Experimental study
of severe accident conditions
in nuclear materials

Supervisor: Prof. Lelio Luzzi
Co-Supervisor: Dr. Dario Manara

Author: Luca Soldi    Matr. 814239

Academic year
2014/2015
Acknowledgements

This work is the result of a unique opportunity that I have had the pleasure to live. I am very glad to have spent some months of my life working with people from all over the world and with great experience in their respective fields. So, I want to thank all the people and institutions that made possible such opportunity.

I am very grateful to Politecnico di Milano for having given to me the possibility to study these five years, opening many ways for my future. I would like also thank very much the European Commission, which has financed my experience abroad through the Graduate and Executive Nuclear Training and Lifelong Education (GENTLE) Project.

A special thank is mandatory to my supervisors who helped me in writing physically this thesis: thank you, Prof. Lelio Luzzi, for having accepted me as your student some months ago and for all the advices and recommendations received from then to now; a truly special thank also to Dr. Dario Manara, for all the patience, support and help during my whole traineeship. Working with you was a pleasure, I hope it will be possible again in future.

I would like to thank also Dr. Maria Betti, Director of the Institute for Transuranium Elements (Joint Research Centre ITU, Karlsruhe, Germany), and Prof. Rudy Konings, Head of the Material Research Unit of ITU, for having accepted me in your structure for my seven-month traineeship. A special thank also to ITU staff, in particular to Davide Robba and Konstantinos Boboridis for all the time spent in laboratory and for the help with the experimental set-up; to Markus Ernstberger for all the days spent in front of the microscope, searching for interesting phases and element diffusion; to David Bottomley, whose energy and enthusiasm were very appreciated during my time in ITU; to Encarnation-Maria Vazquez Mateo and Petra Strube, for all the help in administrative and bureaucratic procedures.

I want to express all my sincere gratitude to my parents, Donatella and Roberto, and my sister, Elisa, for the unconditional support you have given to me in all these years and for making me the person I am. Many thanks also to the people who participated in making so special the time spent in Karlsruhe. To Daniele, who had the burden not only to bear my presence every day at ITU, but also outside the working time: thank you for all the time spent together supporting each other at Waldstadt. To Davide P., for all the funny moments and your precious advices; I hope this is only the beginning of a long friendship. To my officemate Sara, who helped me so much at the beginning of this adventure, you will have a great career for sure. To all the others ITU guys, Fabiola, Tsvety, Luca C., Elisa C., Donato, Nadya and Joaquina, for all lunches, breaks and talks had together. To my lifelong friends Luca B., Valeria, Alessandro, Stefano, Manuel and Daniele P., who have taken care of me during my short returns at home. Thanks to all of you for having been and/or being a part of my life.

And finally, a thank also to those who have the patience to read these acknowledgements till here: I hope it will last till the end of this thesis!
Contents

Sommario...................................................................................................................... VII
Abstract ......................................................................................................................... IX
Estratto........................................................................................................................ XI

Introduzione .................................................................................................................. XI
Apparato sperimentale .................................................................................................. XII
Risultati sperimentali ................................................................................................... XIII

Emissività dello Zircaloy .............................................................................................. XIII
Sistema UO₂-Zr ............................................................................................................... XIV
Sistema U-O-Zr-Al ......................................................................................................... XVIII
Sistemi (U,Pu)O₂-Guaina ............................................................................................ XIX
Lava di Chernobyl ......................................................................................................... XX

Conclusioni .................................................................................................................... XXI

List of figures ................................................................................................................ XXV
List of tables .................................................................................................................. XXIX
List of acronyms ............................................................................................................ XXXI
List of symbols ............................................................................................................. XXXIII

1. Introduction .............................................................................................................. 1
   1.1 The context .......................................................................................................... 1
   1.2 Three Mile Island (1979) .................................................................................. 3
   1.3 Chernobyl (1986) ............................................................................................ 5
   1.4 Fukushima Daiichi (2011) ............................................................................... 7
   1.5 Aim of the present work ................................................................................... 8
   Concluding remarks ................................................................................................. 9

2. State of the art on Severe Accident research ....................................................... 11
   2.1 Research topics .................................................................................................. 11
   2.2 Research programmes on Severe Accidents .................................................... 16
      2.2.1 COLOSS Project ....................................................................................... 16
      2.2.2 SARNET and SARNET2 ........................................................................ 17
      2.2.3 SAFEST .................................................................................................... 18
   Concluding remarks ................................................................................................. 20

3. Experimental methods ............................................................................................ 21
   3.1 Introduction ........................................................................................................ 21
   3.2 Laser-heating facility ......................................................................................... 22
      3.2.1 Autoclave and sample mounting ............................................................. 22
Sommario

Durante un incidente severo in un reattore nucleare, le temperature raggiunte dai materiali diventano critiche, specialmente per il combustibile e la sua guaina, che possono fondersi insieme e formare il corio, una sorta di lava molto pericolosa per l'integrità dell'impianto. E’ di grande attualità lo studio del comportamento e delle proprietà del corio, soprattutto dopo quanto avvenuto a Fukushima. Lo scopo della presente tesi è lo studio sperimentale dell’interazione tra materiali nucleari in queste condizioni estreme, utilizzando la tecnica del riscaldamento laser disponibile presso il Centro Comune di Ricerca, Istituto dei Transuranici (Karlsruhe, Germania). Il sistema maggiormente indagato simula l’interazione tra combustibile e guaina di un tipico reattore ad acqua leggera, riproducendo la geometria che caratterizza una reale barra di combustibile nucleare. Le evoluzioni della temperatura di fusione e dell’emissività durante gli esperimenti sono state usate per osservare il comportamento di questi materiali, dapprima in puro Ar, poi in Ar + 6 vol% H2 e in aria, evidenziando differenze significative. A seguito della fusione e solidificazione, i campioni sono stati osservati al microscopio elettronico a scansione e analizzati tramite spettroscopia elettronica a dispersione per valutare se si siano verificati eventi di segregazione e diffusione. Sono stati eseguiti anche esperimenti preliminari su altri tipi di materiali: per simulare la reazione tra corio e cemento, campioni di UO2-Zr sono stati fusi con Al2O3; successivamente è stata simulata la condizione di un reattore veloce, usando ossidi misti di uranio e plutonio (come combustibile) e acciaio inossidabile (come rivestimento). Infine, sono stati analizzati ad alta temperatura campioni prelevati dalla lava di Chernobyl. I risultati ottenuti mostrano cali significativi nella temperatura di fusione (centinaia di K sotto il valore di riferimento per il combustibile) e la formazione di fasi molto diverse a seconda delle condizioni simulate. Queste informazioni possono essere utili per capire meglio alcuni aspetti legati all’evoluzione di un incidente severo dal punto di vista della scienza dei materiali.
Abstract

During a severe accident, the temperature reached in the nuclear core becomes very critical for the materials involved, especially for the fuel that can melt together with the cladding. This lava-like mixture is called corium and is very dangerous for the nuclear power plant integrity because of its high radioactivity and temperature. Knowing the behaviour and properties of the corium is a crucial task, especially after the events occurred in Fukushima. The aim of the present work is to study the interaction between nuclear materials in such extreme conditions. All experiments are carried out on laboratory-scale samples using the laser-heating facility at Joint Research Centre, Institute for Transuranic Elements (Karlsruhe, Germany). The attention is mainly focused on UO$_2$-Zr system, representative of fuel-cladding interaction in Light Water Reactors. Samples formed by an UO$_2$ disc in contact with a Zircaloy ring are analysed simulating the real nuclear fuel rod geometry. The evolution of the melting temperature and emissivity are key factors to evaluate such interaction. Experiments are repeated in pure Ar, in Ar + 6 vol% H$_2$ and in air, showing different behaviours in these environments. Then, the melted and refrozen interfaces are characterised by Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy, to observe if diffusion and segregation phenomena are occurred. Some other preliminary tests involving different materials are performed. Pellets made by UO$_2$ and Zr in contact with Al$_2$O$_3$ are melted together to simulate the behaviour of corium interacting with concrete. Also first analyses are conducted using mixed uranium and plutonium dioxide as fuel and stainless steel as cladding, representative of fast reactor conditions. Finally, fragments from Chernobyl's lava are tested to observe the behaviour of a real corium system. The presented results show relevant melting temperature drops (even hundreds of K compared with pure UO$_2$) and very different phase formation, depending on the simulated conditions. Such information can be useful especially for a better explanation of a meltdown accident evolution from a material science point of view.
Estratto

Introduzione

Nel tentativo globale di ridurre la produzione di gas serra e, in particolare, di CO₂, è necessaria una forte svolta nella tecnologia finora utilizzata dai Paesi più sviluppati. Questo cambiamento si ripercuote anche sui più importanti processi industriali e, tra questi, sul settore energetico. L’energia elettrica è oggi prodotta per la maggior parte grazie ai combustibili fossili, ovvero carbone, petrolio e gas naturale (IEA, 2015) e, cercando di ridurre le emissioni, queste fonti energetiche devono essere sostituite per quanto più possibile. Gli impianti nucleari sono ottimi candidati per questo ruolo, grazie alle emissioni quasi nulle di CO₂ durante la vita del reattore e alle grandi quantità di energia prodotta e non vincolata da condizioni esterne e aleatorie (come nel caso delle energie rinnovabili, molte delle quali fortemente dipendenti dalle condizioni climatiche). Nonostante i vantaggi offerti, le centrali nucleari trovano con difficoltà il consenso pubblico, soprattutto a causa della pericolosità che ad esse viene comunemente associata e per le disastrose conseguenze che un possibile incidente comporterebbe (Raj Sehgal, 2015).

Molte risorse vengono investite nel campo della sicurezza nucleare, proprio per evitare il rilascio di qualsiasi materiale radioattivo che possa danneggiare la popolazione o l’ambiente. Molto raramente, eventi noti come “incidenti severi” possono accadere. Infatti, come conseguenza di una perdita di refrigerante o per un surriscaldamento delle barre nel noccciolo del reattore (core), una parte o tutto il combustibile qui presente raggiunge temperature ben più alte che nelle condizioni operative. A seguito delle altissime temperature raggiunte (anche oltre i 2500°C), il combustibile si fonde e si mescola con la propria guaina di rivestimento, formando il corio, un materiale dalle sembianze di una lava. Il corio è molto pericoloso per l’integrità dell’impianto, a causa della sua alta temperatura e radioattività e la sua formazione è solo il primo di una catena di eventi molto complicati da modellizzare, che dipendono fortemente dall’evoluzione precedente dell’incidente.

Nel tentativo generale di approfondire la conoscenza di tutti gli eventi che possono intervenire nel corso di un incidente, questa tesi si concentra sull’interazione tra il combustibile nucleare e il suo rivestimento (cladding) nelle prime fasi di questa indesiderata circostanza. Tutti gli esperimenti sono stati condotti su campioni di piccole dimensioni (da laboratorio) portati alla fusione con la tecnica del riscaldamento laser. Sono stati ripetuti vari cicli di fusione/solidificazione osservando come la temperatura di solidificazione cambia al variare della composizione e delle condizioni chimiche. In particolare, l’analisi è iniziativa studiando il comportamento di alcuni campioni provenienti dal progetto COLOSS (Cor Loss during a severe accident), composti da ossidi di uranio naturale e zirconio metallico in quantità note. Le temperature di solidificazione di queste composizioni sono state ricavate e quindi usate come punti di riferimento nel diagramma di fase UO₂-Zr. L’attenzione è stata poi rivolta a campioni più vicini alla reale geometria di una barra di combustibile nucleare utilizzata nei reattori a acqua leggera, in cui i materiali coinvolti sono UO₂ come combustibile e Zircaloy come rivestimento. Gli esperimenti sono stati ripetuti in atmosfera inerte (Ar puro), in presenza di idrogeno (Ar + 6 vol% H₂) e in aria compressa. Alcune prove preliminari sono state condotte pensando alla simulazione di sistemi con materiali differenti. Nello specifico, alcuni esperimenti preliminari sono stati effettuati simulando l’interazione tra corio e cemento (sostituito con Al₂O₃, uno dei suoi principali componenti) e su combustibili a ossidi misti di UO₂ e PuO₂ (MOX) inseriti in rivestimenti di acciaio (vicini alla condizione dei reattori veloci) e Zircaloy (per simulare la situazione nei reattori ad acqua leggera in cui parte dell’uranio nel combustibile ha fatto catture parasite di neutroni ed è decaduto in plutonio). Infine, alcuni esperimenti di fusione/solidificazione sono stati effettuati su frammenti delle lave provenienti da Chernobyl, come esempio di un reale corio.
I campioni risolidificati sono stati caratterizzati con un microscopio elettronico a scansione (SEM), ed in particolare con la tecnica della spettroscopia elettronica a dispersione di energia (EDS) per osservare le fasi formate dopo la fusione e l’eventuale diffusione degli elementi coinvolti.

**Apparato sperimentale**

Tutti gli esperimenti di fusione sono stati effettuati al Centro Comune di Ricerca, Istituto dei Transuranici (JRC-ITU) della Commissione Europea a Karlsruhe (Germania) usando l’apparato sperimentale mostrato in Figura E.1. Il campione viene posto in un’autoclave, che può resistere ad una pressione interna fino a 3 bar. Il gas di riempimento può essere Ar (per i test in ambiente inerte), una miscela di Ar + 6 vol% H₂ (in caso di condizione riducente) o aria compressa (per l’atmosfera ossidante). Il campione è quindi irraggiato da due fasci laser: uno proviene da un laser Nd: YAG TRUMPF, che emette nell’infrarosso (a una lunghezza d’onda di 1064.5 nm) ed è caratterizzato da una potenza massima di 4.5 kW; il secondo proviene da un laser Ar⁺, che emette nel blu (488 nm) con una potenza massima di 0.75 kW (Bottomley et al., 2015; Mastromarino, 2016).

Il campione viene preriscaldata utilizzando il laser infrarosso in modalità continua a bassa potenza, in modo da stabilizzare la temperatura superficiale intorno a 1500 K e ridurre gli sforzi dovuti ai forti gradienti termici che si susseguono durante l’esperimento. Poi una serie di impulsi viene inviata sul campione, portandolo alla fusione; tra un impulso e l’altro il materiale fuso ha il tempo di raffreddarsi e solidificare. Il laser blu è utilizzato a bassa potenza per verificare quando il campione fonde e solidifica. Infatti, in presenza di liquido sulla superficie, il riflesso del laser blu è influenzato dalle piccole oscillazioni dovute alla tensione superficiale del fluido.

Il campione raggiunge pertanto temperature molto elevate e l’intensa radiazione emessa viene analizzata da tre strumenti ottici: un pirometro veloce a due canali, uno spettro-pirometro a 256 canali e una camera a infrarossi. Il pirometro veloce analizza la radiazione emessa a due lunghezze d’onda: la prima è 488 nm e serve per misurare la riflessione del laser blu e, di conseguenza, verificare se la superficie è fusa; la seconda è 655 nm che, calibrata con un riferimento luminoso standard secondo la procedura indicata dall’Organizzazione Internazionale di Metrologia Legale (OIML, 2004), serve per misurare la temperatura di radianza del campione (da cui, conoscendo l’emissività, si ricava la temperatura reale). Lo spettro-pirometro contiene un vettore di 256 sensori, sensibili nel dominio di lunghezze d’onda da 488 nm a 1011 nm. Con questo strumento è possibile misurare la temperatura e l’emissività. Infine, la camera Phoenix™ è usata per osservare l’evoluzione della temperatura su tutta la superficie del
campioncione (mentre gli strumenti descritti precedentemente effettuano solo misure puntuali). Davanti alla camera è stato posizionato un filtro ottico, che permette il passaggio solo alla radiazione di lunghezza d’onda pari a 1.5 µm.

**Risultati sperimentali**

**Emissività dello Zircaloy**

Per il tipo di misure effettuate durante questo genere di esperimenti, la conoscenza delle proprietà ottiche, e in particolare dell’emissività, dei materiali coinvolti è fondamentale per una buona valutazione della temperatura. Inoltre, la particolare configurazione dell’apparato sperimentale è tale da formare un angolo di circa 20° tra la normale alla superficie del campione e la posizione dei pirometri. Per quanto riguarda gli ossidi di uranio e plutonio l’emissività è già stata adeguatamente studiata nel passato (Bober, 1980; Bober et al. 1984; Fink, 2000; Shi et al., 2010; De Bruycker et al., 2011): la dipendenza dalla temperatura è debole, mentre nel campo di lunghezze d’onda qui studiate la dipendenza della frequenza è trascurabile (e quindi vale la così detta ipotesi di corpo grigio); inoltre la natura ceramica dei materiali rende molto limitata anche la dipendenza dall’angolo (almeno per quanto riguarda la presente ricerca). Al contrario, molti meno dati sono disponibili per quanto riguarda lo Zircaloy. Nei reattori ad acqua leggera, i tipi di Zircaloy adottati sono due: lo Zircaloy-2 è usato nei reattori ad acqua bollente (BWR),

![Figura E.2: emissività spettrale dello Zircaloy tra 550 nm e 900 nm nelle due configurazioni analizzate.](image)
mentre lo Zircaloy-4 in quelli ad acqua pressurizzata (PWR). La principale differenza tra le due composizioni (riportate in Tabella E.1) sta nella quasi assenza del Ni nello Zircaloy-4 per ragioni legate alla chimica dell'idrogeno (presente in quantità superiore nei reattori ad acqua pressurizzata). La prima parte degli esperimenti è stata dunque rivolta alla determinazione dell’emissività spettrale alla temperatura di fusione dello Zircaloy-4, utilizzando le misure sia del pirometro, sia dello spettro-pirometro. In particolare, il pirometro è utile per determinare l’emissività alla lunghezza d’onda di 655 nm, mentre grazie allo spettrometro è possibile ricavare il valore dell’emissività spettrale da 550 nm a 900 nm (Figura E.2).

Da i risultati ottenuti, si può assumere che anche per lo Zircaloy-4 possa essere utilizzata l’approssimazione di corpo grigio, come per UO$_2$ e PuO$_2$; tale ipotesi viene utilizzata per tutte le analisi che seguono. In questo modo, è possibile ricavare per ogni spettro di radiazione la temperatura e l’emissività che, sostituite nella legge di Planck

$$L_{\lambda,rb}(\lambda, T) = \frac{2hc_0^2}{\pi^2\lambda^5} \varepsilon(\lambda, T)$$

meglio descrivono la dispersione dei dati sperimentali (dove $L_{\lambda,rb}$ è la radianza di un corpo reale alla lunghezza d’onda $\lambda$ e alla temperatura $T$, $h$ è la costante di Planck, pari a 6.6256·10$^{-34}$ J·s, $c_0$ è la velocità della luce nel vuoto e vale 2.99792·10$^8$ m·s$^{-1}$, $n$ è l’indice di rifrazione del mezzo, $k_B$ è la costante di Boltzmann (1.38047·10$^{-23}$ J·K$^{-1}$), $T$ è la temperatura reale del corpo, $\varepsilon$ è l’emissività in funzione della lunghezza d’onda e della temperatura reale, $T_{\lambda}$ è la temperatura di radiazione, ovvero la temperatura del corpo nero caratterizzato dalla stessa radianza emessa dal corpo analizzato). È’ importante rilevare che è stata riscontrata una certa differenza, evidente nella Figura E.2, nelle misure dell’emissività in direzione normale al campione e nella configurazione corrente, in cui l’asse ottico dei pirometri è inclinato di circa 20° rispetto alla suddetta normale. Per lo scopo di questa tesi le misure qui presentate sono sufficienti, tuttavia per una completa conoscenza delle proprietà ottiche dello Zircaloy-4 sono necessarie ulteriori analisi.

**Sistema UO$_2$-Zr**

Nel tentativo di migliorare la conoscenza delle caratteristiche e delle proprietà del corio che si può formare nei reattori ad acqua leggera, grande importanza è stata data al sistema UO$_2$-Zr. Come primo

![Figura E.3: temperature di solidificazione ottenute per diverse composizioni dei campioni COLOSS in ambiente inerte (a) e in presenza di idrogeno (b), confrontate con il liquidus ottenuto usando CALPHAD (Riprodotto da (Quaini, 2015))](image-url)
passo, sono stati analizzati campioni provenienti dal progetto COLOSS (Adroguer et al., 2003, 2005), in cui pastiglie contenenti biossido d’uranio e zirconio metallico in varie composizioni furono fabbricate per studiare la solubilità del combustibile nello Zircaloy fuso. In questa tesi, tali campioni sono stati utilizzati per osservare il cambiamento della temperatura di solidificazione del sistema UO$_2$-Zr al variare della composizione. Le prove sperimentali sono state ripetute in atmosfera inerte e in presenza d'idrogeno e i risultati sono stati confrontati con il liquidus ottenuto da Quaini (2015) tramite ottimizzazione con CALPHAD (Figura E.3). Il comportamento osservato nei due diversi ambienti chimici è in entrambi i casi qualitativamente concorde con i risultati di Quaini. La presenza di idrogeno non sembra influenzare la temperatura di transizione di fase, tuttavia tutti i campioni fusi in questo ambiente presentano un forte infragilimento, in particolare sono fortemente crepati sulla superficie e talvolta ridotti in polvere. Una spiegazione di tale fenomeno è associata alla formazione di idruri: infatti, l'idrogeno diffonde rapidamente in profondità nel materiale, reagisce con gli elementi presenti e, durante la solidificazione, gli idruri a minore densità vanno a rompere le strutture circostanti, causando le crecche e la polverizzazione riscontrate sperimentalmente.

Guardando ai dati dello spettro-pirometro, è possibile notare che, per i campioni ricchi in zirconio, l’emissività cambia fortemente durante l’esperimento (Figura E.4): quando il campione è fuso e

<table>
<thead>
<tr>
<th>Composizione COLOSS (mol% UO$_2$ – mol% Zr)</th>
<th>Temperatura fusione Pirometro (K)</th>
<th>Temperatura fusione Spettro-pirometro(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar</td>
<td>Ar + H$_2$</td>
</tr>
<tr>
<td>10-90</td>
<td>2305 ± 13</td>
<td>2354 ± 16</td>
</tr>
<tr>
<td>20-80</td>
<td>2230 ± 31</td>
<td>2394 ± 20</td>
</tr>
<tr>
<td>40-60</td>
<td>2390 ± 9</td>
<td>2592 ± 11</td>
</tr>
<tr>
<td>60-40</td>
<td>2641 ± 8</td>
<td>2660 ± 19</td>
</tr>
<tr>
<td>80-20</td>
<td>2781 ± 19</td>
<td>2809 ± 14</td>
</tr>
<tr>
<td>90-10</td>
<td>3066 ± 54</td>
<td>2982 ± 80</td>
</tr>
<tr>
<td>95-5</td>
<td>3065 ± 42</td>
<td>3147 ± 21</td>
</tr>
</tbody>
</table>

Figura E.4: evoluzione dell’emissività (in verde) e della temperatura (in rosso) per un campione COLOSS 20 mol% UO$_2$ 80 mol% Zr.
mantenuto caldo dall’impulso laser, \( \varepsilon \) assume un valore molto simile a un metallo; durante il raffreddamento, il suo valore incrementa leggermente fino alla solidificazione, quando l’emissività assume valori molto simili a una fase ossidata. E’ un fenomeno molto interessante, perché permette di avere informazioni altrimenti non disponibili dal solo termogramma. Infatti, questi forti cambiamenti dell’emissività sono attribuibili a eventi di segregazione che avvengono durante la solidificazione del campione. La formazione di una fase ossidata ricca in U è anche confermata dalla caratterizzazione post-fusione (Figura E.5). Infatti, guardando l’immagine ottenuta con gli elettroni retrodiffusi del microscopio elettronico, nel centro dei campioni fusi è possibile riconoscere un’area più chiara, associabile a un ossido ricco in U, mentre nella periferia è presente una fase più ricca in Zr. Le informazioni combinate di spettro-pirometro e microscopio elettronico consentono di capire quando si formano le fasi presenti dopo gli esperimenti e la loro composizione.

Questi risultati sono quindi usati come punti di riferimento per esperimenti che utilizzano campioni più simili alla geometria di un vero reattore ad acqua leggera di tipo PWR. A questo scopo, sono stati analizzati campioni formati da pastiglie di biossido d’uranio inserite in anelli di Zircaloy-4. Il laser

Figura E.5: immagini al microscopio elettronico con elettroni retrodiffusi (BSE) di un campione COLOSS 20 mol% UO\(_2\) 80 mol% Zr: a) visione globale del campione, in cui si osserva segregazione; b) analisi elementale con EDS, relativa alla presenza di U (in viola) e Zr (in azzurro). L’apparente diminuzione di concentrazione di Zr alla frontiera con il materiale non fuso è un artefatto dovuto alla presenza di una crepa in prossimità dell’interfaccia.

Figura E.6: termogrammi di spettro-pirometro e pirometro veloce, in posizioni diverse della zona fusa. La differenza in temperatura è di circa 100 K.
infrarosso è stato quindi usato per scaldare e fondere questi materiali inizialmente in atmosfera inerte in prossimità del punto di contatto, per vedere come combustibile e guaina possono interagire in caso raggiungano temperature estreme.

L'interazione è molto rapida e avviene già dopo un singolo impulso. Infatti, puntando il pirometro veloce nel centro della zona fusa e lo spettro-pirometro vicino all'interfaccia, la misura della temperatura di solidificazione è diversa tra i due strumenti (Figura E.6). Nello specifico, lo spettro-pirometro rivela una temperatura di circa 100 K inferiore, dovuta al mescolamento tra UO$_2$ e Zr a seguito della fusione. Ripetendo vari impulsi questo mescolamento è sempre più efficace e nella nuova condizione di equilibrio la temperatura scende fino ad un valore 200 K più basso rispetto alla solidificazione del puro UO$_2$. Questo calo può rivelarsi pericoloso per l'integrità del core, in quanto il combustibile può fondere a una temperatura ben più bassa del previsto.

Ripetendo gli stessi esperimenti in presenza di idrogeno, il calo della temperatura di solidificazione è meno marcato del caso precedente (Figura E.7) e i campioni sono caratterizzati dallo stesso infraglimento riscontrato nelle composizioni COLOSS. Una possibile spiegazione di questo diverso comportamento risiede ancora nella formazione di idruri: infatti, l'interazione dell'idrogeno, soprattutto con lo zirconio, può rallentare fortemente la diffusione di Zr nel combustibile fuso, portando a un peggioramento più contenuto della temperatura di solidificazione. Indagini preliminari sono state avviate ripetendo questi esperimenti in atmosfera ossidante: i primi risultati mostrano un ulteriore abbassamento della temperatura di transizione di fase dovuto principalmente alla formazione di ossidi superiori dell'uranio (UO$_3$ e U$_3$O$_8$), ma serviranno ulteriori risultati per comprendere la loro influenza.

La caratterizzazione post-fusione dei campioni fusi in atmosfera inerte mostra la presenza sia di tracce di uranio nell'anello di guaina, sia di zirconio nella pastiglia di combustibile. La diffusione quindi procede in entrambe le direzioni, influenzando le proprietà di entrambi i materiali. A differenza dei campioni COLOSS, in cui la quantità di Zr è approssimativamente costante nella parte fusa del campione, in questo caso la diffusione è molto più eterogenea (Figura E.8). In effetti con questa geometria lo Zr è fisicamente separato dall'UO$_2$ prima dell'esperimento e quindi anche i meccanismi di diffusione sono diversi. Confrontando le temperature di solidificazione ottenute con questi campioni e quelle ottenute

Figura E.7: confronto dell'evoluzione della temperatura di fusione in ambiente inerte e con idrogeno usando impulsi laser con le stesse caratteristiche. Dalle immagini a destra si può notare l'aspetto ben diverso a seguito della fusione nei due diversi ambienti chimici.
sui campioni COLOSS considerate come riferimento, ci si può aspettare che lo zirconio diffuso nel materiale fuso sia compreso tra il 10 mol% e il 20 mol%; l’analisi EDS conferma effettivamente tale previsione, misurando un valore vicino al 18 mol%. Osservando le immagini provenienti dai campioni fusi in presenza d’idrogeno, si osserva che la diffusione dello Zr è molto inferiore (già a poche centinaia di µm dall’interfaccia non viene più rilevato), in accordo con l’interpretazione precedente relativa alla formazione degli idruri.

**Sistema U-O-Zr-Al**

Alcuni esperimenti preliminari sono stati effettuati utilizzando campioni COLOSS con composizione 60 mol% UO$_2$ - 40 mol% Zr all’interno di un anello di Al$_2$O$_3$, per simulare l’interazione tra il corio e il cemento (di cui l’allumina è uno dei principali componenti). I risultati mostrano che il processo di solidificazione è caratterizzato da alcune oscillazioni, non riscontrate nelle precedenti analisi. Questo comportamento si presenta tra i 2830 K e i 2520 K (Figura E.9), probabilmente a seguito dell’interazione tra alluminio e UO$_2$-Zr con formazione di fasi intermedie, che non sono stabilizzate durante il successivo raffreddamento e che pertanto non sono osservabili. La presenza di Al comporta

![Termogramma del campione COLOSS fissato in un anello di allumina.](image)
una riduzione della temperatura di solidificazione di circa 200 K rispetto al valore misurato precedentemente per il corrispondente campione COLOSS. Ripetendo gli esperimenti in presenza di H\textsubscript{2}, non si sono osservati diversi comportamenti alla fusione/solidificazione, mentre le proprietà meccaniche vengono alterate come descritto per i precedenti esperimenti.

La caratterizzazione post-fusione mostra come la presenza dell’alluminio comporti forti differenze non solo dal punto di vista della temperatura di fusione, ma anche della morfologia e delle fasi formate sulla superficie risolidificata. Infatti, al centro della zona fusa (in cui non sono state trovate tracce di alluminio), si possono riconoscere due fasi, una più ricca in Zr, l’altra in UO\textsubscript{2}, riconducibili al campione COLOSS usato per questo test. Invece, alla periferia della zona fusa, possono essere osservate strutture molto diverse dalla precedente e qui l’Al è presente in quantità elevate (Figura E.10).

Certamente ulteriori esperimenti sono necessari per avere una conoscenza esaustiva dell’interazione tra corio e cemento. E’ comunque evidente che l’aggiunta di un semplice ossido come l’allumina può alterare notevolmente le proprietà ad alta temperatura del sistema UO\textsubscript{2}-Zr.

**Sistemi (U,Pu)O\textsubscript{2}-Guaina**

Altri esperimenti sono stati eseguiti utilizzando come combustibile gli ossidi misti di uranio e plutonio (MOX) con rivestimento in Zircaloy-4 (Zy-4) o acciaio inossidabile 15-15 stabilizzato al titanio (Tabella E.3). I campioni analizzati contengono diverse quantità di Pu (Tabella E.4) e in base a ciò si è scelto quale materiale usare come rivestimento. Infatti per il MOX-03 si è scelto lo Zy-4, rappresentativo di un reattore ad acqua (PWR) in cui l’uranio del combustibile durante l’irraggiamento può parzialmente trasmutare in Pu, ma il suo contenuto è limitato a pochi punti percentuali. Al contrario per i MOX-09 e MOX-39 è stato usato l’acciaio, per simulare quanto accade nei reattori veloci. La composizione dell’acciaio usata è infatti la stessa delle guaine del reattore Superphènix (IAEA Nuclear Energy Series, 2012).

Gli esperimenti di fusione/solidificazione sono stati eseguiti come nei casi precedenti, ma i campioni sono stati manipolati all’interno di una scatola a guanti resistente alla radiazione α. I risultati sono stati


<table>
<thead>
<tr>
<th>%</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Ti</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>B</th>
<th>Altri</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>15</td>
<td>15</td>
<td>0.4</td>
<td>1.2</td>
<td>1.5</td>
<td>0.6</td>
<td>0.005</td>
<td>/</td>
</tr>
</tbody>
</table>
inserti nei diagrammi di fase del sistema (U, Pu)O\(_2\) (stechiometrico) e UO\(_2\)-PuO\(_{1.96}\) (ipostechiometrico) pubblicati da Böhler et al. (2014) (Figura E.11). Sperimentalmente si osserva che le temperature di solidificazione misurate cambiano in base al tipo di guaina. Infatti, per MOX-03 a contatto con lo Zr-4 il calo rispetto alla temperatura prevista per il combustibile puro è di circa 100 K, mentre per MOX-09 e MOX-39 fusi con acciaio il calo risulta di appena 50 K (fatta eccezione per MOX-39 nel diagramma ipostechiometrico, in cui la temperatura di fusione risulta più alta del previsto). Anche le analisi al microscopio elettronico danno le stesse indicazioni, rilevando meno componenti dell’acciaio all’interno del combustibile fuso.

Questo effetto può essere spiegato in due modi differenti: in un caso, la presenza di quantità sempre maggiori di Pu può ostacolare la migrazione degli altri elementi, riducendo così l’abbassamento della temperatura di fusione; un’altra spiegazione può risiedere nell’affinità chimica tra il combustibile e i materiali della guaina, in particolare lo Zr sembrerebbe essere più affine del Fe. Un altro effetto molto importante da considerare è la stechiometria dell’ossigeno, che può influenzare fortemente la temperatura di fusione del composto iniziale, così come le fasi che si vanno a formare dopo la solidificazione. Certamente i risultati ottenuti in queste prove sperimentali non sono esaustivi per spiegare questi fenomeni, ma mettono in luce tali problematiche, che dovranno essere analizzate in maggior dettaglio in futuro.

**Lava di Chernobyl**

Gli ultimi esperimenti di questa campagna sono stati condotti su campioni provenienti dalla lava solidificata dell’impianto nucleare di Chernobyl, con lo scopo di studiare il comportamento del corio reale. I frammenti a disposizione sono stati prelevati dal “Piede d’Elefante”, struttura di materiale solidificato che si è formata in un locale al di sotto del reattore esploso.

Eseguendo la stessa procedura degli altri esperimenti, con questi campioni l’arresto termico non è

**Tabella E.4: composizione molare dei campioni MOX analizzati**

<table>
<thead>
<tr>
<th>Campione</th>
<th>% UO(_2)</th>
<th>% PuO(_2)</th>
<th>Guaina</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOX-03</td>
<td>97</td>
<td>3</td>
<td>Zircaloy-4</td>
</tr>
<tr>
<td>MOX-09</td>
<td>91</td>
<td>9</td>
<td>Acciaio</td>
</tr>
<tr>
<td>MOX-39</td>
<td>61</td>
<td>39</td>
<td>Acciaio</td>
</tr>
</tbody>
</table>

![Figura E.11: diagrammi di fase relativi ai MOX e punti sperimentali ottenuti nel corso della presente tesi (riprodotto da Böhler et al., 2014).](image-url)
visibile se la temperatura massima resta al di sotto dei 3000 K, sebbene i frammenti analizzati siano visibilmente fusi; superando i 3000 K, l’arresto termico diventa evidente (Figura E.12). Questo fatto è dovuto alla natura del campione, costituito prevalentemente da Si (proveniente dal cemento e dalle sabbie gettate sul reattore esploso per contenere il rilascio di materiale radioattivo) che gli conferisce un comportamento vetroso. Analizzando più nel dettaglio la composizione e la morfologia dei frammenti testati, è possibile riconoscere una matrice vetrosa in cui sono incorporate delle strutture cristalline, prevalentemente contenenti ossidi di U e Zr (Burakov et al., 1997, Burakov, 2013). Alla luce di queste informazioni, è possibile spiegare il comportamento riscontrato precedentemente: al di sotto dei 3000 K solo la matrice vetrosa fonde e, per via della transizione vetrosa che subisce, l’arresto termico non è visibile (Miller and Liaw, 2008); quando invece viene superata questa soglia qualitativa, anche le inclusioni cristalline fondono secondo una più consueta transizione liquido-solido, caratterizzata dall’arresto termico (in accordo con la legge delle fasi di Gibbs (Findlay, 1951)).

**Conclusioni**

Questa tesi sperimentale è stata rivolta allo studio dell’interazione di diversi materiali nucleari nelle condizioni di un incidente severo, in particolare grande attenzione è stata rivolta all’interazione tra il combustibile e la guaina dei reattori ad acqua leggera. La tecnica usata per simulare queste condizioni di temperatura estreme è il riscaldamento laser con misura ottica della temperatura, seguita da una caratterizzazione post-fusione con microscopio elettronico.

I principali risultati possono essere riassunti nei seguenti punti:

1. I test condotti sul puro Zircaloy (98 wt% di Zr) hanno permesso la determinazione dell’emissività per questo materiale alla temperatura di fusione. Dalle misure dello spettro-pirrometro è possibile assumere il comportamento di corpo grigio per le lunghezze d’onda comprese tra 550 nm e 900 nm.

2. I dati sperimentali sulla temperatura di solidificazione di campioni COLOSS in ambiente inerte sono stati confrontati con il liquidus del sistema UO₂-Zr ottenuto da un’ottimizzazione CALPHAD.
(Quaini, 2015); la corrispondenza qualitativa è buona, pertanto sono stati usati come punti di riferimento per gli esperimenti successivi.

3. La presenza di idrogeno non altera significativamente il comportamento dei campioni COLOSS per quanto riguarda la temperatura di fusione, ma ne cambia fortemente le proprietà meccaniche, a causa del forte infragilimento indotto.

4. L’evoluzione dell’emissività in campioni COLOSS ricchi in Zr può essere molto utile per determinare quando e in che senso avviene la segregazione delle fasi durante il processo di solidificazione. Questa informazione non sarebbe disponibile analizzando il solo termogramma.

5. Prove sperimentali simili in atmosfera inerte sono state ripetute su campioni formati da un disco di UO$_2$ inserito in un anello di Zircaloy-4, per simulare la geometria delle barre di combustibile di un reattore ad acqua leggera di tipo PWR. Si è osservato che, a seguito della fusione tra i due materiali, la temperatura del combustibile è diminuita fino a 200 K rispetto al valore atteso per via della migrazione dello Zr nella matrice di UO$_2$. Confrontando con le temperature dei campioni COLOSS si è stimata una diffusione dello zirconio fino al 20 mol%, dato confermato dalla caratterizzazione post-fusione.

6. Ripetendo gli stessi esperimenti con H$_2$ e riproducendo la stessa geometria, l’abbassamento della temperatura di solidificazione risulta più contenuto del caso precedente. Ciò è stato attribuito alla formazione di idruri, che sembrano rallentare la diffusione dello zirconio e, di conseguenza, anche il cambiamento delle caratteristiche del materiale fuso. Le proprietà meccaniche risultano alterate nello stesso modo riscontrato per i campioni COLOSS. I primi risultati dagli esperimenti in aria mostrano invece un calo maggiore, dovuto alla formazione di ossidi superiori dell’uranio.

7. Un’analisi preliminare è stata effettuata prendendo un disco COLOSS di composizione 60 mol% UO$_2$ - 40 mol% Zr inserito in un anello di Al$_2$O$_3$ per simulare l’interazione corio-cemento. La diffusione di Al è significativa e comporta un abbassamento della temperatura di solidificazione di circa 200 K rispetto al valore precedentemente misurato sul campione UO$_2$-Zr d’origine.

8. Gli esperimenti eseguiti su campioni di ossidi misti di U e Pu (MOX) con piccole percentuali di Pu e usando Zircaloy-4 come guaina non hanno evidenziato differenze sostanziali rispetto alle temperature di fusione misurate sul solo UO$_2$ in una guaina di Zircaloy-4.

9. Anche l’interazione tra MOX con grandi quantità di Pu (fino al 39%) e l’acciaio inossidabile è stata studiata. In questo caso, l’abassamento della temperatura di solidificazione è più contenuto e anche la diffusione del Fe è inferiore rispetto quella osservata per lo Zr. Non è chiaro se ciò sia dovuto a una minore affinità chimica o per la presenza di una maggiore quantità di Pu.

10. È stato possibile analizzare dei frammenti provenienti dalle lave solidificate di Chernobyl. La natura vetrosa di questi campioni ha reso difficile la determinazione dell’arresto termico, evidente solo per temperature oltre i 3000 K, probabilmente dovuto alla fusione e risolidificazione delle inclusioni cristalline, prevalentemente contenenti ossidi di U e Zr.

La ricerca sugli incidenti severi in reattori nucleari riguarda fenomeni molto complessi spesso accoppiati tra loro, particolarmente difficili da modellizzare e prevedere nel dettaglio. Con la presente ricerca sperimentale si sono approfonditi certi aspetti sulla formazione e sulle proprietà del corio, aprendo la
strada a ulteriori indagini. Nello specifico, alcuni dei prossimi passi in continuità con il presente lavoro possono già essere identificati:

- Sarà utile una caratterizzazione strutturale post-fusione (diffrazione dei raggi X, spettroscopia Raman) su tutti i campioni fusi con il laser per studiare le fasi formate a seguito della solidificazione;

- Ripetere le stesse analisi in ambiente ossidante, per vedere come cambia il contenuto di ossigeno nei campioni e, di conseguenza, la temperatura di solidificazione;

- Uno studio più approfondito dell’emissività del corio è necessario, fondamentale anche per studiare gli scambi termici nelle fasi più avanzate dell’incidente;

- L’analisi dell’interazione con il cemento va approfondita, impiegando non più simulanti ma pezzi reali di cemento usato per la realizzazione degli impianti;

- Le prove con i MOX devono proseguire, soprattutto usando campioni con diversi quantitativi di Pu e/o con diversa stecchiometria dell’ossigeno.
List of figures

Figure 1.1: OECD electricity production by fuel type during 2015 (IEA, 2015) ........................................... 1
Figure 1.2: the International Nuclear and Radiological Event Scale (IAEA, 2008) .......................................... 3
Figure 1.3: situation of the core during the evolution of the Three Mile Island accident: a) formation of the metallic crust; b) formation of debris bed (Jacquemain et al., 2015) ........................................ 4
Figure 1.4: final stages of the Three Mile Island accident: c) situation after cold water injection through the PORV; d) drop of the corium as result of crust failure (Jacquemain et al., 2015) ................. 5
Figure 1.5: picture of Chernobyl Unit 4 after the accident ............................................................................. 6
Figure 1.6: comparison between the first four units of Fukushima NPP before (left) and after (right) the accident ........................................................................................................................................ 8
Figure 2.1: main physical phenomena during a severe accident and some emergency systems for preventing it. Water is extracted from the sump, cooled down and then injected from the top of the reactor building to reduce its pressure. Steam explosions and hydrogen combustion are the main hazards that can lead to containment failure and radioactive release in environment (Jacquemain et al., 2015) ... 12
Figure 2.2: different phases of corium behaviour in the lower head: a) fragmentation and debris formation; b) convective movements in corium pool; c) formation of light metallic and oxide layers (Jacquemain et al., 2015) ......................................................................................................................... 13
Figure 2.3: scheme of the interaction between liquid corium and concrete basement (Jacquemain et al., 2015) ........................................................................................................................................... 15
Figure 2.4: UO2-ZrO2 quasi-binary phase diagram studied by Piluso et al. (2005) using VULCANO (reproduced from (Piluso et al., 2005)) ............................................................................................................. 19
Figure 3.1: picture of the laser heating experimental set-up and main devices .................................................. 22
Figure 3.2: schematic view of the main devices of Figure 3.1 ........................................................................... 23
Figure 3.3: example of a thermal arrest in UO2 – Zr system. The starting and ending points are shown, as well as the undercooling ......................................................................................................................... 24
Figure 3.4: schematic view of fast two-channel pyrometer ............................................................................... 26
Figure 3.5: tungsten lamp used for the calibration of 655-nm channels of pyrometer and spectrometer .......................... 27
Figure 3.6: experimental set-up during spectro-pyrometer calibration using the black body .............................. 28
Figure 3.7: block diagram of the Phoenix™ infrared camera electronics .......................................................... 29
Figure 3.8: schematic view of SEM used in the current research ....................................................................... 31
Figure 3.9: representation of the conditions for the constructive interference for X-Rays diffracted by crystalline planes ........................................................................................................................................... 32
Figure 3.10: picture of the shielded Seiffert XRD-3003 .................................................................................... 33
Figure 4.1: spectral emissivity of Zircaloy from pyrometer measurements at 655 nm and at the solidification temperature .................................................................................................................. 36
Figure 4.2: the spectral emissivity of Zircaloy-4 measured in this work from 0.55 µm to 0.9 µm at the solidification temperature .................................................................................................................. 37
Figure 4.3: comparison between thermograms of pure UO2 (a) and Zircaloy-4 (b). The blue laser signal is very helpful to identify the presence of melted materials on the surface ........................................................................... 38
Figure 4.4: solidification temperatures measured in inert atmosphere (3 bar of Ar) for various compositions of COLOSS samples, in the UO2-Zr isopleth phase diagram calculated using CALPHAD (reproduced from (Quaini, 2015)) ........................... 38
Figure 4.5: solidification temperatures measured in reducing atmosphere (3 bar of the mixture Ar + 6 vol% H₂) for various compositions of COLOSS samples, in the isopleth UO₂-Zr phase diagram calculated using CALPHAD (reproduced from (Quaini, 2015)).

Figure 4.6: evolution in time of emissivity (in green) and temperature (in red) in a Zr-rich COLOSS sample (20 mol% UO₂ 80 mol% Zr).

Figure 4.7: normal spectral emissivity measurements of COLOSS molten surface samples (grey body assumption). Experimental data follow with fair approximation an indicative linear behaviour.

Figure 4.8: normal spectral emissivity measurements of COLOSS samples at freezing temperature (grey body assumption). Some experimental data are very different from the linear behaviour (black solid line) due to the occurrence of segregation.

Figure 4.9: evolution of temperature as function of pixels (i.e., space) and time in a COLOSS sample with composition 20 mol% UO₂ 80 mol% Zr.

Figure 4.10: a) BSE image of the COLOSS sample 20 mol% UO₂ 80 mol% Zr, in which a darker ring at the rim of the melted part is clearly visible; b) a line scan performed with EDS, related to the atomic content of uranium (in violet) and zirconium (in light blue). Apparently, the Zr content decreases in the vicinity of the unmelted. It is only an artefact due to the presence of a crack at the interface.

Figure 4.11: SE and BSE images of the COLOSS sample 10 mol% UO₂ 90 mol% Zr and some areas of melted part with higher magnifications. It is clear that the phases formed after the melting/solidification cycles are very different depending on the distance from the centre of the laser spot and on the maximum temperature reached. Compositions of points selected are reported in Table 4.2.

Figure 4.12: diffractogram of COLOSS sample with composition 60 mol% UO₂ 40 mol% Zr. The best fit of the experimental peaks shows the formation of some metallic U.

Figure 4.13: sample components and assembly.

Figure 4.14: thermograms of pyrometer and spectrometer pointed in different positions of the melted area. A difference of about 100 K can be seen.

Figure 4.15: comparison between the thermograms a) after the first shot and b) after the sixteenth. The drop in the thermal arrest is about 200 K.

Figure 4.16: comparison between the phase transition temperatures in inert and reducing atmosphere using shots with the same characteristics. Looking at the pictures of the different samples, the characteristics of the melted part are different.

Figure 4.17: evolution of emissivity and temperature on UO₂-Zr interface.

Figure 4.18: thermograms recorded on UO₂-Zr interface under pressurized air (3 bar).

Figure 4.19: SEM pictures of the sample with Zircaloy: a) SE image of the whole sample; b) BSE image on the interface with higher magnification. The EDS analysis (in mol%) about the atomic content of uranium and zirconium in some interesting spots is reported, revealing the presence of particles richer in Zr.

Figure 4.20: BSE higher magnification image and EDS analysis (in mol%) of point 3 of Figure 4.19b. In the top left corner, an "island" mainly made by zirconium as result of heterogeneous diffusion.

Figure 4.21: SE picture and EDS analysis (in mol%) of UO₂ pellet with Zr cladding melted in presence of hydrogen.

Figure 4.22: thermogram of the COLOSS sample in the alumina ring.

Figure 4.23: temperature measurements from the thermocamera for samples with Al₂O₃.

Figure 4.24: BSE image of the COLOSS sample in alumina ring.

Figure 4.25: higher magnification and EDS analysis (in mol%) of the point 1 of Figure 4.24. Only U and Zr are detected and two phases are recognizable.

Figure 4.26: higher magnification and EDS analysis (in mol%) of the point 2 of Figure 4.24. The morphology here is strongly different from Figure 4.25 and also Al is detected.

Figure 4.27: higher magnification and EDS analysis (in mol%) of the point 3 of Figure 4.24. A part of the plume is recognizable and measurements confirm that Al is its main component.
Figure 4.28: pseudo-binary phase diagram of U, Pu MOX with stoichiometric plutonium dioxide (reproduced from (Böhler et al, 2014)).

Figure 4.29: phase diagram of U, Pu MOX with hypostoichiometric plutonium dioxide (reproduced from (Böhler et al, 2014)).

Figure 4.30: SE picture and EDS analysis (in mol%) of cladding ring of MOX-03.

Figure 4.31: SE picture and EDS analysis (in mol%) of interface in MOX-39.

Figure 4.32: Chernobyl sample before (a) and after (b) a low-power laser heating experiment. In the pictures different areas can be distinguished: 1) graphite holder; 2) ZrO$_2$-based glue; 3) Chernobyl lava sample.

Figure 4.33: different thermograms of Chernobyl's samples. Only if temperature exceeds 3000 K the thermal arrest is observable.

Figure 4.34: Planck's spectra of Chernobyl samples at different temperatures. Above 2050 K, two absorption bands appear at 590 nm and 770 nm.

Figure 4.35: SE image and EDS analysis (in mol%) on the laser-melted/unmolten interface of Chernobyl's particle.

Figure 4.36: a) BSE image of an inclusion in the Elephant Foot before the experiments (reproduced by (Burakov, 2013)); b) SE image of an inclusion in the sample after the melting. The two structures look similar, in particular the second one is larger and better connected as consequence of the melting.
List of tables

Table 2.1: comparison between the compositions (in wt%) of alloying elements in Zircaloy-2 and Zircaloy-4, in addition to Zr (main component)...11
Table 4.1: results about the melting temperature measured for COLOSS samples in inert atmosphere and in presence of hydrogen...39
Table 4.2: EDS analysis (in mol%) of the points selected in Figure 4.11. 43
Table 4.3: composition (in wt%) of stainless steel 15-15 Ti stabilized used in experiments with MOX (IAEA Nuclear Energy Series, 2012)...54
Table 4.4: name, composition (in mol%) and cladding used for the MOX samples. 54
Table 4.5: weight percentages of different samples from Chernobyl. Data of black lava depends strongly from the origin (Burakov, 2013)...57
# List of acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFS</td>
<td>Automatic Feedwater System</td>
</tr>
<tr>
<td>ASTEC</td>
<td>Accident Source Term Evaluation Code</td>
</tr>
<tr>
<td>BSE</td>
<td>Back Scattered Electrons</td>
</tr>
<tr>
<td>BWR</td>
<td>Boiling Water Reactor</td>
</tr>
<tr>
<td>CALPHAD</td>
<td>Computer Coupling of Phase Diagrams and Thermochemistry</td>
</tr>
<tr>
<td>CANDU</td>
<td>CANadian Deuterium Uranium</td>
</tr>
<tr>
<td>CEA</td>
<td>Commissariat à l'énergie atomique et aux énergies alternatives or Alternative Energies and Atomic Energy Commission</td>
</tr>
<tr>
<td>COLOSS</td>
<td>Core LOSS during a severe accident</td>
</tr>
<tr>
<td>COMETA</td>
<td>Corium MEIling Apparatus</td>
</tr>
<tr>
<td>ECCS</td>
<td>Emergency Core Cooling System</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersion X-ray Spectroscopy</td>
</tr>
<tr>
<td>EU</td>
<td>European Union</td>
</tr>
<tr>
<td>EURATOM</td>
<td>European Atomic Energy Community</td>
</tr>
<tr>
<td>EURSAFE</td>
<td>European expert network for the reduction of uncertainties in severe accident SAFety issues</td>
</tr>
<tr>
<td>FCI</td>
<td>Fuel Coolant Interaction</td>
</tr>
<tr>
<td>FP</td>
<td>Framework Program</td>
</tr>
<tr>
<td>FPA</td>
<td>Focal Planed Array</td>
</tr>
<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
</tr>
<tr>
<td>IEA</td>
<td>International Energy Agency</td>
</tr>
<tr>
<td>INES</td>
<td>International Nuclear and Radiological Event Scale</td>
</tr>
<tr>
<td>IRSN</td>
<td>Institut de Radioprotection et de Sûreté Nucléaire or French Institute for Radiological Protection and Nuclear Safety</td>
</tr>
<tr>
<td>ITU</td>
<td>Institut für Transurane or Institute for Transuranium Elements</td>
</tr>
<tr>
<td>JAEA</td>
<td>Japan Atomic Energy Agency</td>
</tr>
<tr>
<td>JNES</td>
<td>Japan Nuclear Energy Safety</td>
</tr>
<tr>
<td>JRC</td>
<td>Joint Research Centre</td>
</tr>
<tr>
<td>KIT</td>
<td>Karlsruher Institut für Technologie or Karlsruhe Institute of Technology</td>
</tr>
<tr>
<td>LWR</td>
<td>Light Water Reactor</td>
</tr>
<tr>
<td>MCCI</td>
<td>Molten Core-Concrete Interaction</td>
</tr>
<tr>
<td>MOX</td>
<td>Mixed OXides</td>
</tr>
<tr>
<td>NIR</td>
<td>Near Infra-Red</td>
</tr>
<tr>
<td>NPP</td>
<td>Nuclear Power Plant</td>
</tr>
<tr>
<td>NUC</td>
<td>Non-Uniform Correction</td>
</tr>
<tr>
<td>OECD</td>
<td>Organization for Economic Co-operation and Development</td>
</tr>
<tr>
<td>OIML</td>
<td>International Organisation of Legal Metrology</td>
</tr>
<tr>
<td>PORV</td>
<td>Pilot Operator Relief Valve</td>
</tr>
<tr>
<td>PTB</td>
<td>Physikalisch Technische Bundesanstalt or National Metrology Institute of Germany</td>
</tr>
</tbody>
</table>
PWR  Pressurised Water Reactor
RBMK  Reaktor Bolšoj Mošnosti Kanalnyj or High Power Channel-type Reactor
RCS  Reactor Coolant System
SA  Severe Accident
SAFEST  Severe Accident Facilities for European Safety Targets
SARNET  Severe Accident Research NETwork
SE  Secondary Electrons
SEM  Scanning Electron Microscopy
TMI  Three Mile Island
US  United States
VVER  Vodo-Vodnyi Energeticky Reaktor or Water-Water Energetic Reactor
WP  Work-Package
XRD  X-Ray Diffraction
Zy  Zircaloy
# List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units/Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Calibration constant of pyrometer (offset)</td>
<td>V</td>
</tr>
<tr>
<td>$B$</td>
<td>Calibration constant of pyrometer (slope)</td>
<td>V·K</td>
</tr>
<tr>
<td>$Counts_{j,av}$</td>
<td>Time average counts of j-th spectro-pyrometer channel</td>
<td>-</td>
</tr>
<tr>
<td>$Counts_{j,i}$</td>
<td>Counts of j-th spectro-pyrometer channel at i-th time</td>
<td>-</td>
</tr>
<tr>
<td>$c_0$</td>
<td>Speed of light in vacuum</td>
<td>m·s$^{-1}$</td>
</tr>
<tr>
<td>$d$</td>
<td>Space between crystal planes</td>
<td>m</td>
</tr>
<tr>
<td>$e$</td>
<td>Electron charge</td>
<td>C</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck's constant</td>
<td>J·s</td>
</tr>
<tr>
<td>$K_j$</td>
<td>Calibration coefficient of j-th spectro-pyrometer channel</td>
<td>W·sr$^{-1}$·m$^{-3}$·s$^{-1}$</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>J·K$^{-1}$</td>
</tr>
<tr>
<td>$L_{\lambda,bb}$</td>
<td>Spectral radiance of black body</td>
<td>W·sr$^{-1}$·m$^{-3}$·s$^{-1}$</td>
</tr>
<tr>
<td>$L_{\lambda,rb}$</td>
<td>Spectral radiance of real body</td>
<td>W·sr$^{-1}$·m$^{-3}$·s$^{-1}$</td>
</tr>
<tr>
<td>$m_e$</td>
<td>Electron mass</td>
<td>kg</td>
</tr>
<tr>
<td>$N$</td>
<td>Natural number</td>
<td>-</td>
</tr>
<tr>
<td>$n$</td>
<td>Refractive index</td>
<td>-</td>
</tr>
<tr>
<td>$P$</td>
<td>Power due to the decays</td>
<td>W</td>
</tr>
<tr>
<td>$P_0$</td>
<td>Nominal power of nuclear power plant</td>
<td>W</td>
</tr>
<tr>
<td>$RLS$</td>
<td>Reflected light signal</td>
<td>V</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Reactor operation time</td>
<td>s</td>
</tr>
<tr>
<td>$T_\lambda$</td>
<td>Radiance temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>Time after reactor shutdown</td>
<td>s</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_{out}$</td>
<td>Signal coming from pyrometer</td>
<td>V</td>
</tr>
<tr>
<td>$v_e$</td>
<td>Electron velocity</td>
<td>m·s$^{-1}$</td>
</tr>
<tr>
<td>$\delta T$</td>
<td>Total temperature uncertainty</td>
<td>K</td>
</tr>
<tr>
<td>$\delta T_{\text{Calibr}}$</td>
<td>Temperature uncertainty due to instrument calibration</td>
<td>K</td>
</tr>
<tr>
<td>$\delta T_{\text{DD}}$</td>
<td>Temperature uncertainty due to data dispersion</td>
<td>K</td>
</tr>
<tr>
<td>$\delta T_\varepsilon$</td>
<td>Temperature uncertainty due to emissivity measurement</td>
<td>K</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Emissivity</td>
<td>-</td>
</tr>
<tr>
<td>$\varepsilon_\lambda$</td>
<td>Spectral emissivity</td>
<td>m$^{-1}$</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Incident X-ray angle</td>
<td>rad</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
<td>m</td>
</tr>
<tr>
<td>$\lambda_e$</td>
<td>Electron wavelength</td>
<td>m</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Transmissivity</td>
<td>-</td>
</tr>
</tbody>
</table>
1. Introduction

Abstract. This thesis deals with the behaviour of nuclear materials under extreme conditions that simulate those caused by a severe accident (SA) in a nuclear power plant (NPP). Particular attention is given to the interaction between the nuclear fuel and the cladding that represents the first barrier against the spread of radioactive fission products. This chapter provides an overview on the importance of the study of severe accidents in NPPs and a general description of the events occurred in the historically most significant SAs: Three Mile Island, Chernobyl and Fukushima. The aim of thesis and its structure are presented as well.

1.1 The context

One of the main goals shared by the most influential countries all over the world consists in responding the ever growing energy demand and, at the same time, in reducing CO$_2$ and, in general, greenhouse gas emissions. In order to do this, the choice of cleaner technologies is mandatory and little by little pervades the life of every person. On a larger scale, a change in industry is needed too, in particular in the field of the electric energy production. Till now, most of the power plants burn tons of fossil fuels (coal, oil or gas) per working day and are responsible for the release of large quantities of CO$_2$ in the atmosphere. In view of reducing the effect of greenhouse gases, the implementation of CO$_2$-free energy sources is mandatory. In this perspective, nuclear power plants can play an important role for the production of large amount of electric energy with low emission of polluting agents. From the data of IEA (International Energy Agency, 2015), 18.1% of the electricity production in OECD (Organization for Economic Cooperation and Development) countries comes from nuclear (Figure 1.1). On the other hand, the development of nuclear industry is nowadays hardly fashionable and supported, especially after the Chernobyl and Fukushima accidents that shocked the world for their consequences on the environment and the population (Raj Sehgal, 2015).

One of the main features driving the conception of a nuclear reactor is the safety for the workers, the public and the environment. IAEA (the International Atomic Energy Agency, founded in 1957) establishes rules and constraints in this sense for the realization of a nuclear reactor. One of the main risks associated to a nuclear power plant is the release of radioactive materials that have different origins: the fission products (as result of nuclear reactions of fissile nuclei), the transuranic elements (from the parasite neutron capture of fertile nuclei) and activation products (from the parasite neutron capture of all the other elements inside the reactor, especially structural materials).

![Figure 1.1: OECD electricity production by fuel type during 2015 (IEA, 2015).](image-url)
In order to avoid any release of radioactive materials, a "defense-in-depth" philosophy is usually adopted in a NPP. It is organized in five levels, each one independent from the others (IAEA Safety Standards, 2012):

1. Any deviation from normal operation and the failure of items important to safety should be prevented, especially paying attention to appropriate design codes and materials, and to the quality control of the plant construction. During all phases of design, construction, operation and decommissioning, the first aim is to reduce the potential for internal hazards through a careful choice of materials and of all the procedures.

2. If deviation from normal operation cannot be avoided, it should be detected and controlled in order to prevent operational occurrences from escalating to accidental conditions. This second level underlines the need for specific safety analysis in order to test the effectiveness of the systems to return the plant to a safe state.

3. If deviation is out of control and an accident occurs, core damaging should be avoided as well as any significant off-site radioactivity release. Return to normal operations should be ensured. In fact, it is conservatively assumed that some unlikely events can possibly develop into accidents. Safety systems must then be conceived for restoring safe conditions.

4. If safety systems fail in the previous point, then effective confinement should be optimized, ensuring that radioactivity release is kept as low as reasonably achievable.

5. In case of radioactive release, consequences should be mitigated, thanks to proper emergency plans and procedures.

In order to fulfill these criteria, the design of nuclear reactors includes a large number of safety systems, conceived to intervene in any situation (theoretically also in the absence of electrical power, the so-called passive systems), and multi-barrier systems, consisting of different barriers aimed at maintaining radioactivity inside the plant. The first barrier is the fuel pellet itself thanks to the porosity that can hold the solid fission products and part of the volatile ones. The entire fuel stack is placed in a cladding that works as the second protection. In case of failure of the cladding, the third barrier is the whole NPP inner vessel (primary system) and, if the accident extends further, the containment building is the last one before the release in the environment.

Nuclear power plants are very complicated systems and the materials employed often operate in extreme conditions, as they are exposed to high temperatures, pressures and intense radiation fields, much more than in most other applications. For these reasons, apparently irrelevant failures can sometimes evolve in unpredictable disasters, and also natural phenomena can interfere with the regular activities. In addition, even if all the nuclear reactions are stopped by inserting the control rods, the fission products, the activated materials and the transuranic elements keep decaying, releasing the so-called decay heat that, if not removed, can cause an uncontrolled increase of the temperature in the core, eventually leading to its melting. In this context, IAEA (2008) formulated a specific seriousness scale to evaluate the magnitude of an incidental or accidental event. This scale, called INES (International Nuclear and Radiological Event Scale, Figure 1.2) and divided in seven levels, is used for fast communication between the public and the nuclear community on the safety significance of events associated with radiation sources. They are classified in events without safety relevance (level 0), incidents (from level 1 to 3) and accidents (from level 4 to 7). Every sequence of events that leads to a partial or total core meltdown is defined as "severe accident". In these conditions, the fuel overheats (for example for a loss of coolant or an insertion of reactivity) up to the melting point and then mixes together with the cladding, forming the so-called corium. Corium is a lava-like material very dangerous for the integrity of the primary system because of its temperature (kept very high by the decay heat even for a long time) and radioactivity. When corium is formed, the first two safety barriers are lost and the risk of radioactive material release in the environment becomes substantial. In the worst accident scenario evolution, the change in core geometry can also lead to a nuclear explosion if a re-criticality configuration is reached (as studied by Bethe and Tait (1956)).
Corium formation leads to various issues in all kinds of reactor, as shown from the experience acquired with the major NPP accidents occurred in history. In particular, the most known SAs in nuclear facilities came about in Three Mile Island (Pennsylvania, 1979), Chernobyl (ex URSS, now Ukraine, 1986) and Fukushima Daiichi (Japan, 2011). In the following, a brief description of the main events happened in these plants will be given.

1.2 Three Mile Island (1979)

The Three Mile Island (TMI) NPP consisted of two units equipped with pressurized water reactors (PWRs): Unit 1 began commercial operations in September, 1974, designed with a capacity of 852 MW$_e$; Unit 2 started electricity production in February, 1978, and had an electrical power of 880 MW$_e$

Some days before the accident (Kemeny et al., 1979), the valves of the Automatic Feedwater System (AFS) were closed during maintenance work in Unit 2. This event was going to be crucial for the whole evolution of the accident. In fact, at 4 a.m. on 28th March 1979 the reactor was operating at 97% of the nominal power, when the feedwater supply of the steam generators stopped working. As a result, the cold leg temperature and primary pressure increased in a few seconds. As planned in this case, the Pilot Operator Relief Valve (PORV) on the top of the pressurizer opened, reducing the pressure and resetting quickly the operational conditions. For the plant safety the reactor was shut down anyway. After reaching the nominal pressure (about 155 bar), the PORV failed in closing and the pressure continued its drop. Meanwhile, on the secondary side, the AFS could not intervene because its valves were accidentally closed. As a result, the steam generators were dried out. After two minutes, the primary system pressure reached approximately 110 bar. The high-pressure Emergency Core Cooling System (ECCS) started automatically and cold water was injected. After few minutes, operators decided to stop manually the ECCS because they thought that the situation was normalized, but they ignored that the PORV was still open. Without any other water injection, the temperature in the primary system increased and steam started to form. Operators did not notice it, as they were focused in restoring the feedwater supply of the steam generators. When they succeeded in it, the decay heat was removed by two different ways: by the working steam generators and by the water and steam mixture discharging through the open valve of the pressurizer (Jacquemain et al., 2015).
Temperature and pressure in the containment building were increasing, so operators decided to turn off the reactor coolant pumps and counted on core cooling by natural convection. As a result, water and steam separated and the coolant level reached the top of the core. The water injected by the chemical and volume control system was not enough to compensate the loss through the PORV, so its temperature increased and evaporation took place, uncovering the top of the fuel bars. After two hours from the starting event, ballooning affected several of the Zircaloy rods, leading to their failure and to the release of some fission products. Only after 142 minutes operators detected the failure of the PORV and succeeded in solving such problem, but half of the height of the fuel bars was uncovered and it was too late to avoid their degradation. The cladding started a strong exothermic oxidation with steam that resulted in an even higher temperature rise, up to melting of most of the metallic structures inside the vessel. The molten materials flowed in the lower part of the core and reached the remaining water, in contact with which they solidified. This led to the formation of a crust made mainly by metallic alloys of Zr, Ag, In, Fe and Ni (Figure 1.3a). Meanwhile, in the upper part the degradation of the cladding materials led to fragmentation and then melting of the fuel pellets. Fragments of both metal and oxide compounds fell on the lower crust, that became a sort of crucible where a mixture of solid and molten debris bed formed (Figure 1.3b). While the crust was cooled by steam convection and by radiative heat transfer, the materials inside were not, so that they gradually started to melt.

At this point, operators decided to restore the coolant circulation, so they switched on one of the reactor pumps. Injected cold water vaporized very quickly because of the overheating of all the structures inside the vessel, and as a result the primary pressure increased. The steam produced in this way allowed the oxidation of the still unreacted zirconium and the generation of hydrogen from this interaction worsened the heat exchange in the steam generators. Another consequence of the cold water injection was the partial quenching and fine fragmentation of oxidized cladding, caused by the strong thermomechanical stresses.

After six minutes from the restarting, the pump was stopped again, because the pressure rise was worrying. To face this emergency, operators decided to re-open the relief valve on the pressurizer. Radioactivity alarms were triggered and the containment building was isolated, interrupting the flow of radioactive materials in other buildings. After 200 minutes from the beginning of the accident, the high-pressure safety system was enabled and a large quantity of water was injected, but unfortunately it was not enough to cool effectively the debris bed (Figure 1.4c). The crust failed and tons of molten corium fell on the bottom of the core. There, a sufficient amount of water still remained to successfully cool all
the debris (Figure 1.4d). On the other hand, the hydrogen produced during all oxidation processes occurring in the vessel ended up in the containment building through the pressurizer valve and was ignited, causing a pressure peak of 2 bar. The structure was damaged by the explosion, but fortunately withstood it, as it was designed to stand for 5 bar overpressures. After 11 hours, the ventilation valve was definitively closed and more water was injected, allowing the re-start of the primary pumps and effective cooling of the core.

The Three Mile Island accident represented an unexpected event in the nuclear era. Until that period, nuclear safety activities were essentially focused on reliability and availability of safety-related reactor components, overlooking the human factor (Lombardi, 2009). From the TMI accident on, even small possible human or technological failures were considered in the safety assessment of a NPP, because errors during the emergency management can lead to consequences as severe as those caused by the major failures. Fortunately, the radioactivity release in the environment was very limited (about 1% of the background radiation dose) thanks to the presence of the containment building that stopped most of the volatile fission products. This last barrier worked very well, avoiding a possible disaster.

1.3 Chernobyl (1986)

The Chernobyl site was formed by four units with RBMK reactors (in Russian, Reactor Bolshoy Moshchnosty Kanalny, or "high-power pressure-tube reactor"). On 25th April, 1986 a test was planned for Unit 4, characterized by a thermal power of 3600 MWth. Its goal was to verify the possibility of using the mechanical inertia of the turbine to power the emergency system in case of loss of offsite electricity supply before the emergency diesel engines were turned on. With this purpose, several safety systems were disabled and reactor operating procedures were violated too. So, on the scheduled day, from 1 a.m. to 1 p.m. the thermal power was decreased from the nominal value to 1600 MWth. Then, the reactor had to be maintained at this level for 10 hours in order to supply the electrical system, leading to core poisoning by xenon. When the power reduction restarted and the value of 850 MWth was reached, operators turned off the medium-power control system, causing another drop in power. In order to continue the test, several control rods were extracted and reactor trip signals were disabled. At 1:15 a.m. on April 26th cold water was injected into the reactor, causing another drop in reactivity. At 1:22 a.m. the
reactivity margin was much below the value that should have to trigger the shutdown of the reactor, but operators proceeded anyway. Slowing of the generator led to slowing of the reactor coolant pumps and then of the water flow rate. The vaporisation in the core increased, resulting in an insertion of reactivity and in a sudden power increase. When the situation was already seriously unstable, the control rods were inserted manually. However, this resulted in an enhanced, and not reduced, reactivity, because the control rod heads were made by graphite, which worked as an efficient neutron moderator. Some seconds after 1:23 a.m. two nuclear explosions occurred, destroying the building in which reactor was contained and spreading most of the radioactivity inventory in the environment (Figure 1.5).

Part of the materials that were not thrown away by the explosions melted because of the high temperature reached in the core. Flows of corium reached the foundations under the basement of the reactor core. To slow the release of fission products, in the following days about 1800 helicopter runs were made to cover the reactor using sand, boron, lead and other materials and, after few months, a structure in concrete and steel was built with the same goal. Such structure is called "sarcophagus". It will be substituted by a new one in 2017, because of a collapse caused also by the high radioactivity field inside the old one. The incandescent debris caused various fires in the surroundings of the plant and a lot of fire-fighters had to face this challenge, being exposed to high dose rate. In particular, a graphite fire begun a few hours after the accident and only after ten days it was declared extinguished. Three workers of the plant died after the explosion and other 28 fire-fighters did too due to the high radiation dose received, while thousands of people who helped in facing the fires and in decontamination of the soils showed health problems. The inhabitants, located in a radius of 30 km, were evacuated. The following fallout involved a large part of Europe (IAEA Safety Series, 1992; Jacquemain et al., 2015).

The Chernobyl accident had the worst consequences, that still now are hard to define completely because of the long-term effects and the wide area involved. Among the causes of such a disaster are some design choices of this kind of Russian reactor, very atypical when compared to the Western ones. A boiling-water cooled, graphite moderated nuclear reactor might be some advantages from a neutronics viewpoint, but in case of accident very exothermic reactions between coolant and moderator can constitute an additional risk source. Also the consequent neutron flux instability makes it difficult to control, especially in emergency conditions. The lack of a proper containment building is another drawback, because the last safety barrier is then missing, a barrier that was decisive in mitigating the Three Mile Island S.A. Moreover, it should not have been possible to disable the safety systems.

![Figure 1.5: picture of Chernobyl Unit 4 after the accident.](image)
manually. Following these events, even more resources were invested in core melt research, including studies of early containment failure. Safety systems have been conceived more conservatively since the Chernobyl SA.

### 1.4 Fukushima Daiichi (2011)

On the 11th of March, 2011, one of the most powerful earthquakes ever recorded occurred at 2:46 p.m. off the eastern coast of Japan, later hit by the resulting tsunami. Built on the coast, the Fukushima Daiichi NPP consists of six boiling water reactors (BWR) Units. As the earthquake had shaken the plant, the automatic shutdown was triggered and control rods were inserted for all the six units, except Unit 4 that was already stopped and under maintenance. The earthquake damaged the electricity grid and caused a blackout, so emergency diesel engines were turned on to cool down the cores even without off-site supply. When the tsunami arrived, its waves were higher than the walls designed to protect the NPP exactly in these cases (15 m vs 5.5 m of the external barriers), and flooded most of the entire site. In particular, the worst damages affected the diesel engines that could no more supply the emergency safety systems. Only one generator connected to Unit 6 withstood the tsunami and it was successfully used later to cool down both Units 5 and 6.

The worst situation occurred in Unit 1 (IAEA, 2015), the oldest among the six reactors. It was equipped with inadequate safety systems, which required electrical power to be activated. Without any information about the status of the coolant in the primary system, operators declared that the fundamental core cooling safety function was lost. The only way to cool the reactor in such conditions was to use the fire protection lines to inject cold water. However, in order to do that, depressurisation was needed, from the operating pressure of 70 bar to the fire protection line value of 8 bar. At 9.51 p.m. a high level of radiations was detected in the Unit 1 reactor building, meaning that some core damages had already occurred. Two hours later, when measurements in the containment vessel became available, the instruments revealed that the pressure had exceeded its design value, so operators started to plan its venting to save the building integrity. At this moment, the core was already damaged and partially melted. At 4 a.m. on 12th March Unit 1 reactor pressure was low enough to allow water injection through the fire protection system, but operators were worried because no other actions were done to fulfil this goal, meaning that a relief had occurred through an unknown path. In a few minutes, the radioactivity level in the building increased by 10 times, confirming that the containment was damaged by the overpressure and uncontrolled radioactive release was still ongoing. From 9 a.m. to 2 p.m., operators opened a path for venting the Unit 1 containment building. Some valves needed to be opened manually and were placed where the radioactivity field was very high, so several operations took more time than the expected. As a result, the pressure decreased quickly, while the dose rate was still very high (about 1 mSv/h).

At 2:53 p.m. on 12th March the fire protection system was shut down, because its tank was almost empty and another source of freshwater was needed. Then, the Site Superintendent decided to use the sea water that had pooled in the Unit 3 pit after the flood. Trying to restore the water injection in Unit 1, a low voltage grid was arranged to use some safety devices, but an explosion damaged both of them before they could be used. The causes of such event are unknown. Some hydrogen might have escaped from the primary containment and then accumulated somewhere in the building. The water injection restarted only at 7 p.m. from both the fire protection system (freshwater) and Unit 3 pit (sea water). Some boric acid was added, too, for ensuring the safety function of the reactivity control.

This procedure continued till March 14th, when, at 1:10 a.m., the Unit 3 pit was almost dried out. Meanwhile, also Unit 3 had been cooled using the same sea water. The water injection restarted at 7 p.m., because an explosion had occurred in Unit 3, slowing down the refilling operations. In the following days, the electrical supply was restored and, then, all safety systems could work properly.
The events happened in Unit 2 and 3 are very similar to Unit 1’s, especially for Unit 3 that experienced a hydrogen explosion, too (at 11 a.m. on March 14th). The main difference is that the newer safety systems of these two Units could face the emergency at the beginning, even without off-site power. However, when conditions worsened and failures happened, core meltdown took place anyway. Unit 4 was fortunately under maintenance, so there was no risk of core meltdown there. Additional risk concerned the spent fuel pool that was no more controlled when the black-out occurred. Fortunately, the water level was high enough to cover all the rods for the whole time of the emergency. An additional explosion occurred at 6:14 a.m. on March 15th, caused by a hydrogen leakage from Unit 3. The explosion damaged the Unit 4 structure but did not affect the conditions of the pool (Figure 1.6). The conditions of Unit 5 and 6 were the less alarming, as an emergency generator of Unit 6 was not damaged by the flood and could be successfully employed in managing the accident. Both the reactors were not running at full power. Unit 5 was not producing steam and Unit 6 was very close to atmospheric pressure. In both cases, the resulting decay heat after the shutdown was limited and could be managed more easily.

1.5 Aim of the present work

In the general effort to develop more efficient and safer plants, the accidental evolution of actual NPPs must be investigated in all its phases. Real corium systems are extremely difficult to model and their exact behaviour is hard to predict. Most of the facilities used to investigate such properties are very complex and expensive because of the large amount of radioactive materials, experimental and safety equipment needed to simulate extreme conditions in nuclear reactors. As a consequence, only rare experimental data are available in this challenging research field. Main goal of the present work is the simulation, on laboratory scale, of some aspects of SA conditions in a NPP, with particular focus on the interaction between fuel and cladding at temperature beyond melting. As a result, thermal property changing depends on the amount of the involved materials and on the chemical conditions in the core. The experiments presented here were performed with the help of a laser-heating, fast pyrometry set-up. This experimental simulation tool permits fast and effective high temperature measurements on real nuclear materials, and the study of interactions between actual fuel
samples and other components of the NPP. In this respect, and in its capability to produce a large amount of data concerning materials under extreme conditions, the current experimental approach is certainly particular and advantageous. The tests were repeated in inert (pure Ar), reducing (Ar mixed with 6 vol% of H2) and oxidising (pressurised air) atmosphere to compare the different behaviours. Moreover, post-melting characterisation (SEM, EDS) was performed to observe the material property evolution after the laser heat treatments at very high temperature. The present experiments are useful for a better understanding of what may happen during the first phases of a core meltdown accident, and what may be the effects, in a SA, of the presence of plutonium or different chemical environments. In addition, the current research is important in that it demonstrates, for the first time, the applicability of laser heating to laboratory simulations of NPP SAs.

Several other experimental facilities and projects exist within and beyond Europe, which focus on particular aspects of the accidental scenario and, in many cases, are needed to predict later phenomena. A brief overview of some of the most relevant research facilities and programs on nuclear SAs is given in the Chapter 2 of this thesis.

Chapter 3 describes the techniques and instrumentations used for the current experimental tests performed at the European Commission Joint Research Centre’s Institute for Transuranium Elements (JRC-ITU) in Karlsruhe (Germany).

Chapter 4 shows the results of the mentioned experiments and their discussion. Most of the results concern the UO2-Zr system as representative of the most common type of NPP fuel element (PWR). Firstly, samples with known compositions were analysed to fix some values in the UO2-Zr isopleth phase diagram. Then, samples more representative of the fuel rod geometry were tested, consisting of fuel pellets (UO2 or (U, Pu) mixed oxides, MOX) enclosed in cladding rings (Zircaloy or steel). The latter results were compared and discussed in comparison with the previous ones. Some other preliminary tests were performed to observe the interaction between the fuel and the cladding of a possible fast reactor (in perspective of the Generation IV) and between the corium and a concrete simulant (for this purpose, Al2O3 was used). There was also the possibility to perform similar tests on samples coming directly from the Chernobyl lavas. Such results are shown as last part of Chapter 4.

Finally, the last chapter sums up the main conclusions of this experimental campaign and shows some possible improvement and perspectives of the current work.

**Concluding remarks**

NPPs play an important role in the global energy supply and could represent a good low-CO2 emission alternative to more traditional fossil fuel power plants. Unfortunately, even if a lot of resources are invested in implementing the safety, malfunctions and failures can lead very unlikely to core damage. Such events are called severe accidents. The main risk associated to them is the release in the environment of large amount of radioactive materials. Severe accident consequences are very difficult to evaluate, because of their long-time effects and large areas involved, as experienced in the past.

The aim of the present thesis is the experimental study of interaction between nuclear materials in SA conditions, especially focusing on nuclear fuel and cladding in LWRs. The tests are performed using a laser-heating technique on laboratory-scale samples representing different material systems.
2. State of the art on Severe Accident research

Abstract. In the present chapter, an overview about the research on Severe Accidents in LWRs is given. The melting of fuel and cladding represents a very critical event and, as a result, the radioactive material release risk becomes substantial. If not properly cooled, the formed corium falls to the bottom of the pressure vessel, interacting with both water (if still present) and steel. Corium pool formation leads to erosion and failure of primary system. Part of the molten materials can escape and interact with the concrete of the basement. During all the evolution of the accident, hydrogen is produced as result of Zr oxidation and can cause an explosion. All these events are complicated and coupled each other, so several research programs focused on their understanding are needed. A few European projects are here described.

2.1 Research topics

When a severe accident occurs, the corium formation is only one of the first dangerous events for the integrity of a NPP. Several other physical phenomena are involved in the possible complete sequence of events. In order to design effective countermeasures and to be prepared for any situation, all the possible phenomena that can take place after the corium formation need to be considered. So, the worst possible accident for a Light Water Reactor (LWR) is modelled to enhance the safety of existing and future nuclear power plants.

In general, the accidental event starts from a cooling failure, caused by some dysfunctions and/or human errors in the emergency procedures. Depending on what operators do and on the starting fault, the initial sequence can change, but the main effect is a loss of coolant efficiency inside the core. In the worst case, it can lead to uncovering and, then, overheating of the fuel rods. In fact, even if the fission reactions are stopped, the radioactive decay heat still remains and is not negligible especially after shutdown (because of the great amount of short-life fission products). It can be modelled as:

\[ P(t) = 6.48 \cdot 10^{-3}P_0[t^{-0.2} - (t - T_0)^{-0.2}] \]  

(2.1)

where \( P \) is the power due to the decays, \( P_0 \) is the nominal power of the plant, \( t \) is the time in seconds after the shutdown and \( T_0 \) is the reactor operation time in seconds (Nichols, 2002). With increasing temperature, two events can take place: the cladding oxidation and the fuel melting. In a LWR, the fuel is made mainly by enriched uranium dioxide pellets, put in cladding rods made in a zirconium alloy.

Table 2.1: comparison between the compositions (in wt%) of alloying elements in Zircaloy-2 and Zircaloy-4, in addition to Zr (main component).

<table>
<thead>
<tr>
<th></th>
<th>Zircaloy-2</th>
<th>Zircaloy-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>1.2%</td>
<td>1.2%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.12%</td>
<td>0.22%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.07%</td>
<td>0.07%</td>
</tr>
<tr>
<td>Ni</td>
<td>0.03%</td>
<td>&lt;0.007%</td>
</tr>
</tbody>
</table>
called Zircaloy (Zy). Two types of Zy exist, Zircaloy-4 in PWR and Zircaloy-2 in BWR (Table 2.1). The major difference stays in the composition and, in particular, in the presence of nickel. In fact, Ni is almost absent in the nominal composition of Zircaloy-4 because of the chemical affinity with hydrogen (the concentration of which is much higher in PWR) that can affect the chemical and mechanical properties of the rod. When zirconium is heated beyond approximately 1300 K, it reacts with steam as follows:

$$\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2$$  \hspace{1cm} (2.2)

The oxidation is very exothermic, (about 630 kJ per mole of reacted zirconium) and produces some hydrogen, dangerous for the further evolution of the accident. In this phase, the situation becomes very worrying when the temperature reaches 1600 K (Jacquemain et al., 2015), because the only convection of the steam is no more sufficient to remove the heat generated by the oxidation, resulting in a rapid increase of reaction rate (Steinbrück et al., 2010). In this condition, the depth of the oxide layer on the surface of the rod increases exponentially (in accordance with Arrhenius law) and affects all the mechanical properties of the material. Another event directly linked to overheating of the fuel is melting of the fuel itself. In LWR, the fuel is enriched uranium dioxide UO$_2$, characterized by a melting point above 3100 K. The formation of plutonium during the in-pile fuel operational life can decrease such melting point, but for the general explanation of the phenomena this effect is not considered here. When the melting temperature is reached, the fuel melts starting from the centreline of the rods and, interacting with the cladding, mixes together with the Zircaloy and eventually with other NPP core and structural elements, forming the corium (Figure 2.1).

Both the oxidation of zirconium and the formation of corium cause the failure of the cladding, because of the degradation of its mechanical properties from the outside and the interaction with melted fuel from the inside. The situation is even worse if depressurisation of primary system occurs. In this case, the cladding internal pressure can exceed the external one, causing ballooning of the fuel element, adding more stresses to the rod and reducing the flowing area of the coolant. When the rod integrity is
lost, a large part of fission products inventory is released, in particular the volatile and semi-volatile ones (like Xe, Kr, Cs, I).

The problem of overheating can affect the control rods too. Although there is no power generation inside these rods, as the decay heat there is negligible compared with the one typical of the fuel, the materials involved have lower melting temperatures (above 1100 K for Ag-In-Cd alloy, 1500 K for B₄C) and exothermally react with steam, producing hydrogen in a similar way as zirconium. The melted material can then damage the unbroken fuel rods through chemical interaction.

After rupture of the cladding, the corium flows through the degraded core and can solidify in its colder areas, blocking some sub-channels and worsening the general cooling efficiency. Meanwhile, the metallic Zr still remaining in the corium continues to oxidise because of its direct contact with steam, and the production of hydrogen is increased. In this phase, the molten material composition and properties change continuously. Even if these phenomena are fairly known theoretically, their modelling and experimental validation is very difficult in practice, because of the extreme complexity of the materials and environment involved.

If the accident proceeds and a larger part of the core melts, a "molten pool" forms and incorporates all the rods and their support grids in the pressure vessel. The corium pool is characterised by a low surface/volume ratio, so it is very difficult to cool, even by flooding (Miassoedov, 2015). From the support grids, the corium can fall or flow to the lower head, usually still filled with water. The interaction between water and corium has two main consequences: corium fragmentation and steam explosions. In fact, corium has such a high temperature that water in contact with it evaporates very wildly, causing a pressure peak and, if the primary system was depressurised, a steam explosion too (Piluso, 2015). The occurrence of the explosion is very critical for the mechanical resistance of the vessel. If strong enough, the explosion can damage the vessel walls and lead to fine-grained fragmentation of the corium into particles. Then, all the debris falls to the bottom of the vessel, forming a "debris bed" (Figure 2.2a). If not sufficiently cooled, the debris bed is very compact and presents a low permeability, because part of the corium is not solidified, otherwise it is composed of porous fragments. Especially in the first case, the debris bed is cooled very ineffectively and gradually dries the lower vessel head from the remaining water. The temperature then increases, leading to melting of the steel supports placed here and of the fragments themselves. During these events, all the metallic materials (mainly remaining zirconium from the cladding and steel from the vessel) can oxidise in contact with water, producing more hydrogen (which accumulates in the upper vessel head or also in other parts of the primary system) and changing the properties of all the melted materials (that can affect the further evolution of the accident).

These conditions will lead to the formation of a corium pool at the bottom of the vessel, made by melted fuel, cladding and steel (Figure 2.2b). This new configuration is much more difficult to cool.

Figure 2.2: different phases of corium behaviour in the lower head: a) fragmentation and debris formation; b) convective movements in corium pool; c) formation of light metallic and oxide layers (Jacquemain et al., 2015).
down (even with the additional injection of water). At this stage, the only ways heat can be removed from the corium are conduction through the wall, convection through a possibly water layer on top of the corium mass, and radiation from the free surface. These heat transfer mechanisms affect natural convection movements of the molten materials in the corium pool. Such movements are mainly turbulent, although some stratified layers appear in the vicinity of the walls where no convection takes place (Zhang et al., 2015).

In general, the corium pool is made by two different immiscible liquid phases at the equilibrium, one metallic and the other consisting of oxides (Kim et al., 2015). Depending on the previous oxidation processes, the composition of the mixtures can be very different. In general, the metallic one is mainly composed of steel, in average less dense than the heavy-metal containing oxides, resulting in a configuration in which the metallic layer is on the top of the pool (Figure 2.2c). On the other hand, depending on the oxygen potential of the system corium + water + atmosphere, also metallic uranium and zirconium can be present, making the metallic phase denser. This can eventually lead to the precipitation of the metallic layer to the bottom of the pool. The stratification of the corium pool is hardly predictable, because it depends on complex factors, such as oxidising processes, coupled phenomena at the interface (for example mass exchange) and flow dynamics. The challenge now is to predict under what conditions the metallic layer lies on the top. In such a configuration, the heat flux in the reactor vessel is "concentrated" in the metallic layer (the contribution of conduction is greater if the thickness is lower than 50 cm) and it is called "focusing effect". In a first-order approximation, the heat flux exchanged with the vessel walls is inversely proportional to the molten metal layer thickness, concentrating the heat transfer only in the contact region and leading locally to exceed the critical heat flux and then to vessel failure (Seiler and Froment., 2000). In fact, the vessel can resist in such conditions only if properly cooled by external water (at this point of the accident, the reactor pit should have been flooded) and reaching the critical heat flux causes a bad worsening of the cooling efficiency.

In addition, radiative contribution to the heat transfer is limited because of the low emissivity of metals. Another danger is constituted by the possible formation of Fe-U-Zr eutectic mixtures that can interact and dissolve the steel of the walls and bottom starting at about 1360 K (while the melting point of steel is above 1600 K), leading to the erosion of the vessel itself, especially in contact with the oxide phase.

With the formation of the corium pool, the conditions of the vessel can become quickly critical by the strong heat exchange with the metallic layer and the corrosion from the oxide one. In addition creep phenomena can occur, too, starting at about 1300 K. Therefore, the steel mechanical properties can deteriorate strongly, causing the failure of the main vessel. Three parameters are very important to understand the severity of the latter events: the moment when the vessel fails, which depends on the composition of the corium pool and the hydrogen produced previously, the position of the break and its size, which are linked to the location and extension of the corrosion phenomena and by the steel properties and composition. The vessel rupture can also be initiated in one of the several "penetration holes" bored for the insertion of instruments to measure the neutron flux. If these passageways fail, water, steam, fission products and corium may leak from the reactor vessel and end up in the containment building.

After the vessel failure, the containment building is the only remaining barrier between radioactive materials coming from the nuclear core and the environment. Its integrity is very important to mitigate the consequences of the accident scenario. The primary system pressure and the containment building one are normally very different. The first is close to operational value (around 160 bar, but it can be lower in case of depressurisation of the primary system), while the second is only few bars. If the primary vessel fails, corium and a mixture of steam, hydrogen and, probably, water are therefore ejected in the containment, as a direct consequence of the pressure difference, and this flow depends on the size and the position of the break. After the ejection, the corium can come in contact with water (used to cool the vessel externally) and then be fragmented in small pieces that oxidise very rapidly, producing hydrogen, as happened previously, and steam explosions. Steam and hydrogen produced in this way lead
to the rise of containment building temperature and pressure. In particular after an explosion, the pressure peak can damage the whole structure. These events can cause the failure of the containment building. Moreover, if big quantities of hydrogen (above the flammability limit) are produced and accumulate in the containment building dome, the increasing temperature can lead to its burning and, in certain conditions, to hydrogen explosion, very critical for the whole structure, as experienced in three reactors in Fukushima (see Chapter 1.4 "Fukushima accident"). The flammability and detonation limits depend on temperature, pressure and composition of the gas mixture in the dome. Therefore the magnitude and characteristics of the flow outgoing from the vessel determine the following events in the containment building. Conditions for hydrogen burning can also be reached locally, causing minor damages comparing with more extended explosions.

The corium ejected from the vessel, after the (possible) reaction with water, ends up on the basement of the reactor building, starting the so called Molten Core-Concrete Interaction (MCCI). In fact, the residual decay heat cannot be removed through the basement because of its thickness, the low thermal conductivity of concrete and the almost negligible contribution of the radiative heat transfer from the surface of the corium. Then, the corium heats up to the melting temperature of oxide materials from the core (UO$_2$ and ZrO$_2$) and metals from the vessel, forming a corium pool on the floor of the containment building. The temperature reached here is most probably higher than the concrete decomposition temperature, starting a process of erosion and ablation, the rate of which depends directly on the heat flux on the interfaces. As a result, a cavity is formed in the basement (Figure 2.3). Its properties depend strongly on the composition of the concrete itself. For example, in the case of siliceous concrete, the behaviour is more anisotropic since the erosion proceeds more in the axial direction, while for silico-calcareous one it proceeds in both axial and radial directions (Journeau, 2015).

In this way, the main components of the concrete (SiO$_2$, CaCO$_3$, Al$_2$O$_3$, and H$_2$O) interact and their decomposition leads to the release of gaseous phases (especially H$_2$O and CO$_2$) into the pool, promoting natural circulation of the melted materials and oxidation/erosion of more basement. All these phenomena are still under investigation, because using an effectively representative corium is difficult. Finally, the contact between hot corium and colder concrete can lead to local solidification and formation of a crust, partially slowing the degradation of the structure (solidified materials work as a

![Figure 2.3: scheme of the interaction between liquid corium and concrete basement (Jacquemain et al., 2015).](image-url)
barrier that interferes with this interaction). In order to mitigate the consequences after the escape of some corium from the vessel, the core catcher is designed. It is placed under the vessel and, in case of failure, collects the corium flow. Such corium is then distributed in a large pool of a sacrificial material, with the specific goal of ensuring the cooling of the hot material. In this way, the damages to the containment building are surely minor.

2.2 Research programmes on Severe Accidents

The previous section reported a brief description of the main events occurring in a severe accident in a NPP and of the possible failures of its components. The entire evolution is very complex and depends on the whole reactor life and accident history and, for this reason, predicting the exact sequence of events is very hard. NPP Safety systems are designed to be effective in every circumstance and operators are trained to stop failures and avoid the release of radioactivity in the fastest way possible. More comprehensive knowledge about the accident evolution can be obtained by improving our insight into the events involved, through combined experimental and modelling campaigns aimed at a full understanding of the main phenomena that can affect the integrity of the entire plant. Because of the large number of these phenomena, many different research projects dealing with specific aspects of the accidental scenario have been conceived in the last four decades.

In this general framework, extended co-operations between different countries have been carried out in order to support the high costs of these studies and to share the acquired knowledge about accidental events. In particular, the European Union interest on nuclear safety has always been a key point of the nuclear research and, after the events of Fukushima, efforts have even been intensified. A description of some research programmes particularly relevant to the present work will follow in this section.

2.2.1 COLOSS Project

The COre LOSS during a severe accident (COLOSS) Project was a 3-year shared-cost action, which started in February 2000 (Adroguer et al., 2003, 2005). The goal of such Project was to improve severe accident codes focusing on risk-relevant events that can occur during the starting phases of the accidental scenario. The 19 partners, spread in all Europe and Russia, studied these aspects of SAs through an experimental campaign divided in four topics:

- dissolution of fresh and high burn-up UO$_2$ and MOX by molten Zircaloy;
- simultaneous dissolution of UO$_2$ and ZrO$_2$ by molten Zircaloy;
- oxidation of U-O-Zr mixtures;
- degradation-oxidation of B$_4$C control rods.

The results were then used for model development for SA codes, especially the ones regarding H$_2$ production and melt generation.

All the work was divided in four work-packages (WP). The first one concerned small-scale experiments on all the topics listed above. Fuel dissolution by molten Zircaloy was studied by using firstly an UO$_2$ crucible and secondly short fuel rods, heated using steam and argon atmospheres. The main results showed differences between the two approaches because the gap in rod geometry plays a crucial role in the interaction between cladding and fuel. The data collected were compared with the results of three different codes and were useful to their improvement and validation. The agreement was good, except only for some discrepancies on ZrO$_2$ thickness, related to the steam quality during the heating. More tests were carried out using irradiated fuel (both UO$_2$ and MOX), to evaluate the effect of burn-up on fuel dissolution. The results showed clearly that the dissolution of irradiated fuel is enhanced and more heterogeneous, because of the presence of several cracks and fission gas bubbles, which foster fuel melting. During U-O-Zr system oxidation tests, H$_2$ release was analysed. Oxide spalling and sample cracking are responsible for enhanced oxidations and hydrogen produced in this way is much more than
the one coming from pure Zircaloy in the same conditions. Another important topic of this WP regarded the oxidation of control bars that can lead to higher production of hydrogen and affect the chemical conditions in the primary system. Such oxidation process results to be very complex and strongly dependent on the oxygen partial pressure and the steam flow-rate.

The second WP was about large-scale experiments on three representative fuel rods bundles (one coming from a Water-Water Power Reactor, or VVER, and two from a PWR). Tests were performed to understand the evolution of rod degradation in different conditions and with different materials involved. Results confirmed the previous analyses, since the control rods were the first to melt. However, none of the codes could predict the temperature evolution and only qualitatively the H$_2$ release. These experiments gave a good basis for the improvement of safety codes, for a better prediction of the possible evolution of an accidental scenario.

The third WP consisted in the model development and coupling of different SA codes used by industries and safety authorities about the events analysed in previous experiments. Big improvements were done especially about the degradation of B$_4$C control rod and fuel dissolution in different conditions. Collected data were also useful to extend the previous revised model to irradiated fuel.

Finally, the fourth WP was concerned with plant calculations to assess the new experimental data and models on crucial SA events leading to core degradation for different plant designs. The main goal was to assess the ability of SA codes to predict the core damage after an accidental event, to improve them using the data collected in previous experiments and, finally, to evaluate the new results coming from the revised models.

The experimental campaign was very useful to better understand the hydrogen production caused by control rod degradation and the corium relocation in the vessel. Evaluating the safety implications of these results, the hydrogen rate production in early core heat up (coming from control rod and, in general, U-O-Zr system oxidation) is as important as the total H$_2$ released by Zircaloy oxidation, from the point of view of hydrogen explosion risk. This contribution was underestimated by previous codes, especially in the first phases of the accident evolution. Another point deals with the corium behaviour, strongly depending on the metallic-oxidic composition and the burn-up at the accident onset. These phenomena are hard to model, although more experimental tests are being performed to better understand them.

### 2.2.2 SARNET and SARNET2

SA research has always been difficult for the complexity of the involved phenomena and expensive for the high cost of experiments with real materials. For this reason, in 2004 the European Commission deemed it necessary to better coordinate the efforts of Europe in order to optimise all the available expertise and experimental facilities in the aim of enhancing safety of existing and future NPPs. Hence, the Severe Accident Research NETwork of excellence (SARNET) (Van Dorsselaere et al., 2015) was launched, involving 43 organizations spread in 22 countries. All principal nuclear safety research centres were included, and also a few important non-European organisations (from USA, Canada, Korea, India). Collaboration with Japanese JAEE and JNES has started too. The whole program was renewed in 2009, with the name SARNET2.

The first task of this huge program was to rank the priorities in SA research. The list made by EURSAFEP5 Project was taken as reference (Magallon et al., 2005). Two criteria were used to order all the phenomena to analyse: importance for safety and level of knowledge (considering the whole international background). The topics considered to have highest priority are listed as follows, taking also into account, since 2011, the Fukushima accident impact:

- Core coolability during reflooding and debris cooling in the vessel;
- Ex-vessel melt pool configuration during MCCCI, ex-vessel corium coolability by top flooding;
• Melt relocation into water, ex-vessel Fuel Coolant Interaction (FCI);
• Hydrogen mixing and combustion in containment;
• Oxidising impact on source term (release of ruthenium in oxidising conditions/air ingress for high burn-up and Mixed OXide (MOX) fuel elements);
• Iodine chemistry in Reactor Coolant System (RCS) and in containment.

For each of these events occurring during a SA, a review of the available knowledge, past experiments and models was conducted, encouraging experimentalists and modellers to work together. New improved tests could be conducted and the results were implemented in simulation codes. Lacking a reference European integral code, ASTEC (Chatelard et al., 2014) was selected to merge the whole severe accident knowledge. It was developed initially by IRSN in the late 90s, but during SARNET most partners could access to the source code and improve it with new models and modules.

Without going into detail, improvements were achieved for each topic, in particular from the modelling point of view. Recreating conditions similar to real SA cases has helped the development of 2D or 3D models and the implementation of simulation approaches taking into account more complicated conditions. ASTEC was strongly improved in predicting accidental evolution, also in reactor as BWR or CANDU. Another great contribution of SARNET consisted in the dissemination of SA knowledge through education courses for young researches and students, conferences, technical papers.

2.2.3 SAFEST

After the events in Fukushima, SA research received even more attention from the nuclear community. Lessons learned from the Fukushima accident and experimental research can be combined to improve the safety of current and future NPPs. Several research areas dealing with phenomena occurred in Fukushima were identified. The particular need for appropriate research facilities was analysed. In this scenario, the European Commission’s Seventh Framework Programme has founded the Severe Accident Facilities for European Safety Targets (SAFEST) Project from 2014 to 2018 (Journeau et al., 2016). This collaboration initially addressed to European Countries, is being extended to Japan, Russia and other potential international partners. Roadmaps for joint experimental research on SA topics are being drawn within SAFEST, taking into account the lessons learned from Fukushima accident and the results of stress tests conducted in all European nuclear facilities thereafter. Corium behaviour and properties are still a priority in SA research, because they are crucial for all the subsequent phenomena in the accidental evolution.

The ranked list of SA topics and priorities drawn by SARNET constituted a good starting point also for SAFEST roadmaps. Eleven high priority and nine medium priority issues were selected, regarding very different phenomena as debris coolability, corium behaviour in lower head, hydrogen production, Molten Core-Concrete Interaction (MCCI), direct containment heating, effect of impurities in water on corium behaviour etc. All experimental results will be compared to the material analyses on Fukushima corium samples. In future, more studies will be needed for modelling potential recriticality in reactor core and in spent fuel pools, taking into account the possible change in geometry or material composition as consequence of accidental evolution.

Analysing these topics and having the possibility to validate experimental results with measurements in Fukushima site, the general understanding of SA evolution and the designing of more efficient protection system will improve NPP safety.

Several EU experimental facilities are involved in SAFEST. SAFEST supports the upgrade of these facilities and international access to them. They study different phenomena occurring during a SA. Several of these facilities are useful for the general understanding of corium properties, on a larger scale than the current experiments. Some of them, listed here, are therefore particularly relevant for the general background of the present work.
COMETA (Corium Melting Apparatus) is a facility used in UJV Rêz (Nuclear Research Institute) in Czech Republic. It is used to heat pulverized oxide materials with melting temperature up to 3000°C. The most used compound is UO$_2$ to simulate different types of coria interacting with different materials (concrete, steel, Zircaloy…). It is used also for studying the chemical effects of impurities.

COMETA can contain only up to 1 kg of material. A bigger facility is needed for larger scale experiments. Such facility is VULCANO (CEA Cadarache, France), a furnace that can contain up to 50 kg of materials. All the constituents of corium are added as powders and the composition of the resulting mixture can be adjusted during the test. When the melting is complete, the corium simulant is poured into a concrete test vessel. This amount of material is suited to simulate in a proper way the real MCCI and permits the study of the behaviour of different corium compositions. Moreover, VULCANO results are very useful to design a proper core catcher that, in case of vessel failure, can help in moderating the consequences. This facility has been used largely to study the UO$_2$-ZrO$_2$ system at high temperature (Piluso et al., 2005) (Figure 2.4).

The VITI facility (CEA Cadarache) is mainly devoted to the measurement of thermodynamic and thermophysical properties of corium through aerodynamic levitation, especially density, viscosity and surface tension. A furnace heats and melts the materials, allowing the study of corium formation and the following stratification. Corium behaviour in different chemical environments (oxidant, reducing or inert) can be analysed by VITI. Then, a droplet can be sampled and used to measure some properties of the molten material.

ATTHILA (CEA Saclay) is a versatile experimental set-up which allows high temperature measurements on different kinds of materials (metal, oxides, etc.). Samples are heated by a CO$_2$ laser emitting at 10.6 µm. The sample levitates in a stream of gas, for example compressed air, pure Ar or Ar and 20 vol% O$_2$. When the sample melts, its thermo-physical properties change, as density, viscosity and so on. Adjusting the parameters of the gas stream, the levitation is maintained stable and the properties are investigated. This technique can be applied to the study of small samples (around 100 mg) containing natural uranium or non-radioactive materials.

![Figure 2.4: UO2-ZrO2 quasi-binary phase diagram studied by Piluso et al. (2005) using VULCANO (reproduced from (Piluso et al., 2005)).](image-url)
Finally, the QUENCH facility (Karlsruhe Institute of Technology, Karlsruhe, Germany) consists of a cylinder in which several fuel rod simulants can be placed inside Zr-alloy claddings. The rods are electrically heated. Forced convection is maintained in the system using different gas mixtures. The main goal of QUENCH is to simulate the reactor vessel conditions especially to test the core coolability in different cases and the hydrogen generation during corium flooding. It will be very useful also to analyse the behaviour of accident tolerant fuels and the chemical effects of water impurities. Compared to the listed facilities, the laser heating set-up used in this work is suited for the very-high temperature (potentially between 1500 K and over 5000 K) characterisation of small amounts of nuclear materials (100 mg – 1 g), under controlled atmosphere. It is the only technique available for the study of highly radioactive materials (including transuranium elements) under such extreme conditions. For its unicity, and complementary to other techniques, it is also part of the SAFEST-associated facilities.

Concluding remarks

The evolution of a LWR SA is still difficult to predict because of the large numbers of complex and coupled phenomena involved. The formation of corium is only the first and, depending on the efficiency of safety systems and the countermeasures taken by the operators, can lead to different scenarios. Therefore, corium properties and behaviour must be studied as much as possible. In this way, several facilities have been built to collect experimental data. Collected results are then implemented in software partially capable to predict the further evolution. International research programs have been launched to improve the general understanding of all these complex phenomena, combining both experimental and modelling approaches. Especially after Fukushima, more resources have been invested in this direction.
3. Experimental methods

Abstract. This chapter contains a brief description of the tools used for the present experimental campaign. Firstly, the laser heating facility of JRC ITU is shown. The attention is focused on the description of the current fast-pyrometer and spectro-pyrometer, very crucial for all the tests performed. Then, a concise description of the post-melting characterisation techniques follows, in particular as far as Secondary Electron Microscopy and X-Ray Diffraction are concerned.

3.1 Introduction

As shown in the previous chapters, NPP SAs are the focus of considerable research involving substantial human and financial resources in a few research facilities worldwide. The research field encompasses many challenging phenomena, complicated by very high temperatures (often exceeding 3000 K) and presence of radioactive materials. An international approach to nuclear safety is required because a nuclear accident might have negative consequences for countries well beyond national borders, as highlighted by the European Commission in a 2009 Directive (EU, 2009). A more recent amendment to this Directive requires EU countries to give highest priority to nuclear safety at all stages of the lifecycle of a nuclear power plant (EU, 2014). This includes carrying out safety assessments before the construction of new nuclear power plants and ensuring also significant safety enhancements for old reactors.

In this context, a controlled atmosphere laser-heating and fast radiance spectro-pyrometry facility has been implemented at the European Commission JRC-ITU for the laboratory simulation, on a small scale, of NPP core meltdown. Thanks to the limited sample size (typically on a cm and 0.1 g scale), the high efficiency and remote nature of laser heating and the controlled atmosphere under which experiments can be performed, this laboratory simulation tool permits fast and effective high temperature measurements on real nuclear materials, including plutonium and minor actinide-containing nuclear fuel samples (Bottomley et al., 2015). In this respect, and in its capability to produce a large amount of data concerning materials under extreme conditions, the current experimental approach is worldwide recognized as unique. In fact, other complementary investigation techniques based on induction heating have been shown to suffer from the rapid high-temperature interaction between sample material and containment (Kato et al., 2008). In order to minimize this effect, the sample should be exposed to high temperature for limited time and the contact area with its containment minimized. In addition, if on one hand such techniques allow and, mostly, need larger amounts of material for the analysis, they are less suited than the present one for the investigation of real nuclear materials, due to the samples' high radioactivity and limited availability.

The current experimental method permits to separate and experimentally analyse several of the many complex physicochemical mechanisms related to the sequence of events described in Chapter 2. Corium formation can be potentially studied in the presence of different atmospheres (inert gas, air, traces of hydrogen or steam), producing important reference data for a comprehensive understanding of SAs. In addition, the spectral radiance emitted by the hot sample is simultaneously recorded on several wavelengths in the visible and near-infrared domain. Such analysis, essential for the determination of the sample’s real temperature through the spectral emissivity, permits also an in-situ study of some optical properties of the studied surface. This constitutes a further supporting tool for the identification of high-temperature phenomena, such as phase transitions, chemical reactions between condensed material and gas phase, or segregation effects.
The present approach, particularly suited for the laboratory investigation of high-melting materials, has been employed also for the successful analysis of other refractory compounds, such as zirconium, tantalum and hafnium carbides, metallic superalloys, calcium oxide etc. An essential part of the present research is represented by the post-melting materials characterisation. In this work, this has been mostly carried out with the help of scanning electron microscopy (SEM) and, preliminarily, X-Ray Diffraction (XRD). The current chapter describes the main experimental techniques and equipment used in this research.

3.2 Laser-heating facility

The laser-heating facility implemented at JRC-ITU is unique for simulating the extreme temperature occurring during a NPP SA (Bottomley et al., 2015). All the devices used for in this set-up are shown in Figure 3.1 and in a schematic view in Figure 3.2. The set-up is formed by an autoclave (for containing the sample), two lasers, a fast two-channel pyrometer, a spectro-pyrometer and an infrared camera.

3.2.1 Autoclave and sample mounting

The autoclave is a cylindrical vessel, in which sample and holder are placed. It has two windows: the first one is in sapphire (characterised by a transmittance of 0.86) and is passed through by the laser beams; the other is in fused silica. The autoclave is connected with a pump system that permits setting pressures between primary vacuum and overpressures up to 3 bar, needed to limit the surface evaporation during the experiments. The chamber can be filled with different gas mixtures, in particular for the present experiments pure Ar (inert condition), Ar + 6 vol% H₂ (reducing) and pressurized air (oxidising). Between two experiments, some few Ar + H₂ flow cycles are repeated in the autoclave in order to purify the working environment (Manara et al., 2008). The samples analysed are in general fixed in the chamber in a graphite or alumina holder by three screws of the same material.

3.2.2 Laser heating and thermal arrest technique

The current technique uses a continuous-wave infrared laser as a method of rapid heating to high temperatures (> 3000 K). The TRUMPF Nd: YAG laser used emits coherent light with a wavelength of 1064.5 nm and with maximum power of 4.5 kW. Although this laser works in a continuous-wave mode, short pulses (minimum duration of 1 ms) can be programmed through a computer code driving the
laser’s pumping system and a mechanical chopper. Typically, laser pulses lasting from a few tens ms to a few s are used to heat refractory samples beyond melting. The temperature to which the sample is heated is then recorded by a pyrometer, the most appropriate device to measure high temperatures (often greater than 3000 K) and high rates of heating and cooling (up to 100000 K/s).

A second laser is used as probe for verifying the occurrence of surface melting. It is an Ar+ laser, emitting at 488 nm (in the blue field of the visible spectrum) and with a maximum power of 0.75 kW. This laser works in a continuous-wave mode throughout the test duration. The beam emitted by it and reflected by the sample surface is detected by the fast two-channel pyrometer, one wavelength of which is tuned exactly at 488 nm. In fact, every morphological variation caused by phase transition on the surface changes the blue light reflection and therefore the value recorded by the pyrometer (Mastromarino, 2016).

The sample is put in an autoclave and here, before shooting with intense laser pulses, is preheated at low laser power for a few seconds (at a temperature of approximately 1500 K) in order to reduce the thermal stresses and to avoid rupture of the pellet during the heating/cooling cycles. Then, it is heated to very high temperature using more intense laser pulses. The emitted thermal radiation is collected and analysed by the fast pyrometer, the spectro-pyrometer and the camera. After each laser pulse, the sample cools and a traditional thermal analysis can be performed on the thermogram (the temperature versus time curve yielded by the pyrometer). Thermal arrests can be seen more or less clearly, corresponding to phase transitions. Looking at a typical thermogram, the heating rate is very fast and no thermal arrest is present on melting because of the non-thermodynamic-equilibrium conditions produced by the intense laser heating. On the other hand, the natural cooling conditions result in obvious thermal arrests, corresponding to the phase transition. Theoretically, a congruent freezing process (and in general any congruent, first order phase transition) should lead to a temperature plateau according to Gibb’s phase rule (Findlay, 1951). This means that the temperature is constant during all the phase transition process because of the co-existence of more phases and the latent heat release. On the other hand, in the presence of a non-congruent transition (two phases co-exist with different compositions) the thermogram displays only a change of slope, once more in agreement with Gibbs’ phase rule. In the current experimental conditions, the molten material produced during the laser flash pulses forms a pool contained in the unmelted part of the sample. The relative solidification dynamics is rather complex, as clarified in some earlier computer code calculations (Welland et al., 2011). When solidification occurs in the cooling stage, the phase transition starts from the solid/liquid interface acting as a large crystal nucleation site and, in some milliseconds, reaches all the volume of the melt. On the other hand, the temperature measured by the pyrometers is referred to the outer surface, reached by the solidification front in a finite time interval. During this time interval, only liquid is present on the outer surface, and,
respecting Gibb’s phase rule, its temperature keeps decreasing even below the equilibrium phase transition value (Figure 3.3). This phenomenon is called undercooling and it is very common in solidification experiments. When the outer surface finally starts to freeze too, then its temperature shows a quick increase, due to the latent heat release, up to the equilibrium transition point, level at which it stays constant throughout the solidification process. The surface temperature then begins to decrease again after completion of such process. The starting and ending points of the phase transition can be observed in the example thermogram of Figure 3.3. For the kind of experiment performed, the cooling rate is fast although still slower than the heating one and, in general, the ending point of the freezing is the most obviously visible, so it is taken as representative of all the process.

3.2.3 Two-channel pyrometer

The only instruments that can measure temperatures between 2400 K and 10000 K are optical pyrometers (also called radiance thermometers). This type of instrument measures the temperature of a sample through the determination of the intensity of electromagnetic energy (radiance) emitted from the sample surface at a wavelength $\lambda$ (nm or $\mu$m) and the temperature $T$ (K). In particular, the fast pyrometer employed here has two channels that allow the measurement of radiation emitted at 488 nm (here used only to analyse the information coming from the blue laser) and at 655 nm (used effectively to yield the temperature).

The relationship between temperature and spectral radiance of an ideal blackbody is given by Planck's law:

$$L_{\lambda, bb}(\lambda, T) = \frac{2hc_0^2}{n^2\lambda^5} \exp\left(\frac{hc_0}{n\lambda k_BT}\right)$$

where $L_{\lambda, bb}$ is the spectral radiation (radiance) at the wavelength $\lambda$ and the absolute temperature of the black body $T$, $n$ is the refractive index of the medium, $c_0$ is the speed of light in vacuum ($2.99792 \times 10^8$ m·s$^{-1}$), $h$ is Planck’s constant ($6.6256 \times 10^{-34}$ J·s), $k_B$ is the Boltzmann constant ($1.38047 \times 10^{-23}$ J·K$^{-1}$). If $n\lambda T \ll h c_0 k_B^{-1}$, then the approximation of Wien can be exploited:
This approximation is accurate to 1% of the absolute radiance if $\Delta T < 3\,100\,\mu\text{m} \cdot K$.

Since the conditions of an ideal black body are never realized in practice, the equation of Planck must be corrected for the emissivity of the surface investigated, defined as the ratio between the radiation emitted from the surface of a real sample at temperature $T$ and the radiation emitted from an ideal blackbody at the same temperature. The emissivity, the value of which is always between 0 and 1 ($0 \leq \varepsilon \leq 1$), depends on the nature and the morphology of the surface and is, in general, a function of $\lambda$ and $T$. Furthermore, when the temperature of the sample is measured optically, the radiated intensity is attenuated by the optical elements present on the light path between hot sample and detector. In general, the factor by which the intensity is attenuated, the transmittance $\tau$ ($0 \leq \tau \leq 1$), depends on the temperature of the optical element (generally fixed at room temperature) and the radiation wavelength. Given that every optical element is normally kept at room temperature and the $\lambda$-dependence of $\tau$ is usually known, the transmittance can be straightforwardly inserted as a known parameter in the correction equations, and will be not considered in the following description (Mastromarino, 2016).

Therefore, a real body (rb) and a black body at the same temperature have different spectral radiance as the first absorbs part of the radiation while the black body has emissivity 1 and does not absorb radiation. The relationship between them is:

$$L_{\lambda,\text{rb}}(\lambda, T) = \varepsilon(\lambda, T)L_{\lambda,\text{bb}}(\lambda, T)$$

$$= L_{\lambda,\text{bb}}(\lambda, T_{A})$$

(3.3)

from which the temperature of radiance $T_{A}$ is defined starting from the temperature of a black body that emits the same spectral radiance of the real one at a certain wavelength. Combining equations (3.1) and (3.3), the radiance emitted by the real body can be written as:

$$L_{\lambda,\text{rb}}(\lambda, T) = \frac{2hc_{0}^{2}}{n^{2}\lambda^{5}}\left[\exp\left(\frac{hc_{0}}{n\lambda k_{B} T_{A}}\right)-1\right]^{\varepsilon(\lambda, T)}$$

$$= \frac{2hc_{0}^{2}}{n^{2}\lambda^{5}}\left[\exp\left(\frac{hc_{0}}{n\lambda k_{B} T_{A}}\right)-1\right]$$

(3.4)

In the spectral region where is valid the approximation Wien, from Equation (3.4) one gets an expression that links the real temperature and the temperature of radiance:

$$\frac{1}{T} = \frac{1}{T_{A}} + \frac{n\lambda k_{B}}{hc_{0}}\ln\varepsilon(\lambda, T)$$

(3.5)

Equation (3.5), fundamental for pyrometry, permits to obtain the real temperature of a sample from the radiance temperature $T_{A}$, which was directly measured by the device, and the sample’s emissivity $\varepsilon(\lambda, T)$. When the value of emissivity is not known a priori, the measurement obtained by the spectro-pyrometer is used to obtain the right temperature of the analysed sample through Equation (3.5).

Each pyrometer is equipped with an optical system for the collection of the thermal radiation emitted from the focal spot on the sample, a mono-chromator unit (generally a grating or a prism), a radiation detector (a photodiode), an operational amplifier and an analogue/digital converter. The radiance
temperature $T_\text{L}$ is obtained after calibration of the device against a known light source (see following sections).

**Optical system**

Figure 3.4 shows the pyrometer’s focussing unit. It is composed of an objective lens (2) which collects the thermal radiation coming from a spot of 0.5 mm in diameter on the sample surface (1). The radiation is then focused on a mirror with a diaphragm (4) and passes through an optical filter that separates the spectral components at different wavelengths. The radiation is focused on Si photodiodes (5) mounted in a metal box, maintained at 25°C thanks to a high precision thermostat. The output current of each photodiode is directly proportional to the light detected. A second mirror (8) reflects the image of the sample in a telescope that is used to align the pyrometer on the area of interest. The signal from the photodiode is then converted into voltage with logarithmic amplifiers. An oscilloscope is used as AD converter for these voltage signals. It displays the digitised signals and sends them to a personal computer where they are converted into temperature through the calibration equation reported further in this section.

**Calibration**

During the laser heating experiments, only the pyrometer channel at 655 nm is used for measuring the temperature of radiance. This channel was calibrated at 655 nm with two tungsten ribbon lamps: the first one was used for the temperature range between 1100 K and 1800 K, the second between 1800 K and 2500 K (Figure 3.5). Both lamps were accurately calibrated by one of the German standard reference institutions, the Physikalisch Technische Bundesanstalt (PTB, 2010). For calibration, the recommendations given by the International Organization of Legal Metrology (OILM, 2004) were followed.

From such procedure, one can derive a linear relationship between the lamp’s temperature of radiance and the pyrometer output signal, thanks to the use of a logarithmic amplifier in the system. By combining the response of the pyrometer with the expression of Wien for the blackbody spectral radiance, shown in Equation (3.5), one gets:

$$V_{\text{out}}(T) = A + \frac{B}{T_\lambda}$$  \hspace{1cm} (3.6)
where A and B are two constants determined experimentally from the linear fit of the data to calibrate the pyrometer and $T_A$ is the lamps’ radiance temperature (known through PTB calibration).

### 3.2.4 Spectro-pyrometer

To convert the temperature of radiance at a given wavelength into absolute temperature through equation (3.5), it is necessary to know the normal spectral emissivity of the target at a certain wavelength. In this context, a multichannel pyrometer is used. In this way, the determination of temperature and emissivity from the measurement of spectral radiance at different wavelengths is possible. This device consists of a linear array of 256 silicon photodiodes, allowing a complete spectral analysis in the wavelength range between 488 nm and 1011 nm. The instrument has a memory buffer that can record 256 full spectra. As a result, the final information is contained in a 256x256 array, in which each row represents a radiance spectrum at a different time and each column gives the evolution of the signal at a given wavelength during the entire experiment.

### Calibration

The procedure to calibrate the 655 nm-channel of spectrometer is the same described for the 655 nm-channel of fast-pyrometer. Using a 4 ms integration time, this calibration follows the same indication given by the OILM.

For calibrating the whole photodiode array, a blackbody at 1200°C was used (Figure 3.6). The black body is a graphite tube, fixed at a graphite holder inside a metallic box, closed by two fused silica windows. Because of the high temperature reached by such instrument, a water cooling system is needed. Also an argon flow is maintained inside the chamber, to avoid any condensation of carbon vapours on the window or graphite oxidation, which would affect the calibration.

After the lamp calibration of the 655-nm channel, the actual temperature of the black body is measured using the same spectro-pyrometer channel. Each channel records 256 counts. In order to obtain the
calibration coefficients for each channel, an averaging operation for each wavelength is made at a fixed blackbody temperature:

\[
\text{Counts}_{j,\text{av}}(\lambda_j, T) = \frac{\sum_{k=1}^{256} \text{Counts}_{j,k}(\lambda_j, T)}{256}
\]  

where \(\text{Counts}_{j,\text{av}}\) are the average counts at wavelength \(\lambda_j\) and temperature \(T\), and \(\text{Counts}_{j,k}\) are the counts at wavelength \(\lambda_j\), \(k\)-th time from triggering and temperature \(T\). From such averages, the calibration coefficients \(K_j\) for each wavelength \(\lambda_j\) are obtained as:

\[
K_j(\lambda_j) = \frac{L_{\lambda_j,\text{bb}}(\lambda_j, T)}{\text{Counts}_{j,\text{av}}(\lambda_j, T)}
\]  

In fact, the black body radiance \(L_{\lambda_j,\text{bb}}\) can be calculated from Equation (3.1) (using the \(T\) coming from the previous calibration at 655 nm), while \(\text{Counts}_{j,\text{av}}\) are obtained directly by spectro-pyrometer measurements.

**Spectral emissivity measurement**

The calibration coefficients \(K_j(\lambda_j)\) calculated in this way allow obtaining the radiance directly from the counts measured by the optical device. Unfortunately, as already pointed out in the fast pyrometer section, real body are characterised by a certain emissivity \(\varepsilon\), depending on wavelength \(\lambda\) and temperature \(T\), as shown in Equation (3.4). The evaluation of emissivity \(\varepsilon\) can be obtained in two different ways.

Knowing the real temperature \(T\) of the sample thanks to the previous calibration at 655 nm and knowing the wavelength \(\lambda\) of interest, the black body radiance \(L_{\lambda,\text{bb}}\) is calculated through Equation (3.1) and real body radiance \(L_{\lambda,rb}\) is directly obtained by the calibration coefficients and the counts at wavelength \(\lambda\). So, emissivity can be calculated as:
\[ \varepsilon_\lambda(\lambda, T) = \frac{L_{\lambda,rb}(\lambda,T)}{L_{\lambda,bb}(\lambda,T)} \]  

(3.9)

In this way, emissivity is calculated at a certain wavelength and temperature without any assumption. This procedure can be applied to real materials whenever a well-established reference temperature can be measured in the investigated system (e.g. the solidification point of Zircaloy). Otherwise emissivity \( \varepsilon \) and temperature \( T \) as must be considered as free parameters of Equation (3.4). Then, emissivity and temperature are obtained as the best values that fit the whole spectrum. This procedure is numerically accurate if the grey body assumption is valid, i.e. emissivity does not depend on wavelength, which is mostly true for the materials investigated in this work. Otherwise, further assumptions on the emissivity wavelength dependence are needed.

**Temperature measurement uncertainty**

Measurement uncertainty is calculated according to error propagation law (Manara et al., 2005), considering the formula:

\[ \delta T = \sqrt{\delta T_{\text{Calibr}}^2 + \delta T_{\varepsilon}^2 + \delta T_{\text{DD}}^2} \]  

(3.10)

where \( \delta T_{\text{Calibr}} \) is the uncertainty related to the calibration of the instruments, \( \delta T_{\varepsilon} \) the one from the emissivity determination, and \( \delta T_{\text{DD}} \) the one associated to the data dispersion during the measurements. Considering all these contributions, all the measurements of the present work have an uncertainty of \( \pm 1\% \) in a confidence interval of 95%.

**3.2.5 Infrared Camera**

Phoenix\textsuperscript{TM} is an infrared camera (Indigo, 2002), useful to see the time evolution of the temperature on several pixels distributed on the whole surface of the analyzed sample. A schematic representation of this device is shown in Figure 3.7. Its sensors consist of thermoelectric-cooled Indium Gallium Arsenide detectors, sensitive in the wavelength range between 0.9 µm to 1.7 µm, organized in a 320x256 array called Focal Planed Array (FPA). The spatial resolution between two pixels is approximately 0.4 mm. In the present work, a mono-chromator at 1.5 µm is used to cut all the other wavelengths. The raw data are then elaborated using a “Non-Uniform Correction” (NUC) process that optimises the signal depending on the temperature range of the test. It is used to select the best integration time and window size,
which constitute essential information to convert the final counts into temperature. After this correction, the analogue signal is converted into a digital one and analysed by a computer. As result of such elaboration, a picture is displayed on a screen and a line can be drawn on it. The counts from each intercepted pixel are then converted into temperature, knowing the NUC set before and the emissivity of the material.

3.2.6 Summary

When the sample is heated using the infrared laser, the radiance emitted by the hot surface is analysed by the fast pyrometer, the spectro-pyrometer and the camera. The information from the 655 nm-channel of fast pyrometer is used to determine the radiance temperature and, through Equation (3.5), the real one. The average uncertainty associated to this measurement is ±1%, meaning that at 3000 K the accumulated error is estimated in ±30 K. The signal from the 488 nm-channel is independent from the previous one and is used to determine the instant at which the fusion and the solidification of the sample surface occur. Such information is available thanks to the reflection of argon ion laser at low power, pointed on the heated area. In fact, the molten material causes a change in light reflection due to surface-tension induced vibrations, resulting in a variation of the signal. Meanwhile, the spectro-pyrometer collects all the spectra between 0.488 µm to 1.011 µm and allows having information on temperature and emissivity. Firstly, the emissivity is determined as function of wavelength because the optical behaviour of some materials is not known. Then, after having verified that grey body assumption is valid for the system analysed, the emissivity is calculated as the result of the best Planck’s law fitting of the spectra collected. Finally, the camera is used to observe the line temperature profile evolution of some samples. Unfortunately, the spatial resolution is hardly high enough to accurately follow the temperature evolution at the interfaces (see Chapter 4), still the information obtained is sometimes useful to support the results coming from the other devices.

3.3 Post-melting characterisation

Another important part of the present work is the post-melting characterisation of the samples. In particular, diffusion of the systems’ main elements is analysed and the formation of new phases is observed. Segregation is sometimes observed and causes optical property changes. The techniques used for these purposes are the Scanning Electron Microscopy and, preliminarily, X-Ray Diffraction (Ashcroft and Mermin, 1976).

3.3.1 Scanning Electron Microscopy (SEM)

Electron microscopy can produce a high magnification image. Electrons instead of light are used as probe source. An electron beam is produced from a heated tungsten filament, and is accelerated in a high vacuum chamber, where it hits the surface of the sample. The acceleration potential used is very high (from 1 kV to tens of kV). In these conditions, the wavelength associated to electrons \( \lambda_e \) is much shorter (~ \( 10^{-3} \) nm) than that of visible light (380 - 710 nm), in accordance with the De Broglie equation:

\[
\lambda_e = \frac{h}{m_e v_e}
\]  

(3.11)

where \( m_e \) and \( v_e \) are respectively the mass and the velocity of one electron, and \( h \) is the Planck constant. From the above formula, the wavelength of the electrons can be reduced, increasing their momentum and, in particular, changing the potential \( V \) causes a change in velocity \( v_e \) too, according to the formula:
\[ v_e = \sqrt{\frac{2eV}{m_e}} \]  

(3.12)

where \( e \) is the electron charge. The minimum wavelength related to the electron defines the spatial resolution of the method, linked to the phenomenon of diffraction which occurs when the size of the observed object is comparable with the wavelength associated with the probe.

In SEM, the electron beam scans the surface of a sample. The electrons are scattered from the surface both elastically and inelastically. Elastic scattering with the sample atoms lead to the detection of the most energetic backscattered electrons (Back Scattered Electron, BSE). At the same time, secondary electrons (SE) are emitted by the sample as a result of the inelastic interaction with the beam (Figure 3.8).

Since SE have low energy, measurements are performed under high vacuum, in order to enable them to reach the detector. Moreover, only conductive materials can be analysed. Insulators can only be analysed if they are coated with a thin layer of gold, in order to avoid the accumulation of a net local electrical charge on the sample surface.

Detection techniques are related to the energies of the electrons of interest. As for the secondary electrons, they are deflected toward a photomultiplier, going through a grid biased at 400 V, in order to accelerate them. The backscattered electrons are detected by a coaxial annular detector, a semiconductor device or a photomultiplier, in order to maximize the efficiency of the geometric detection. On the other hand, backscattered electrons have a high kinetic energy, and therefore they do not need to be further accelerated.

The images resulting from the back-scattered electrons provide qualitative information on the distribution of elements on the surface. If an electron is back-scattered from a heavy element, it keeps most of its initial energy, so that the resulting image is brighter than that obtained when scattering occurs from a relatively light element. Thanks to BSE images, areas more or less rich in heavy elements can be distinguished. Most of the images reported in Chapter 4 are BSE type because the main interest is to identify different phases on the post-melting surface.

In the current research, the SEM used is equipped with an EDS (Energy Dispersive X-ray Spectroscopy) detector. The characteristic X-rays emitted by atoms present on the surface when they are hit by the impinging electrons can be used for semi-quantitative chemical analysis. However, due to a number of experimental factors, such as absorption of the vacuum chamber window, overlap of the

Figure 3.8: schematic view of SEM used in the current research.
peaks, surface roughness, such method can only be used in a qualitative way for light elements. The analysis can be considered as semi-quantitative for the elements heavier than sodium. A Philips XL40 scanning electron microscope operating at 20 kV and installed in a glove box is employed in the present work for the analyses of samples containing Pu.

### 3.3.2 X-Ray Diffraction (XRD)

X-ray diffraction is a technique based on elastic scattering resulting from the interaction of an electromagnetic beam with the atoms in a crystal lattice. The wavelength of X-rays is typically of the order of 1 Å, comparable with the interatomic distances in the crystals, so this technique is suitable to obtain information about the crystal structure.

An electron can be considered as an electromagnetic field that oscillates with its own frequency. When an X-ray beam hits an atom, electrons around the nuclei begin to oscillate with the same frequency of the incident beam. These electrons become secondary sources of X-rays with the same energy of the incident beam (coherent scattering). In almost all directions, it results in a destructive interference, the X-rays are scattered out of phase compared to those incidents. However, atoms in a crystal lattice are arranged in a regular way, and in some directions a constructive interference occurs. In these directions, the scattered waves are in phase with the incident giving rise to the phenomenon of diffraction. Constructive interference is obtained when the incident beams respects equation:

\[
\overline{AB} + \overline{BC} = N\lambda
\]  

(3.13)

As shown in Figure 3.9 and in equation (3.13), when the phase difference between the wave fronts diffused by two adjacent atoms is equal to a \( N \) integer multiple of the wavelength, the interference is constructive. These geometrical conditions for constructive interference are summarized by Bragg's law:

\[
N\lambda = 2d \sin \theta
\]  

(3.14)

where \( d \) is the space between crystal planes and \( \lambda \) is the wavelength of the incident beam. The various orders of constructive interference \( n \) result only for specific values of the angle \( \theta \). Each diffracted beam identifies the reflection from a family of lattice planes characterized by Miller indices. The diffractogram is then clearly mathematically correlated to the structural arrangement of the atoms which causes scattering (Mastromarino, 2016).

Each solid possesses a crystalline structure. When irradiated by monochromatic X-rays, it gives rise to a diffraction pattern which characterizes the crystalline structure uniquely. The position and intensity of

---

Figure 3.9: representation of the conditions for the constructive interference for X-Rays diffracted by crystalline planes.
the peaks are characteristic of the crystallographic structure and the atomic composition of the material. In the present work XRD analysis was preliminarly performed only on a single sample, but further investigations are needed to understand more clearly the compounds formed after the melting. The device used for this work is a Seifert XRD-3003 X-ray diffractometer, dedicated to room temperature analysis of pulverised polycrystalline materials. The equipment is placed in a shielded glove-box which allows the measurement of irradiated samples (Figure 3.10). The configuration used is θ-θ, i.e. both the X-ray source and the detector rotate during the measurement. It is equipped with a point detector. This diffractometer is not equipped with a monochromator. The Cu Kα line is used as X-ray source, whereas a nickel filter is used to remove the Cu Kβ radiation. The data acquisition time is usually from 2 hours to 12 hours, depending on the required data accuracy. This machine is primarily intended to perform phase analysis and unit cell measurement.

**Concluding remarks**

The laser-heating facility at JRC-ITU is here described. Thanks to this unique technique, samples are heated at very high temperature in few milliseconds, reducing the interaction with the containment and limiting sublimation phenomena. The most important instruments for the present thesis are the fast pyrometer and the spectro-pyrometer. The first returns the radiance temperature of the sample, while the second is fundamental to know the emissivity of the analysed material. Combining such information, the real temperature is yielded. In particular, thermal arrest evolution will be deeply analysed in the following chapter. Also post-melting characterisation is very important for the present study. SEM and EDS have been largely used to identify the phases formed after the solidification of the samples.
4. Results and discussions

Abstract. In the present chapter, all the experimental results are described and analysed. In particular, most of them regard the system UO$_2$-Zr, representative of LWR, the most common NPP type used in the world. A laser heating technique was used to simulate a sudden temperature increase due to an accidental condition and, then, to study the interaction between nuclear fuel and cladding material. Post-melting characterisation is another important part of the present work, in particular elemental analysis performed with EDS. Preliminary tests were performed also using U, Pu MOX fuel (mainly to simulate a fast reactor condition) or Al$_2$O$_3$ (to study the interaction between corium and concrete). Finally, results about Chernobyl lava samples are discussed.

4.1 Introduction

The present chapter shows the results of this experimental work, focused mainly on the study of melting behaviour and post-melting characterisation between nuclear fuel and cladding material in case of severe accident on laboratory-scale samples. A first objective of the present research consists of establishing whether lower-melting compounds can be formed in real fuel-cladding systems, and, in case, what the resulting melting temperature depression would be. In order to answer this question, the melting behaviour of pure and mixed fuel compounds should first be soundly assessed, which therefore constitutes an even more paramount goal of the current approach. In fact, this situation must be controlled especially in the nuclear core, where the fuel is stored and fission reactions take place. As already described in Chapter 2, in the most common NPP type (i.e., LWR), the fuel consists of enriched uranium dioxide and the cladding of Zircaloy (for compositions, see Table 2.1). When the temperature rises up to the melting point, the fuel and the cladding start to interact and mix together. As largely described in the Introduction to this thesis, the resulting corium mass has different properties compared with unmelted fuel and cladding. Understanding the behaviour of such material and characterising the post-melting composition will be important for the prediction of the accident evolution and, in the worst case, the mitigation of its consequences. For these reasons, the UO$_2$-Zr system needs to be analysed in details, which is the main focus of the present work. Preliminary tests were also performed using different materials. UO$_2$-Zr pellets were put in an alumina ring, in order to simulate and study the interaction between the corium and the concrete. In another test, U, Pu MOX fuel was used in stainless steel cladding to simulate the resulting interaction as consequence of a SA in fast reactors. Finally, the melting behaviour of some fragments coming from Chernobyl's lava was studied as well, as an example of a real corium system.

4.2 Emissivity of Zircaloy-4

For contact-less pyrometric temperature measurements, the spectral emissivity $\varepsilon$ of the investigated materials must be known.

The emissivity is in general a function of temperature, wavelength and angle of measurement and depends also on the morphology and characteristics of the analysed surface. In particular, the normal spectral emissivity (NSE) of uranium and plutonium dioxides is well known (Bober, 1980; Bober et al., 1984; Fink, 2000; Shi et al., 2010; De Bruycker et al., 2011). For these compounds the grey body hypothesis is applicable in the visible/ near infrared (NIR) spectral range. It means that the wavelength
has a negligible role on the value of NSE. The influence of angle is not relevant too, at least within the scopes of this work.

On the contrary, NSE of Zircaloy (Zy) has not been established in the visible/NIR range such in detail, so some analyses are needed. The main interest is to study the spectral emissivity of Zy at the melting/freezing temperature and at angles between 0° and 20° from the normal direction, due to the complex positioning and alignment of the current optical instruments. For the measurements, both the fast two-channel pyrometer and the 256-channel spectro-pyrometer are used. Using the fast pyrometer, the Zy spectral emissivity at the solidification point at wavelength of 655 nm can be obtained directly through its definition, by dividing the experimental radiance spectra (obtained without any emissivity correction) by the theoretical Planck intensities at the melting temperature and various wavelengths (see Chapter 3). Such direct determination is possible in this particular case, because the melting/solidification temperature of Zircaloy is to be 2120 K (IAEA, 2006).

Some measurements were done in two different positions, with angles of 0° and 20° between the pyrometer and the normal to the surface of the sample. From the results of eighteen tests (Figure 4.1), the normal emissivity is higher than the 20° one, in particular the values obtained are \( \varepsilon_{655,\text{norm}} = 0.32263 \pm 0.00922 \) and \( \varepsilon_{655,20°} = 0.30309 \pm 0.00430 \).

Using the spectro-pyrometer, analysis of the spectral emissivity is possible. In particular, the evaluation of emissivity from 550 nm to 900 nm has been investigated using the method without assumptions, described in Chapter 3. Considering the two different alignment geometries reported above, also in this case the normal spectral emissivity is higher than the 20° one, in agreement with the behaviour shown by the pyrometer. For wavelengths in analysed range, Figure 4.2 shows that the grey body approximation can be applied to Zy too. In fact, the trend of \( \varepsilon_\lambda \) is very close to be flat, in contrast with Teodorescu (2007), that reported decreasing emissivity at increasing wavelength. This disagreement is actually only apparent, because of the different wavelength range used for his tests (from 1 µm to 16 µm), much larger than the one used in the present work. The current analysis displays emissivity values decreasing with wavelength only starting at approximately 0.8 µm. Spectro-pyrometer emissivity averages can be calculated and compared with the pyrometer values, yielding \( \varepsilon_{\text{norm,av}} = 0.32248 \pm 0.00886 \) and \( \varepsilon_{20°,\text{av}} = 0.30653 \pm 0.00643 \). In according with the present results, all further emissivity evaluations are conducted by best fit of the Planck’s law for real body.

![Figure 4.1: spectral emissivity of Zircaloy from pyrometer measurements at 655 nm and at the solidification temperature.](image)
These analyses are enough for the scopes of the present tests. However, a deeper investigation on the behaviour of optical properties of Zy as function of the angle is needed because the change in emissivity is not negligible, even for small angles. This angle-dependent emissivity change, larger than what one would expect for a metallic alloy (DeWitt and Nutter, 1988), is probably partly attributable to the optical effect of the autoclave window.

4.3 The UO$_2$-Zr system

The study of the melting behaviour (using the laser heating technique) and of the composition (thanks to post-melting characterisation) is crucial to improve the knowledge of corium properties, also in different chemical environments. As pointed out before, LWRs represent the most important system for the nuclear safety, so the analysis was first focused on UO$_2$-Zr samples produced in the COLOSS Project. Successively, the high-temperature interaction of real samples of fuel pellets with cladding material, more representative of the real fuel rod geometry in the reactor case, was experimentally investigated.

The current analysis started with the experimental determination of the melting/solidification points of pure UO$_2$ and pure Zr (Zy). Because these phase transition points are relatively well established, such a check constituted also a good test of the accuracy of the present experimental approach. Thermograms recorded on UO$_2$ and Zy are shown in Figure 4.3. The observed solidification arrest temperatures obtained by using the emissivity values reported above, are in good agreement with accepted literature data: 3105 K ± 3 K for UO$_2$ and 2125 K ± 4 K for Zy, to be compared respectively with 3120 K and 2120 K (IAEA, 2006).
In the framework of the COLOSS Project (Adroguer et al, 2003, 2005), samples made by metallic zirconium and uranium dioxide were produced to study the dissolution of the fuel in molten Zircaloy. In this work, the same samples are used to simulate the characteristics of "ideal coria" with known compositions, in order to determine phase boundaries in the UO$_2$-Zr isopleth phase diagram. In fact, only few data exist about such a system. They are due to Juenke and White (1970) and Kleykamp and Pejsa (1991). Only very recently, thanks to the work of Quaini (2015), new experimental data have been collected and phase boundaries have been optimised using a CALPHAD approach.

Samples are heated above the melting temperature by the TRUMPF laser at 1064.5 nm. As the laser beam is switched off, during the sample’s cooling stage, the liquid-solid transition temperatures are clearly visible as thermal inflections or arrests on the thermograms detected by pyrometer and spectropyrometer. Such experimental transition temperatures are then placed in the phase diagram at the corresponding nominal composition and compared with the CALPHAD optimised phase boundaries.

![Thermograms](image)

Figure 4.3: comparison between thermograms of pure UO$_2$ (a) and Zircaloy-4 (b). The blue laser signal is very helpful to identify the presence of melted materials on the surface.

### 4.3.1 COLOSS samples

In the framework of the COLOSS Project (Adroguer et al, 2003, 2005), samples made by metallic zirconium and uranium dioxide were produced to study the dissolution of the fuel in molten Zircaloy. In this work, the same samples are used to simulate the characteristics of "ideal coria" with known compositions, in order to determine phase boundaries in the UO$_2$-Zr isopleth phase diagram. In fact, only few data exist about such a system. They are due to Juenke and White (1970) and Kleykamp and Pejsa (1991). Only very recently, thanks to the work of Quaini (2015), new experimental data have been collected and phase boundaries have been optimised using a CALPHAD approach.

Samples are heated above the melting temperature by the TRUMPF laser at 1064.5 nm. As the laser beam is switched off, during the sample’s cooling stage, the liquid-solid transition temperatures are clearly visible as thermal inflections or arrests on the thermograms detected by pyrometer and spectropyrometer. Such experimental transition temperatures are then placed in the phase diagram at the corresponding nominal composition and compared with the CALPHAD optimised phase boundaries.

![Phase Diagram](image)

Figure 4.4: solidification temperatures measured in inert atmosphere (3 bar of Ar) for various compositions of COLOSS samples, in the UO$_2$-Zr isopleth phase diagram calculated using CALPHAD (reproduced from (Quaini, 2015)).
Laser heating

Repeating the measurements for different compositions in inert atmosphere (3 bar of Ar), the phase transition occurs at different temperatures, in particular it is higher in UO$_2$-rich samples. This observation is coherent with the properties of the materials involved, characterised by very different melting temperatures (2120 K of metallic zirconium versus 3120 K of uranium dioxide). These values are put in the UO$_2$-Zr isopleth phase diagram (as shown in Figure 4.4). Phase boundaries here correspond to the CALPHAD optimisation, made by Quaini (2015). It should be noted, incidentally, that this isopleth section cannot be re-conducted to a pseudo-binary diagram, as the composition of the present phases can be obtained only using the complete 3D ternary system (the tie lines lie outside the plane in multi-phase domains). For this reason, it only makes sense, in the phase diagram of Figure 4.4, to compare the present experimental points with the dotted liquidus line. It is clear that the trends of both data sets are in good qualitative agreement, even if the transition temperatures measured in the present work with both pyrometer and spectro-pyrometer are higher than the CALPHAD lines by up to 400 K. The fabrication of these multi-phase samples is a crucial step. Probably different preparation

Table 4.1: results about the melting temperature measured for COLOSS samples in inert atmosphere and in presence of hydrogen.
ways can influence the oxygen distribution between uranium and zirconium, which would affect the experimentally observed liquid/solid transition temperatures. It should also be noticed that it is hard, with the current method, to detect both solidus and liquidus transitions for a complex isopleth phase diagram like the UO$_2$ – Zr. Therefore, the current thermal arrests are assumed to be related to total fusion or first solidification of the surface, i.e. the liquidus transition. The present results are shown in Table 4.1. Regrettably, also the liquid miscibility gap hypothesised in the CALPHAD optimisation between 55 mol% and 85 mol% of UO$_2$ could not be clearly detected with the present approach, probably because of the limited amount of latent heat released by the separation or two liquid phases. Despite these few discrepancies, the present results are very promising in a field with only few experimental data and can help in improving the knowledge of such system, the high temperature behaviour of which determines the first phases of a severe accident.

The same tests have been repeated in 3 bar of a mixture of Ar and 6 vol% of H$_2$, to observe the influence of hydrogen on the behaviour of these materials. H$_2$ can actually be formed in the reactor.

**Figure 4.6:** evolution in time of emissivity (in green) and temperature (in red) in a Zr-rich COLOSS sample (20 mol% UO$_2$ 80 mol% Zr)

**Figure 4.7:** normal spectral emissivity measurements of COLOSS molten surface samples (grey body assumption). Experimental data follow with fair approximation an indicative linear behaviour.
environment by hydrolysis and under accidental conditions due to the reaction of water with Zircaloy leading to Zy oxidation. Comparing with the previous melting/solidification results, no big differences can be noted (Figure 4.5), so it seems that hydrogen has no relevant effect on the melting behaviour of the investigated materials. However, all the samples melted in presence of hydrogen are characterised by the formation of numerous cracks on the surface. If put in contact with air, they are strongly pyrophoric and are quickly turned into powder. This fact is most probably due to the formation of hydrides of lower density that, by expanding, destroy the surrounding structures.

Another important part of the present analysis regards the emissivity of the different COLOSS compositions. From the spectro-pyrometer measurements, the spectral emissivity is obtained within the grey body assumption. This information is very important in this kind of temperature measurements, because assuming a wrong emissivity leads to bad temperature measurements. An interesting feature of Zr-rich samples is the strong emissivity change during the melting/freezing experiments both in inert and reducing environment (Figure 4.6). In fact, the emissivity fitting through Planck’s law shows three different steps during the tests: the melted hot material has a value very close to metallic phase; then, when the cooling starts, it slightly increases; and finally, after completion of the phase transition, it rises up to an obviously higher value, characteristic of an oxide phase. Emissivity evolution can be very useful to detect other phenomena, otherwise not recognizable in the thermogram. In this case, emissivity steps indicate that the composition of the surface is changing, in particular during the freezing, when zirconium segregation occurs and a UO$_2$-richer phase appears in the centre of the refrozen pool, as shown by the successive electron microscopy analysis reported in the next section.

This information is also observable by looking at the evolution of the emissivity as function of composition in different moments of the tests. The behaviours in two particular conditions are analysed: the hot liquid surface (Figure 4.7) and the freezing point (Figure 4.8). In Figure 4.7, the experimental data follow reasonably well an indicative linear increase from the emissivity value of pure Zr to the one of pure UO$_2$, meaning that the composition of the liquid is very close to the nominal one. On the other hand, observing Figure 4.8, for some compositions the emissivity is higher than the linear trend, and very close to the urania value. This behaviour is typical of Zr-rich samples, especially with 60 mol% and 80 mol%, and depends also on the chemical environment. This effect is not observable for the
composition with 90 mol% of Zr, probably because the UO$_2$ content is too low for allowing the segregation.

**Thermocamera**

During some of the current laser heating experiments, also the Phoenix™ Camera System was used to understand the temperature evolution in time and space across a sample. Figure 4.9 shows the time evolution of the temperature profile on the vertical diameter of a COLOSS sample with composition 20 mol% UO$_2$ 80 mol% Zr. As expected, the temperature is higher in the centre of the heated part and, when the laser pulse ends, it decreases quicker than in the periphery. Looking at different profiles, it can be noted that the temperature in the central part is more uniform during the cooling than during the heating. This is consistent with the fact that the freezing temperature is an invariant property of the material (i.e., it is independent of the maximum temperature reached locally). It can also be seen that the freezing arrest recoalescence is apparently higher in the central part of the sample, as shown by orange and red spots in Figure 4.9. This effect is in reality due to the emissivity increase following the segregation of an oxide phase during the freezing, as pointed out in the previous section and shown in Figure 4.6.

Figure 4.10: a) BSE image of the COLOSS sample 20 mol% UO$_2$ 80 mol% Zr, in which a darker ring at the rim of the melted part is clearly visible; b) a line scan performed with EDS, related to the atomic content of uranium (in violet) and zirconium (in light blue). Apparently, the Zr content decreases in the vicinity of the unmelted. It is only an artefact due to the presence of a crack at the interface.
After the laser melting experiments, the samples are analysed using scanning electron microscopy. The main goal of the analysis is observing the formation of different phases and the elemental composition on different areas of the samples. Areas richer in heavier elements (typically U as opposed to Zr) can be easily recognized in BSE images. This tool is very helpful in detecting the different phases formed on the surface. Comparing the behaviour of different compositions, it is possible to see that in the melted and refrozen area uranium and zirconium are generally well mixed together although sometimes segregation and non-congruent vaporisation/condensation phenomena occur, leading to zirconium-richer areas. In some Zr-rich compositions, a dark ring is clearly visible around the melted part (Figure 4.10). The brighter area is richer in uranium while the presence of such BSE-darker ring, richer in zirconium, is the result of segregation occurred during the freezing, as explained before during the melting/solidification cycles are very different depending on the distance from the centre of the laser spot and on the maximum temperature reached.

Compositions of points selected are reported in Table 4.2.

### Scanning electron microscopy

Figure 4.11: SE and BSE images of the COLOSS sample 10 mol% UO$_2$ 90 mol% Zr and some areas of melted part with higher magnifications. It is clear that the phases formed after the melting/solidification cycles are very different depending on the distance from the centre of the laser spot and on the maximum temperature reached.

<table>
<thead>
<tr>
<th>Point</th>
<th>% U</th>
<th>% Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.43</td>
<td>95.57</td>
</tr>
<tr>
<td>2</td>
<td>36.80</td>
<td>63.20</td>
</tr>
<tr>
<td>3</td>
<td>2.89</td>
<td>97.11</td>
</tr>
<tr>
<td>4</td>
<td>52.93</td>
<td>47.07</td>
</tr>
<tr>
<td>5</td>
<td>2.19</td>
<td>97.81</td>
</tr>
</tbody>
</table>
analysis of the emissivity evolution. Another possible cause for the formation of this ring can be sought in the vaporisation of Zr from hotter central part of the molten zone, with consequent condensation in contact with the cooler rim. This second explanation is however more awkward, it would not explain the apparent directional crystal growth in image Figure 4.10b nor why this vaporisation/condensation mechanism would involve Zr more than U. In both cases, SEM images are consistent with the emissivity evolution reported in Figure 4.6. The separation of areas richer in one compound changes properties and phases of the post-melted material.

Figure 4.11 shows some results of a SEM analysis carried out on a sample with 10 mol% of UO₂ and 90 mol% of Zr. The presence of different structures is observable. In the middle of the melted part, the material is organised in an anisotropic phase, in which uranium and zirconium are well mixed together. Moving to the external part, uranium and zirconium segregate in different ways, depending on the distance from the centre. Closer to the hottest part, uranium forms little particles spread in a matrix of zirconium (brighter spots on a dark background in the BSE image). In the vicinity of the interface with the unmelted material, one can observe BSE-brighter strips richer in uranium. The obvious separation of phases with markedly different composition is in qualitative agreement with the complex phase boundaries reported in Figure 4.4 and Figure 4.5.

Energy-Dispersive Spectroscopy (EDS) confirms these interpretations, giving a semi-quantitative elemental analysis of the different phases. However, it is not possible to determine, with the present approach, if some oxygen stoichiometry changes have occurred during the melting/solidification cycles. Such changes can be important, especially for the formation of uranium oxides, as UO₃ and U₃O₈, characterised by very different material properties.

**X-Ray Diffraction**

XRD analysis was performed on one COLOSS sample as a preliminary test of post-melting phase characterisation. The diffractogram resulting from a measurement performed on a 60 mol% UO₂ - 40 mol% Zr sample is shown in Figure 4.12. It was hard to separate the laser melted and refrozen part from the unmelted bulk. Therefore, XRD analysis was performed on 50 mg of a mixture, containing mostly melted and re-solidified material, but certainly also some unmolten parts. Fitting of the experimental peaks, also reported in Figure 4.12, was performed with the help of Powdercell®. It shows

![Diffractogram](image)

**Figure 4.12:** Diffractogram of COLOSS sample with composition 60 mol% UO₂ - 40 mol% Zr. The best fit of the experimental peaks shows the formation of some metallic U.
that the sample mostly contains a face centred cubic fluorite-like oxide phase, the lattice parameter of which would be correspond to a $\text{U}_{0.9}\text{Zr}_{0.1}\text{O}_2$ composition. The remaining materials peaks are harder to attribute. The best fit is nonetheless obtained by considering a Zr-U alloy and traces of metallic U. The Zr-U alloy is partially oxidised, although it is not possible to determine its exact oxygen content with this approach only. Because of this partial oxidation, it is also impossible to accurately assess the uranium content in the alloy. It is anyway shown that some Zr can migrate into the oxide phase and some metallic uranium can be produced during the melting/freezing process.

### 4.3.2 $\text{UO}_2$-Zircaloy samples

#### Sample preparation

In order to simulate the geometry of a nuclear fuel rod placed in a NPP core, special samples are prepared with two components. The first one is a disc of natural uranium dioxide, the second a Zircaloy-4 ring, with the inner diameter a little greater than the pellet one. Like in a real LWR fuel element, the fuel pellet is placed inside the cladding ring and, in this way, the geometry of a generic bar is well reproduced (Figure 4.13). The sample is held in the experimental vessel in the vertical position, so the pellet is in perfect contact with the cladding in the lower part while a variable gap is produced in the rest of the circumference. Main interest of this experimental campaign is to study the direct interaction between fuel and cladding. Therefore, the heating laser is focussed on a spot, on the fuel sample, close enough to the contact area. Both thermal analysis during the melting/freezing cycles and post-melting characterisation are here mostly performed on the fuel-cladding interface. In future work, the influence of the gap can be studied too, especially evaluating how it delays the melting of the cladding and the mixing with the fuel. This investigation will be very useful to compare the different situations potentially occurring in the rod in case of a fuel melting event. Usually, a tungsten disk is used to fix the pellet with the cladding (not shown in Figure 4.13). It is placed where the gap is largest and does not interfere with the measurements that are performed on the other side of the sample, around 1 cm away. Such distance has been checked to be largely sufficient to rule out any possible effect of the tungsten disks.

#### Laser heating

The samples described are put in the autoclave in an inert atmosphere of Ar where they are hit by laser pulses close to the contact area between the fuel pellet and the Zircaloy ring. Even after one single shot, the melted area involves both the fuel and the cladding and the properties of the mixed re-solidified material change. In fact, when one points the pyrometer in the centre of the laser spot and the spectrometer on

![Figure 4.13: sample components and assembly.](image-url)
the interface, there is a difference of about 100 K in the thermal arrest measurement (Figure 4.14). Without interaction, the phase transition temperature should be the same for the two instruments (within the uncertainty range of about ±30 K). The observed difference certainly comes from the expected inter-mixing of Zy and urania during the melting/freezing process, producing a mixed material similar to the COLOSS samples presented in the previous section. Evidence of mixing is even clearer when several successive laser shots are repeated in the same area and each time the solidification thermal arrest is measured. The transition temperature decreases by about 200 K, from the 3120 K of the first shot (corresponding to the melting temperature of pure uranium dioxide) to about 2900 K of the sixteenth (Figure 4.15). After each shot, the quantity of mixed material increases. Therefore, the main reason for such a drop is most likely the diffusion of zirconium, characterised by a lower melting temperature than uranium dioxide. This fact can be dangerous from the safety point of view, because melting of the fuel can occur before the expected design values thus increasing the probability of a severe accident scenario in case of uncontrolled overheating of the fuel.

Repeating the same tests in reducing atmosphere (mixture of Ar and H\textsubscript{2}), the behaviour is a little different. In fact, the drop in the phase transition temperature is lower than that observed in inert atmosphere (Figure 4.16). An explanation of this effect is that hydrogen interacts with zirconium forming hydrates and, in this way, the diffusion phenomena are slowed, reducing the phase transition temperature change. From the mechanical point of view, however, the presence of hydrogen causes a strong embrittlement of the whole structure and even the Zircaloy ring is sometimes cracked or damaged (picture in the right part of Figure 4.16). The eventual formation of hydrides affects both

![Figure 4.14: thermograms of pyrometer and spectrometer pointed in different positions of the melted area. A difference of about 100 K can be seen.](image)

![Figure 4.15: comparison between the thermograms a) after the first shot and b) after the sixteenth. The drop in the thermal arrest is about 200 K.](image)
thermal and mechanical properties of the corium, leading to its fragmentation. On the other hand, one cannot exclude that the presence of H$_2$ remove most oxygen impurities, hindering the trance formation of higher uranium oxides (like U$_3$O$_8$ and UO$_3$) having a lower melting point. However, this latter interpretation would not explain, alone, the more limited Zr diffusion observed in the UO$_2$ matrix by post-melting analysis. Probably both phenomena co-operate in the current experiments.

By comparing the evolution of the thermal arrest temperatures with the COLOSS ones reported in Figure 4.4 and Figure 4.5, suggests that zirconium diffusion in the fuel pellet should stabilize the interface composition at about the 20 mol% of Zr dissolved in UO$_2$ for samples laser heated in Ar. By using this approach, the interface composition of samples laser heated in the presence of hydrogen would be between 5 mol% and 10 mol% of Zr dissolved in UO$_2$.

From the spectro-pyrometer measurements, the emissivity evolution can be used again for

![Figure 4.16: comparison between the phase transition temperatures in inert and reducing atmosphere using shots with the same characteristics. Looking at the pictures of the different samples, the characteristics of the melted part are different.](image)

![Figure 4.17: evolution of emissivity and temperature on UO$_2$-Zy interface.](image)
understanding what happens on the surface. Looking at Figure 4.17, the emissivity is very close to the UO₂ value till freezing occurs. Then it decreases a little and stabilizes on the new lower level affected by the zirconium diffused in the fuel pellet.

Finally, some preliminary laser heating experiments were carried out on a UO₂ disk in a Zy ring under an oxidising atmosphere (pressurised air at 3 bar). The goal of these tests is to check how the melting behaviour of the investigated UO₂-Zr mixture evolves in a strongly oxidising environment. Figure 4.18 shows two thermograms recorded at the interface between an UO₂ pellet and a Zy ring during the first and the fifth laser pulses, respectively, of a series of eight melting/freezing cycles. It can be seen that the solid/liquid transition occurs at lower and lower temperatures over the successive laser pulses. The solidus arrest stabilizes around 2500 K. This temperature is certainly lower than the solidus/liquidus temperatures assessed by Piluso et al. (2005) or Quaini (2015) for the system UO₂-ZrO₂. Therefore, such a low solidus point can most probably be ascribed to the formation of higher uranium oxides like U₃O₈.

Unfortunately, for this kind of samples, thermocamera data were not useful to understand the evolution of the temperature on the interface, because spatial resolution is not high enough.

Figure 4.18: thermograms recorded on UO₂-Zr interface under pressurized air (3 bar).

![Figure 4.18](image)

Figure 4.19: SEM pictures of the sample with Zircaloy: a) SE image of the whole sample; b) BSE image on the interface with higher magnification. The EDS analysis (in mol%) about the atomic content of uranium and zirconium in some interesting spots is reported, revealing the presence of particles richer in Zr.

<table>
<thead>
<tr>
<th></th>
<th>% U</th>
<th>% Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.65</td>
<td>85.35</td>
</tr>
<tr>
<td>2</td>
<td>79.24</td>
<td>20.76</td>
</tr>
<tr>
<td>3</td>
<td>13.06</td>
<td>86.94</td>
</tr>
<tr>
<td>4</td>
<td>82.12</td>
<td>17.88</td>
</tr>
</tbody>
</table>
Scanning electron microscopy

As for the previous samples, also the UO$_2$ – Zy specimens are analysed using the SEM. In this case, there is no evidence of formation of different phases in the melted part and even in the interface between pellet and ring. The most interesting fact is that it is possible to detect some zirconium inside the uranium dioxide pellet, even at hundreds of µm from the interface, and some traces of uranium are measured in the cladding, too. One can conclude that the diffusion goes in both directions, from the fuel pellet to the cladding ring and vice versa, changing the properties of both materials, in particular decreasing the fuel melting point.

On the interface, the zirconium content can change locally, because of segregation and evaporation phenomena, as in the COLOSS samples. These phenomena are more pronounced than in the previous situation because zirconium is here physically separated from uranium before the tests, and therefore, during the melting/freezing process the mixing is more heterogeneous. Towards the centre of the laser-heated zone, further away from the interface, EDS analysis performed on a sample laser-heated in Ar shows that the average zirconium content in the melted and refrozen zone is about 17 mol% (Figure 4.19), although Zr-rich particles can be recognized in the refrozen fuel (Figure 4.20). This value is in agreement with the one estimated in the previous section by comparing the melting point depression

<table>
<thead>
<tr>
<th></th>
<th>% U</th>
<th>% Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.31</td>
<td>93.69</td>
</tr>
<tr>
<td>2</td>
<td>77.66</td>
<td>22.34</td>
</tr>
<tr>
<td>3</td>
<td>55.20</td>
<td>44.80</td>
</tr>
<tr>
<td>4</td>
<td>74.81</td>
<td>25.19</td>
</tr>
</tbody>
</table>

Figure 4.20: BSE higher magnification image and EDS analysis (in mol%) of point 3 of Figure 4.19b. In the top left corner, an "island" mainly made by zirconium as result of heterogeneous diffusion.

<table>
<thead>
<tr>
<th></th>
<th>% U</th>
<th>% Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>31.61</td>
<td>68.39</td>
</tr>
<tr>
<td>3</td>
<td>17.68</td>
<td>82.32</td>
</tr>
<tr>
<td>4</td>
<td>9.22</td>
<td>90.78</td>
</tr>
</tbody>
</table>

Figure 4.21: SE picture and EDS analysis (in mol%) of UO$_2$ pellet with Zy cladding melted in presence of hydrogen.
caused by Zr diffusion into UO$_2$ and the results obtained on COLOSS samples. As one can see in Figure 4.21, the zirconium diffusion is much less pronounced if the melting occurs in presence of hydrogen. In fact, in this condition the EDS analysis shows that Zr has diffused only in the vicinity of the interaction, while in the remaining melted part no Zr traces are detected. This fact seems to confirm that the formation of hydrides inhibits the zirconium diffusion in the urania pellet, slowing the fuel melting temperature drop.

4.3.3 Concluding remarks

The tests performed on the uranium dioxide-zirconium samples are useful to investigate the properties of the corium in the first steps of a hypothetical core meltdown severe accident scenario. Even if some compositions are not directly representative of the reactor situation, the results obtained on COLOSS samples can help in the general understanding of the system UO$_2$-Zr, especially for the new data on solid/liquid transition temperatures and the detected post-melting phase separation. Considering also the experiments carried out in a geometry closer to the real LWR fuel element, results are well consistent. Zirconium diffusion is the most likely reason for the changing of fuel properties, in particular the melting/freezing temperature decrease. In these experiments, Zircaloy-4 was used as cladding material. Because of the small concentration of other alloying metals in Zy, Zy-4 can be considered to be representative of the case in which Zircaloy-2 is used, too, at least for the measurements performed in Ar. In fact, zirconium diffusion drives the main changes in the material properties and the role of the other alloying elements, present in a low concentration, is hardly relevant in the general evolution of the system, also considering the uncertainty of the present measurements. In the presence of hydrogen, however, it is not possible to extend the present results, because even a tiny quantity of nickel, very sensitive to hydrogen, could change the behaviour of the mixed material. Incidentally, for this reason, in an environment potentially richer in hydrogen, like the PWR, any trace of nickel is avoided.

4.4 U-O-Zr-Al system

A few preliminary experiments have been carried out using a COLOSS pellet (with composition 60 mol% UO$_2$ - 40 mol% Zr) inserted in an alumina (Al$_2$O$_3$) ring. The goal of these preliminary tests is to study the interaction between a hypothetical corium mass and the concrete of the reactor building basement, i.e. the simulation of the Molten Core-Concrete Interaction (MCCI). MCCI research studies, in general, the erosion of concrete carried on by the convective movements of molten corium, but high temperature fosters diffusion and chemical interaction too. These coupled phenomena are responsible for the failure of the reactor building basement and possible leakage of corium through the ground. The choice of the composition for the corium simulant is done imagining a large damage in the reactor core. However, selecting the most realistic composition is very hard, for the large number and the complexity of all the phenomena occurring from the meltdown to the ex-vessel interaction. As for the concrete alumina was taken for this preliminary test as one of its main components. In these first exploratory experiments, also the presence of steel components (mostly Fe) was neglected in the corium composition. On the other hand, some tests on the interaction between a UO$_2$-Zr mixture and steel have already been performed at JRC-ITU in recently published research (Bottomley et al., 2015).

Laser heating

As in the previous experiments, the sample is placed in the autoclave and shot with the infrared laser in the vicinity of the contact area between pellet and Al$_2$O$_3$ ring. Looking at the thermograms, the shape of the thermal arrests is sometimes original. In fact, some hardly reproducible fluctuations are present.
during the cooling stage, very different from the other tests reported in the previous sections. Probably, the presence of aluminium in the ring results in the formation of complex intermediate phase solidifying at different temperatures. Unfortunately, it is hard to study these apparent thermal arrests more in details in the present campaign, because possible intermediate phases are not observed after quenching the sample to room temperature. After these oscillations occurring from a temperature of 2830 K to 2520 K, a long solidification plateau is observed at 2460±20 K, lasting for about 500 ms (Figure 4.22). Such temperature is about 200 K lower than the melting one of the pure COLOSS sample with the same composition (which was observed to be above 2600 K, as in Figure 4.4). This suggests that interaction with alumina is another reason of property degradation from the original fuel ones. There is no obvious effect, on the melting behaviour, of the presence of hydrogen, while the mechanical behaviour is worsened by H₂ as seen in the previous section.

Figure 4.22: thermogram of the COLOSS sample in the alumina ring.

Figure 4.23: temperature measurements from the thermocamera for samples with Al₂O₃.
Thermocamera

Also for these samples, some information was extracted by the thermocamera data. As before for the COLOSS samples, another emissivity change occurring during the freezing is observable, but it is much less pronounced than the previous case (Figure 4.23). In fact, the mixture 60 mol% UO₂ 40 mol% Zr was used, in which no segregation of an oxide phase was observed in previous tests. Adding that no aluminum was found in the center of melted part, its diffusion and/or segregation cannot explain totally such phenomenon. A more reasonable explanation of this temperature increase during the cooling can be attributed to the undercooling, occurring during the solidification of the melted surface.

Scanning electron microscopy

Looking at the image of an (UO₂)₀.₄₅Zr₀.₅₅ + Al₂O₃ sample laser-melted in Ar, a dark plume is visible at the periphery of the melted part (Figure 4.24). In the present case, EDS analysis revealed that aluminium is the main component of this darker area, and not Zr like in the COLOSS samples previously investigated. Also the morphology is different from the previous case of the Zr-rich ring in COLOSS samples. Looking at higher magnification in different areas of the sample, different morphologies can be distinguished. In particular, in the centre of the melted part, two different phases appear, containing U and Zr, representative of the condition of the COLOSS sample nominal composition (Figure 4.25). Close to the interface, an interesting morphology is detected (Figure 4.26), where uranium, zirconium and aluminium are mixed together and form rather well-ordered dendritic structures, obviously originating from the nucleation and growth solidification dynamics.

From the BSE image in Figure 4.27, three different areas can be recognized: externally, the unmelted part of the sample is dirtied by some aluminium vapours (point 1); then, a darker part is recognizable, very rich in aluminium, possibly due to Al condensation from the hottest area in the middle of the laser spot (point 2); finally, in the centre of the laser shot, the lighter part is formed by a mixture of uranium, zirconium and aluminium, the composition of which changes as a function of the distance from the centre of the melted area. In particular, the Al content decreases in the vicinity of the centre, as shown in points 3, 4 and 5. This observation is consistent with the observed accumulation of Al in the darker ring. Similar SEM analyses performed on (UO₂)₀.₄₅Zr₀.₅₅ + Al₂O₃ samples laser-melted in the presence of H₂ showed no obvious effects of hydrogen on evaporation and diffusion phenomena, the only clear

![BSE image of the COLOSS sample in alumina ring.](image_url)
influence being limited to the mechanical behaviour, as already discussed in the previous section. Even far from the interface with the Al₂O₃ ring (about 1 mm), aluminium is present in the mixture, underlining that its diffusion is very strong even beyond the ring-pellet interface region. This fact must be taken into account during the MCCI analysis, in order to evaluate the change of property in the deep layers of the interacting materials in the accident late phases.

4.5 MOX-cladding system

Having analysed in details the UO₂-Zy interaction representative of PWR conditions, some preliminary tests were performed in inert atmosphere also using U, Pu MOX as fuel and both Zircaloy-4 and stainless steel 15-15 stabilized with Ti (SS) as cladding. This composition of SS (Table 4.3) is chosen because it is the same employed in the Superphénix reactor (IAEA Nuclear Energy Series, 2012). Three different MOX compositions were used, as reported in Table 4.4. The two samples richer in Pu were melted in SS rings to simulate fast reactor conditions, in which usually the coolant is a liquid metal, imposing a different material choice for the cladding compared with LWRs. The sample with the lower
quantity of PuO₂ was melted in Zr-4 ring as representative of PWR fuel partially transmuted by neutron absorption of 238U. The main goal of these first tests is to compare the magnitude of fuel-cladding interaction between fast and thermal reactors and evaluate if the Pu presence plays a role in the diffusion and melting behaviours analysed in previous sections.

Because of the presence of Pu, these samples were manipulated exclusively in an α-tight glove box in N₂ atmosphere. Cladding and fuel were fixed to the holder using a refractory zirconia-based glue. The rest of the set-up was the same as for the laser-heating experiments depicted in the previous sections (Figure 3.1), save for the camera, which could not be aligned when the sample was placed in a glove-box.

**Laser heating**

Several laser shots were performed on the MOX + cladding samples described above. The average temperatures at which solidification thermal arrests were measured are compared with the urania-plutonia phase-diagram recently published by Böhler et al. (2014). Two different sections of the U-Pu-O system are used, corresponding to the conditions in which UO₂ is mixed with stoichiometric (Figure 4.28) or hypo-stoichiometric (Figure 4.29) PuO₂. Due to the presence of metallic cladding, which can

<table>
<thead>
<tr>
<th></th>
<th>% U</th>
<th>% Zr</th>
<th>% Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>51.85</td>
<td>21.28</td>
<td>27.87</td>
</tr>
<tr>
<td>2</td>
<td>7.84</td>
<td>3.46</td>
<td>88.70</td>
</tr>
<tr>
<td>3</td>
<td>37.86</td>
<td>15.03</td>
<td>47.11</td>
</tr>
<tr>
<td>4</td>
<td>32.27</td>
<td>19.96</td>
<td>47.77</td>
</tr>
<tr>
<td>5</td>
<td>57.73</td>
<td>37.07</td>
<td>5.20</td>
</tr>
</tbody>
</table>

Table 4.3: composition (in wt%) of stainless steel 15-15 Ti stabilized used in experiments with MOX (IAEA Nuclear Energy Series, 2012).

<table>
<thead>
<tr>
<th>Ei</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Ti</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>B</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0.1</td>
<td>15</td>
<td>15</td>
<td>0.4</td>
<td>1.2</td>
<td>1.5</td>
<td>0.6</td>
<td>0.005</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 4.4: name, composition (in mol%) and cladding used for the MOX samples.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>% UO₂</th>
<th>% PuO₂</th>
<th>Cladding</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOX-03</td>
<td>97</td>
<td>3</td>
<td>Zircaloy-4</td>
</tr>
<tr>
<td>MOX-09</td>
<td>91</td>
<td>9</td>
<td>SS 15-15</td>
</tr>
<tr>
<td>MOX-39</td>
<td>61</td>
<td>39</td>
<td>SS 15-15</td>
</tr>
</tbody>
</table>
act as an oxygen getter, the hypo-stoichiometric case is most probably better representative of the present experimental system. In case of hypo-stoichiometric PuO$_2$, MOX-39 and MOX-09 have a melting temperature of about 50 K lower of the solidus reported by Böhler et al.(2014). In the stoichiometric case MOX-39 shows a solidification temperature 50 K higher than the literature solidus. MOX-03 shows in both cases a drop of about 100 K with respect to the literature value. This different behaviour is probably due to the different diffusion phenomena involving Fe and Zr. To confirm such behaviour, more tests are needed using SS as cladding.

Results between pyrometer and spectro-pyrometer are not always in agreement. Measurements carried out in near, but different spots, can result in different experimental data as already pointed out in Chapter 4.3.2. Another reason for discrepancies between the two devices can be sought in the placement of two windows (one of the glove box and one of the autoclave) between the hot sample and the pyrometers that can affect in different ways the signal. Given that the spectrometer is closer to the normal direction of the sample surface, its measurements are considered more reliable than the pyrometer ones.

Plotting the current data in sections of the ternary U-Pu-O system corresponding to oxygen hypo-
stoichiometric uranium and plutonium dioxides, the present measurements can fall in areas where the formation of different solid phases is foreseen at lower temperatures, especially in samples rich in Pu. In further investigations, the formation, upon solidification, of oxygen-deficient phases should be taken into account to understand properly its influence on the properties of the quenched material.

**Scanning electron microscopy**

As for previous tests, EDS analyses performed on MOX samples support and partially explain the temperature measurements performed above. In fact, looking at the interface between MOX-03 and the Zy ring, the diffusion of zirconium is observable (Figure 4.30). Moving from the ring to the melted part, the content of zirconium is decreasing and, even at some hundreds of µm, some traces are found. On the other hand, in MOX-09 and MOX-39 the diffusion of iron and other alloying elements is hardly detectable, even close to the interface. In particular, looking at Figure 4.31 only a few Fe percentages are found in the melted area, while higher content is detected on the interface. This is probably due to segregation phenomena that occur during the freezing as happened previously in COLOSS samples. However, the quantity of diffused Fe is lower of Zr. Probably this fact can be explained in two ways: high Pu content can affect the diffusion of other elements in the MOX pellet and, from the tests performed, this influence is more evident for samples with stainless steel cladding; chemical affinity of Zr is higher than Fe and this fact results in an higher diffusion in the fuel. Both of these explanations are not experimental proved. For this reason, more tests are needed on this kind of system.

![Figure 4.30: SE picture and EDS analysis (in mol%) of cladding ring of MOX-03.](image)

<table>
<thead>
<tr>
<th>% U</th>
<th>% Pu</th>
<th>% Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.83</td>
<td>66.17</td>
</tr>
<tr>
<td>2</td>
<td>47.40</td>
<td>44.15</td>
</tr>
<tr>
<td>3</td>
<td>88.07</td>
<td>1.97</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% U</th>
<th>% Pu</th>
<th>% Fe</th>
<th>% Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>79.34</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>57.19</td>
<td>10.47</td>
<td>2.59</td>
</tr>
<tr>
<td>3</td>
<td>84.60</td>
<td>11.67</td>
<td>2.71</td>
</tr>
</tbody>
</table>

![Figure 4.31: SE picture and EDS analysis (in mol%) of interface in MOX-39.](image)
To complete the laser heating experimental campaign on NPP SA materials, the current experimental approach was used to study the high-temperature behaviour of some real frozen corium from Chernobyl. Details about the origin and composition of these unique samples were published by Burakov et al. (1997) ten years after the Chernobyl accident.

Depending on the location from where they were sampled, three types of lava specimens can be distinguished, different for morphology and composition: brown and black lavas (having the same origin, but differing for composition and inclusions) and porous ceramics (resulting from practically instantaneous solidification of brown lava in contact with water). The composition of these samples is given in Table 4.5. The samples recently shipped to JRC-ITU come from a location called “The Elephant Foot” in a steam corridor beneath the failed reactor and are classified as black lavas.

### Laser heating

Lava fragments were put in the glove box autoclave and fixed to the graphite holder using the above-mentioned ZrO$_2$-based refractory glue. The glue was necessary in this particular case, because the irregular shapes of the lava samples made it impossible to fix them to the holder with graphite screws only (Figure 4.32). Post-melting analysis showed no visible interaction between samples and glue during the laser heating experiments. Chernobyl samples were heated using laser pulses like the previous ones. However, no freezing arrest was observed on the thermograms recorded on samples heated to a maximum temperature lower than 3000 K, even if some melted material was obviously visible on the surface (Figure 4.32b). Only by reaching very high temperature (above 3000 K) a solidification arrest

---

**Table 4.5: weight percentages of different samples from Chernobyl. Data of black lava depends strongly from the origin (Burakov, 2013).**

<table>
<thead>
<tr>
<th>Types of &quot;lava&quot;</th>
<th>Fe</th>
<th>Na</th>
<th>Si</th>
<th>Al</th>
<th>Mg</th>
<th>K</th>
<th>Ca</th>
<th>Zr</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous ceramic</td>
<td>0.2</td>
<td>0.5</td>
<td>35.2</td>
<td>3.8</td>
<td>4.5</td>
<td>2.3</td>
<td>7.5</td>
<td>4.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Brown &quot;lava&quot;</td>
<td>0.2</td>
<td>0.6</td>
<td>36.6</td>
<td>4.0</td>
<td>4.4</td>
<td>2.3</td>
<td>7.2</td>
<td>2.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Black &quot;lava&quot;</td>
<td>0.3±6.7</td>
<td>0.4</td>
<td>37.2</td>
<td>3.8</td>
<td>1.3±3.2</td>
<td>2.7</td>
<td>8.2</td>
<td>3.7</td>
<td>3.2</td>
</tr>
</tbody>
</table>

---

**Figure 4.32:** Chernobyl sample before (a) and after (b) a low-power laser heating experiment. In the pictures different areas can be distinguished: 1) graphite holder; 2) ZrO$_2$-based glue; 3) Chernobyl lava sample.
was clearly observed (Figure 4.33). In fact, this kind of lava is not characterised by a typical thermodynamic liquid-solid transition (clearly represented by the thermal arrest, according to Gibbs’ phase rule (Findlay, 1951)), but by a glassy transition. The usual phase transition temperature is due to the release of the latent heat, occurring when the solid phase becomes thermodynamically more stable than the liquid, but in glass-like materials the latent heat is released in a larger temperature range and there is no evidence of it in the thermogram (Miller and Liaw, 2008). These lava samples are actually mostly glassy because of their high content of Si, coming from the interaction between nuclear core melted materials and sand and concrete used in the early phases of the emergency to cover the destroyed reactor. Various types of crystals are embedded in such glassy matrix. Probably the thermal arrest is visible only when these crystalline structures melt and then re-freeze. Being made mainly by uranium and zirconium oxides (Burakov, 2013), their melting can occur above 3000 K as measured in the current tests.

The spectro-pyrometer measurements yielded very characteristic Planck’s spectra. In fact, for temperatures exceeding approximately 2050 K, two intense absorption bands appear at two specific wavelengths, 590 nm and 770 nm (Figure 4.34). Probably during the heating of these lavas, some sodium and potassium are released, having absorption peaks exactly at 589.6 nm and 769.8 nm.

Figure 4.33: different thermograms of Chernobyl’s samples. Only if temperature exceeds 3000 K the thermal arrest is observable.

Figure 4.34: Planck’s spectra of Chernobyl samples at different temperatures. Above 2050 K, two absorption bands appear at 590 nm and 770 nm.
(Fredrickson and William, 1927). However, the mechanism through which this release occurs should be still unknown.

**Scanning electron microscopy**

Looking at the surface, the morphology is very different between the laser-melted and unmelted parts (Figure 4.35). Even if the points analysed are not very different in composition, the melted part looks more homogeneous while in the periphery a sort of bubbles can be seen. Such morphology was absent before the laser heating tests, so it is probably caused by the quick cooling of the external heated area.

Another interesting aspect regards the inclusions. In fact, Burakov (2013) shows very different types of inclusions, depending on the lava sample origin. In particular, one of the typical inclusions of the Elephant Foot is a chain made by a mixture of UO$_x$ and Zr embedded in the glass matrix. A very similar structure is found also in the melted sample (Figure 4.36). However, these inclusions in the laser-heated material are bigger than the original inclusions, probably because, during the experiments, they started to melt, losing their very characteristic shape and, when cooling occurred, a more interconnected structure was quenched.

To summarize, it has been possible to investigate, on laboratory experiments, the melting behaviour of these samples of real Chernobyl lava in this work for the first time. A glassy behaviour has been observed, as expected, but also the presence, in the lava, of refractory crystal inclusions melting and solidifying above 3000 K. Further research is ongoing to determine the nature of these crystallites.

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Si</th>
<th>Ca</th>
<th>Fe</th>
<th>Zr</th>
<th>In</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.03</td>
<td>59.80</td>
<td>3.68</td>
<td>1.88</td>
<td>3.55</td>
<td>7.15</td>
<td>2.91</td>
</tr>
<tr>
<td>2</td>
<td>18.31</td>
<td>55.40</td>
<td>4.42</td>
<td>2.94</td>
<td>6.52</td>
<td>8.95</td>
<td>3.46</td>
</tr>
<tr>
<td>3</td>
<td>26.48</td>
<td>50.72</td>
<td>4.57</td>
<td>1.50</td>
<td>5.10</td>
<td>8.27</td>
<td>3.36</td>
</tr>
</tbody>
</table>

Figure 4.35: SE image and EDS analysis (in mol%) on the laser-melted/unmolten interface of Chernobyl’s particle.

(Figure 4.36: a) BSE image of an inclusion in the Elephant Foot before the experiments (reproduced by (Burakov, 2013)); b) SE image of an inclusion in the sample after the melting. The two structures look similar, in particular the second one is larger and better connected as consequence of the melting.)
Concluding remarks

In the present chapter, all the experimental results obtained during this campaign have been discussed. The interaction between nuclear materials in SA conditions is analysed by freezing temperature evolution point of view. Great importance is given to the system UO$_2$-Zr (i.e., to LWR fuel-cladding interaction). The main results are here summarised:

- Zircaloy-4 shows an almost constant emissivity in the wavelengths analysed, so the grey body assumption can be applied on it;
- UO$_2$-Zr system is analysed using two different types of samples. Firstly, the behaviour of COLOSS pellets with known compositions is studied in inert atmosphere to fix some reference points in the phase diagram. Also the emissivity evolution shows an interesting behaviour, especially in Zr-rich samples. In fact, it can be used to determine when segregation occurs. Post-melting characterisation confirms the formation of different phases detected using optical properties. Repeating the same tests in presence of hydrogen, the melting temperature shows almost the same behaviour, but a strong embrittlement affects the samples, probably due to hydrides formation;
- The second type of UO$_2$-Zr samples is formed by a fuel disc inserted in a Zircaloy-4 ring. The interaction results in a drop of solidification temperature because of Zr diffusion. Comparing the temperature of the post-melting mixture with the values fixed before, the amount of migrated zirconium can be estimated. Such evaluations are then confirmed by EDS analysis. In presence of H$_2$, the freezing temperature drop is lower. The explanation is that hydrides not only affect mechanical properties of the samples, but also hinder Zr diffusion, as confirmed by post-melting characterisation;
- First tests using COLOSS pellets and Al$_2$O$_3$ rings show that also aluminium can diffuse largely in the melted material. As a result, melting temperature can decrease of about 200 K;
- Some preliminary experiments have been conducted also on MOX. In low-Pu MOX with Zy-4 cladding, the observed behaviour is very similar to the previous ones. On the other hand, using high-Pu MOX with stainless steel cladding, the freezing temperature drop is lower. Such system needs more investigations;
- Fragments from Chernobyl’s solidified lava are analysed as example of a real corium. The study of such system is more difficult than before because of the glass-like behaviour of the samples.
5. Conclusions and Perspectives

The materials employed in a NPP are subject to very special conditions because of the high temperature and pressure and the intense radioactivity field in the reactor core. In case of a severe accident, materials can experience even more extreme situations, in which their behaviour is still partly hard to predict. As consequence of failures and malfunctions in the coolant system, the temperature of the fuel can increase in an uncontrolled manner, reaching the melting point. Then, melted fuel mixes together with cladding, forming the corium, a lava-like mass very dangerous for the NPP integrity. Knowing the behaviour and properties of such material is crucial in the general understanding of accidental evolution and, in case, in order to mitigate the consequences of such event.

The main goal of this work was to study the interaction between the nuclear fuel and the cladding material when the core meltdown accident starts, and the post-melting characterisation of the resulting mixture. All the experiments were performed on laser-heated laboratory-scale samples, using a new approach in this kind of research. The main system analysed was the UO$_2$-Zr as representative of the most common reactor type (i.e., LWR), but some preliminary tests were performed also on other materials to simulate fast reactor conditions (MOX and stainless steel) or to analyse the interaction between corium and concrete (Al$_2$O$_3$). Samples coming from Chernobyl’s lava were studied, too, as an example of a real corium system.

The conclusions of the present work can be summarised in the main following points:

1. Pure metallic Zircaloy (98 wt% Zr) and Zr-rich samples were successfully melted with the current laser heating set-up. This allowed also performing some original measurements of metallic zirconium emissivity at the melting temperature. The results show that the grey body assumption is reasonable for Zy between 550 nm and 900 nm. Such assumption is used for all the results discussed below.

2. Experimental data about the melting temperature in inert atmosphere of different COLOSS samples are in qualitative agreement with the CALPHAD-optimised liquidus in the UO$_2$-Zr isopleth system. (Quaini, 2015) These results are used as reference points for the other experiments discussed in this thesis.

3. The presence of hydrogen has limited effects on the melting point of COLOSS samples, but it affects their mechanical properties. In fact, all the mixtures melted in this reducing atmosphere are more brittle than the same compositions heated in inert gas and are sometimes turned partially or totally into powder.

4. Emissivity evolution of liquid UO$_2$-Zr samples is monotonically increasing with the U content. A different behaviour was observed for Zr-rich compositions at solidification temperature. In these cases, segregation occurring during freezing affects the optical properties of the surface. Two phases are recognizable as result of this process, one in the centre of the melted part (oxidised and richer in U) and one in the periphery (richer in Zr), as shown by EDS analyses.

5. Tests were performed on samples more representative of the LWR fuel rod geometry by mounting an UO$_2$ disk in a Zy ring. After repeating several laser heating pulses in the vicinity of their contact point, the new melting temperature of the mixture resulting from the inter-diffusion of molten UO$_2$
and Zy stabilizes at a value corresponding to the one measured for the COLOSS composition with up to 20 mol% of Zr. Such composition was confirmed by post-melting electron-microscopy characterisation.

6. Repeating the same experiments in the presence of hydrogen showed that the formation of hydrides might hinder the zirconium diffusion in the nuclear fuel, resulting in a lower final drop in the melting temperature. Even the mechanical properties of such samples are affected by the presence of H₂, as discussed before.

7. Preliminary laser heating experiments were carried out melting UO₂ disk in a Zy ring under pressurized air. In this strongly oxidising atmosphere, the solid/liquid transition occurs at lower and lower temperatures over the successive laser pulses. The solidus arrest stabilizes around 2500 K, most probably corresponding to the formation of higher uranium oxides like U₃O₈.

8. In preliminary tests performed on UO₂-Zr disks mounted in an alumina ring, extensive Al diffusion was observed in melted UO₂-Zr mixtures. This resulted in a significant melting temperature drop of over 200 K with respect to the original UO₂-Zr composition.

9. Experiments performed using low-Pu MOX as fuel and Zy as cladding show a similar behaviour as previous samples with UO₂. The presence of a few mol% of Pu seems to have limited effect on Zr diffusion and on melting behaviour.

10. Few tests were performed using Pu-rich MOX (up to 39 mol% of Pu) in a stainless steel ring. Apparently, Fe diffusion in the nuclear fuel is more limited than Zr one, and the resulting influence on the melting temperature is lower too. It is not well understood if this is due to a poorer chemical affinity between Fe and the fuel or to the high content of Pu.

11. Samples coming from a real corium system were analysed too. Some fragments of Chernobyl’s lava were tested by laser heating. The melting temperature was hardly detectable because of the glass-like behaviour of the material analysed. Nonetheless, it was possible, with fast pulses, to heat the lava samples to very high temperature (above 3200 K). In these latter tests, a clear thermal arrest was detected around 3000 K. Such a thermal arrest is most probably ascribable to the melting and the successive solidification of refractory crystals embedded in the glassy matrix.

Nuclear severe accident research regards several complex coupled phenomena very difficult to fully understand and model properly. The present work has dealt with some aspects of the corium formation and behaviour, opening the way to additional studies. In particular, some further steps can be identified, that might complete the present investigation in the near future:

- Post-melting structural analyses (e.g., XRD, Raman spectroscopy) on all laser-melted samples will clarify the nature of the phases formed in the solidification process;

- The same laser heating tests should be repeated in an oxidising atmosphere on more samples, in order to check up to which extent the sample oxygen content changes and to evaluate its effects on the melting behaviour;
A study of the corium crust emissivity will be crucial for a realistic modelling of the radiative heat transfer from the lava mass, and for a deeper understanding of the NPP thermal balance in a SA scenario;

More tests should be performed simulating the MCCI, especially using real concrete pieces instead of simulants;

The investigation of MOX-cladding interaction can be deepened, using different compositions and/or changing oxygen stoichiometry.
References


IAEA, 2015, The Fukushima Daiichi Accident: Report by the Director General, Vienna.


Journeau, C., 2015, Ex-Vessel Phenomena, Short Course on Severe Accident Phenomenology, Stockholm, 6-10 July 2015.


Miasseodov, A., 2015, *Late In-Vessel Phase*, Short Course on Severe Accident Phenomenology, Stockholm, 6-10 July 2015.


Raj Sehgal, B., 2015, *Environmental and Socio-Economic Impact of a Severe Accident*, Short Course on Severe Accident Phenomenology, Stockholm, 6-10 July.


