on investigating the reasons of the coating failure by trying to coat with 30  $\mu$ m chromium layer and/or different sputtering parameters.

Another potential coating material could be CVD SiC deposited after the joining treatment. This could be an interesting solution because of CVD SiC good properties against corrosion and because tubes are coated with the same materials. SAY joined tubes will be coated with CVD SiC by CEA to explore this solution.

# To date, SAY requires further investigation on its suitability as uncoated joining material. If classified as unsuitable, coatings could be used to protect it from corrosion allowing to take advantage of the good temperature stability and of the pressure-less joining process provided by this joining material.

Assessment of coated Mo-wrap joints must be conducted. This material was severely damaged by the static autoclave exposure, but protective coatings could be the key to make it suitable for the application.

Joined SiC/SiC tubes will be mechanically tested at CEA to assess the shear strength provided by SAY glass-ceramic. Future works will also focus on the optimisation of joint design: the main challenge will be the joining of the tube to the end cap.

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