INER-F0751 **INER-F0751**

出國報告（出國類別：其他）

赴大陸寶雞參加第二屆亞洲鋯合金研討會

服務機關：核能研究所
姓名職稱：陳仁宏　副研究員
派赴國家：大陸
出國期間：102 年 10 月 14 日~102 年 10 月 20 日
報告日期：102 年 11 月 22 日

摘要

此次赴大陸寶雞主要目的爲參加第二屆亞洲鋯合金研討會發表一篇鋯合金研究成果，以及參觀「國核寶鈦鋯業股份公司」之鋯合金生產製造工廠。由大陸國家核電主辦之第二屆亞洲鋯合金研討會，參與人員分別來自日本、韓國、大陸與台灣等有核工業的亞洲國家，計 4 人來自日本、27 人來自韓國、1 人來自台灣、及大陸地區 31 人，共有 63 人註冊參與此次研討會，總共發表 46 場次鋯合金相關研究成果，探討內容包括：鋯合金材料設計與基礎冶金、腐蝕、照射後性質、護套完整性與氫化、及組件製程與機械性質等研究領域。

研討會結束後，主辦單位安排參觀位於寶雞市之國核寶鈦鋯業股份公司的鋯合金生產製造工廠。此工廠生產線包括核級海綿鋯製造、鋯合金熔煉、管板帶材加工等，其生產目標爲年產 4000 噸海綿鋯、2000 噸鋯合金錠、1000 噸鋯材製品，西屋公司是其技術引進之合作對象。

關鍵詞：鋯合金研討會，國家核電，陝西寶雞

目　　錄

（頁碼）

一、目的

第二屆亞洲鋯合金研討會主要提供東亞區擁有核工業之國家，如日本、韓國、大陸等，從事核燃料護套鋯合金材料研發人員之技術交流平台，主要參與者爲核能相關研發機構，及參與合作計畫的大學相關實驗室。本所爲台灣核能研究機構之代表，長期進行核燃料護套鋯合金之腐蝕、氫化、機械性質等項目之研究工作，藉參與此會議進行研究成果交流，獲取最新研發結果與國際研發趨勢訊息，對核燃料運轉實績研究工作有極大助益，進而達成提昇核能安全目標。

大陸有三大核工業集團，分別是最早(1955)成立的「中國核工業集團」，簡稱「中核集團」，接著在1994有「中國廣核集團」，簡稱「中廣核」，2007年最晚成立的「國家核電技術公司」，簡稱「國家核電」。本次研討會主辦單位爲「國家核電」，而「國核寶鈦鋯業股份公司」屬其集團單位之一，負責研發與生產鋯合金材料。故研討會結束後，主辦單位安排參觀「國核寶鈦鋯業股份公司」之鋯合金生產製造工廠，增進研發人員了解鋯合金材料實際生產過程，對於沒有鋯合金生產工廠的台灣，能有機會參訪此類工廠極具意義，故此次赴大陸具有參訪與會議研發成果交流之雙重目的。

二、過程

日期	內容
102/10/14	去程：桃園機場飛往西安咸陽機場 咸陽機場至寶雞
102/10/15	研討會報到註冊
102/10/16 ≀ 102/10/18	參加第二屆亞洲鋯合金研討會
102/10/19	參觀國核寶鈦鋯業股份公司的鋯合金生產製造工廠，搭乘火車至西安
102/10/20	回程：西安咸陽機場飛往香港 香港至桃園機場

(一) 亞洲鋯合金研討會簡介

緣起於亞洲國家人員常參加以核燃料爲主題國際會議，此類會議之議題過於廣泛與參與人數眾多，對於專責於鋯合金研究工作者，不易獲得所需求資訊及同行之交流機會，因此由大陸工程院院士周邦新、韓國 KAERI（韓國核能研究所）核材料組長 Dr. Yong Hwan JEONG、日本 NFD（日本核燃料開發株式會社）代表等人共同發起籌辦亞洲鋯合金研討會，以促進亞洲國家在核燃料護套鋯合金材料的研究發展與成果交流。

第一屆亞洲鋯合金研討會於 2011 年由韓國 KAERI 在大田主辦，其主辦單位聘請 EPRI（美國電力研究院） Bo CHENG 當顧問，籌備第一次的鋯合金研討會，Bo CHENG 則推薦臺灣核研所參與此研討會，是以本所有機會派二員鋯合金研究工作者參加第一屆亞洲鋯合金研討會。第一屆亞洲鋯合金研討會順利舉行後，決定每二年舉行一次，並由韓國、大陸、日本依序輪流主辦。

(二) 第二屆亞洲鋯合金研討會地點與參加人員

第二屆亞洲鋯合金研討會由大陸三大核電集團之一：國家核電旗下位於陝西

省寶雞市之國核寶鈦鋯業股份公司主辦。研討會地點在寶雞高新君悅國際酒店，酒店大樓如圖 1 所示。

圖 1．研討會地點：寶雞君悅國際酒店

此次研討會參與人員分別來自日本、韓國、大陸與台灣等有核工業的亞洲國家，計 4 人來自日本、27 人來自韓國、1 人來自台灣、及大陸地區 31 人，總共 63 人註冊參與此次研討會，所有與會人員合影留念如圖 2 所示。

圖 2.全體與會人員合影

（三） 第二屆亞洲鋯合金研討會內容

研討會探討內容包括：鋯合金材料設計與基礎冶金、腐蝕、照射後性質、護套完整性與氫化、及組件製程與機械性質等研究領域。三天議程共發表 46 場次研究成果，主辦單位不提供簡報內容，僅可獲得所發表論文摘要內容，如附錄一所示。三天議程分述如下：

第一天：October 16th, 2013 (Wednesday)

Opening 8:30-9:00	Opening Address Gaihuan Yuan (SNZ)
Session Chairs: Wenjin. Zhao (NPIC)	
9:00-9:20	Effect of Niobium on the Anisotropic Growth of Oxide Layer Formed on Zirconium Alloys
9:20-9:50	Developments of HANA Alloys for Advanced Fuel Cladding
9:50-10:10	Role of Alloying Elements in Hydrogen Pickup Mechanism of Zr-based Alloys
10:10-10:40	Group Photo and Coffee Break
10:40-11:00	Effect of Nb and Fe on the Recrystallization behavior of Zr-based Alloys
11:00-11:20	Basic Study on the Development of a Metal Cladding with Protective Sic Composites
11:20-11:40	Properties Evaluation of Reground Die and Die Materials for Increasing Life Time of Pilger Die
12:00-14:00	Lunch
Session Chairs: Yong Hwan Jeong (KAERI)	
14:00-14:20	Comparison Characteristics of HANA-4 Tube Shells with Manufacturing Process
14:20-14:40	ID Grit Blasting for tubing
14:40-15:00	The High Temperature Oxidation Kinetics of Zr-alloys claddings in Air/Steam
15:00-15:20	Effect of Dissolved Oxygen in Water/Steam on the Corrosion Behavior of Zirconium Alloys
15:20-15:40	Coffee Break
15:40-16:00	Effect of the Manufacturing Process on the Composition and Size of Second Phase Particles in N36 Tubes
16:00-16:20	The Effect of Heat Treatment and Reduction Process to the Second Phase Particles and the Texture

16:20-16:40	The Effect of Annealing Process on the Surface Residual Stress of Zr Alloy Plate
16:40-17:00	Study of Second Phase Particles with Stripes in Zr-1Nb-0.1Fe Alloys

第二天：October 17th, 2013 (Thursday)

Session Chairs: Gang Li (SNZ)	
8:50-9:10	Irradiation Performance of HANA Alloy Tested in Halden Reactor
9:10-9:30	Effect of Bi on the Corrosion Behavior of Zirconium Alloys
9:30-9:50	Influence of Waterside Corrosion on Integrity of PWR Fuel under Power Transient
9:50-10:10	Microstructure and Corrosion Resistance of Zr-XSn-1Nb-0.3Fe Alloys
10:10-10:30	Coffee Break
10:30-10:50	Investigation on Corrosion Properties of CZ1 and CZ2 New Zirconium Alloys
10:50-11:10	Effect of Ge on the Corrosion Resistance of Zr-1Nb-0.7Sn-0.03Fe-xGe alloys Corroded in Lithiated Water
11:10-11:30	Iodine Induced Stress Corrosion Cracking of N36 Zirconium Cladding
11:30-11:50	High Temperature Creep Behavior of N36 Cladding Tube
12:00-14:00	Lunch
Session Chairs: Kan Sakamoto (NFD)	
14:00-14:20	Research on Tensile Property of New Zirconium Alloys Used in Fuel Cladding
14:20-14:40	Radial Texture of SZA-1 Alloy Tube
14:40-15:00	The Out-reactor Performance of New Zirconium Alloys
15:00-15:20	Application of BP Network Technology Optimized by Genetic Algorithm in the Optimization of Cladding Tubes' Flooding-focused Ultrasonic Detection Parameters
15:20-15:40	Coffee Break
15:40-16:00	Stress-reorientation of Hydrides in N36 Zirconium Alloy Cladding Tube

16:00-16:20	Separation Efficiency of Impurities from Zirconium Scrap by Electrorefining with Electrolyte Composition
16:20-16:40	The Characterization of SZA-6 Strip and Tube
16:40-17:00	Effect of Initial Texture on Deformation Mechanisms and Dynamic Recrystallization in Zirconium Alloy during Uniaxial Compression

第三天：October 18th, 2013 (Friday)

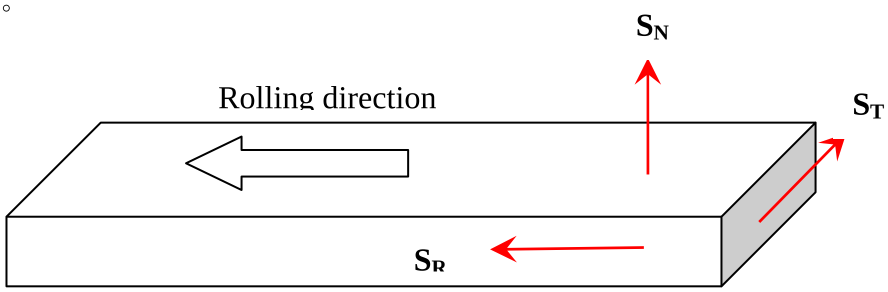
Session Chairs: Zhongkui Li (NIN)	
8:50-9:10	Study of the SZA-6 New Zirconium Alloy
9:10-9:30	Effect of Mo on Microstructure and Mechanical Properties in Zr-based Alloys
9:30-9:50	Effect of Pre-deformation on Growth Behavior of Second Phase Particles in a Zr-Sn-Nb Alloy During 600-700 ℃ Aging after β Quenching
9:50-10:10	The Effect of Temperature and Cooling Rates on Hydride Reorientation of High Burnup Cladding under Interim Dry Conditions
10:10-10:30	Coffee Break
10:30-10:50	Study on Direct Zirconium Powder Production by Bubble Injection of ZrCl4
10:50-11:10	Effect of Sn Content on the Phase Transformation Temperature of Zr-Sn-Nb-Fe Alloys
11:10-11:30	Effect of Pre-hydriding on the Burst Behavior of the Zirconium Cladding under Loss-of-Coolant Accident Condition
11:30-11:50	Study on Hydride Reorientation of Cladding Tubes Simulating Spent Nuclear Fuel under Interim Dry Storage
12:00-14:00	Lunch
Session Chairs: Kyu Tae Kim (Dongguk Univ.)	
14:00-14:20	High Temperature Stability of Delta-phase Zirconium Hydride
14:20-14:40	A Study on the Effects of Dissolved Hydrogen on Zirconium Alloys Corrosion
14:40-15:00	Hydrogen Effect of Zircaloy-4 on the High Pressure Steam Oxidation
15:00-15:20	Influence of Second-phase Particles on Hydrogen

	Absorption and Desorption Behavior of N36 Cladding
15:20-15:40	Coffee Break
15:40-16:00	**Effect of Hydrogen on the Oxidation Kinetics of Zircaloy-4 Cladding at 650℃ in Air (Presented by INER)**
16:00-16:20	Curve-fitting on the Thermophysical Properties of N36 Alloy
16:20-16:40	Some Investigation in the Zircaloy Pickle Salts
16:40-17:00	Effect of Anneal temperature on the Hydrogen Orientation of Zirconium Alloy
16:40-17:10	Closing

三天研討會總共發表 46 篇研究論文，其中 15 篇來自韓國，如上表藍色字體所顯示之標題，4 篇由日本發表，如紅色字體所示，1 篇由**本所簡報**，以**粗黑體**顯示，其餘 26 篇皆由大陸地區眾多單位代表所發表，所有與會之論文摘要請參考附錄二。明顯地，主要以主辦的大陸及韓國爲主要多數，而日本與台灣成爲少數參與者，論文數量多寡似可反映核能在該國被重視的程度。茲將此次研討會特邀的三篇”Plenary talks”論文，分述如下：

(1)Effect of Niobium on the Anisotropic Growth of Oxide Layer Formed on Zirconium Alloys

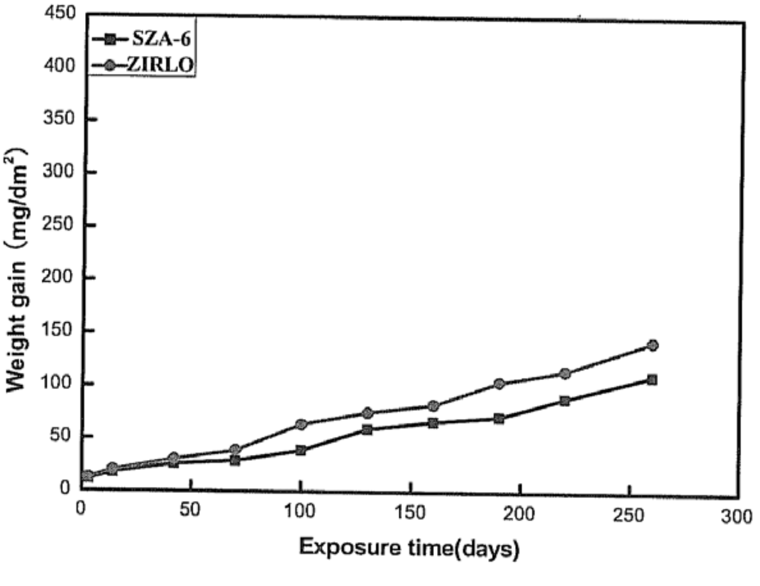
演講者爲上海大學材料研究所周邦新院士。此項研究將三種不同成份的鋯合金，分別爲 Zircaloy-4, ZIRLO, N18，其中 N18 爲大陸自行發展之鋯合金，成份接近 ZIRLO，經過相同滾軋加工後，形成非等方向性的組織(texture)之板狀試片，如下圖所示共有三個方位存在，分別是 normal direction “S_N”, rolling direction “S_R”, transverse direction ”S_T”，經由 360℃含 LiOH 水中與 420℃蒸汽之腐蝕試驗探討三種材料在三個方位的腐蝕速率差異。



Zr-Sn-Nb plate for corrosion

結果顯示只有 Zircaloy-4 在 S_N,S_R,S_T 三個方位的氧化層厚度有所差異，另外兩種 ZIRLO 與 N18 合金則此現象，而 ZIRLO 與 N18 與 Zircaloy-4 成份最大的差異爲前二者有含鈮(Nb)，Zircaloy-4 則無鈮的添加，故得到鈮具有抑制非等向性氧化之效應，同時亦得到含鈮的合金 ZIRLO 與 N18 有較 Zircaloy-4 爲低的腐蝕速率。

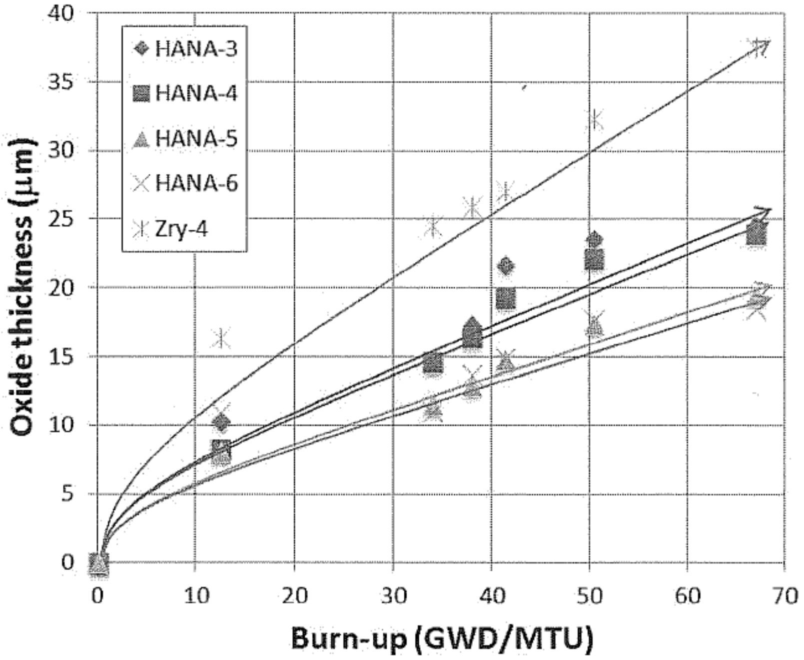
另外在其它的腐蝕試驗中，採用另一系列自行發展的新合金材料，稱爲”SZA”，主要成份爲 Zr-Sn-Nb-Fe-Si，此組成規範更貼近 ZIRLO 成份，目標是發展出較 ZIRLO 更好的腐蝕抗性。同樣經過 360℃含 LiOH 水的壓力釜 400 天以上試驗，結果如下圖所示，明顯地看出 SZA-6 的腐蝕速率較 ZIRLO 爲低，曾有與會者提問其原因爲何，是否有其它未公佈的添加成份，但大陸方面不願告知 SZA-6 確實成份規範，因而無法得知其可能機制，但由其它場次所發表論文內容，筆者推測除微量元素氧含量的控制外，可能添加微量鍺(Ge)，此元素可能進入二次相析出物(secondary phase particles; SPPs)，而含鍺二次相析出物會對氧化層結構的轉變產生延緩效應所致。


Corrosion of SZA-6 and ZIRLO

(2) Development of HANA Alloys for Advanced Fuel Cladding

演講者爲韓國核能研究所 Dr. Jeong-Yong Park，內容介紹韓國自行發展的鋯合金”HANA”，取名自 High performance Alloy for Nuclear Application 之縮寫。初始目標是應用於高燃耗的燃料棒護套，燃耗(burn-up)高達 70GWD/MTU。大量的基礎研究，如成份元素、二次相析出物、製程參數等對 HANA

腐蝕抗性的效應，均已完成，並根據實驗結果，逐步發展HANA-3, HANA-4, HANA-5,至HANA-6。爐外腐蝕試驗以Zircaloy-4 爲比較對象，確認HANA系列合金較Zircaloy-4 有較低腐蝕速率後，遂將HANA合金送到挪威Halden research reactor進行爐內測試，如下所示，HANA合金經接近 70 GWD/MTU高燃耗目標值的照射實驗結果顯示，HANA系列合金之爐內腐蝕抗性較Zircaloy-4 優異 30~50%。



Corrosion behavior of HANA and Zircaloy-4 claddings tested in the Halden research reactor

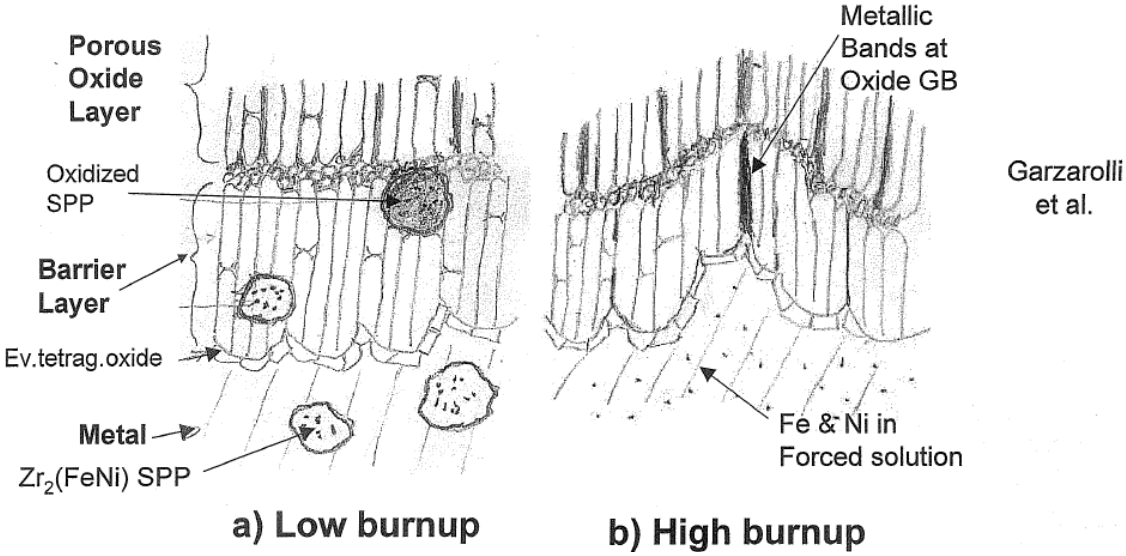
同樣地，在Halden的潛變試驗亦顯示，HANA系列合金較Zircaloy-4有較佳潛變強度。目前已選定二座PWR廠進行先導實際測試(lead test)，分別是西屋的PWR與韓國自行設計的OPR 1000 (Optimized Power Reactor)，預計運行三個週期後，開始熱室的照射後檢驗(Post Irradiation Examination; PIE)工作。

(3) Role of Alloying Elements in Hydrogen pickup Mechanism of Zr-based Alloys

演講者爲日本NFD主任研究員Dr. Kan Sakamoto。此項研究緣起於BWR廠的燃料護套在高燃耗時(>50 GWD/MTU)，產生加速腐蝕與高吸氫量之現象，更進一步的分析此現象時，發現同樣在BWR環境高燃耗條件下，Zircaloy-4的吸氫較Zircaloy-2爲低，因而認爲Zircaloy-2與Zircaloy-4的成份差異，在

累積高劑量照射後，某些合金元素扮演重要關鍵角色。已有學者提出解釋機制，如下圖所示。

Hypothesis: After Ni contaning SPPs are dissolved under irradiation at high burnup, metallic Ni segregates at grain boundaries (oxide and/or metal) and act as H window by resulting accelerated hydrogen pickup

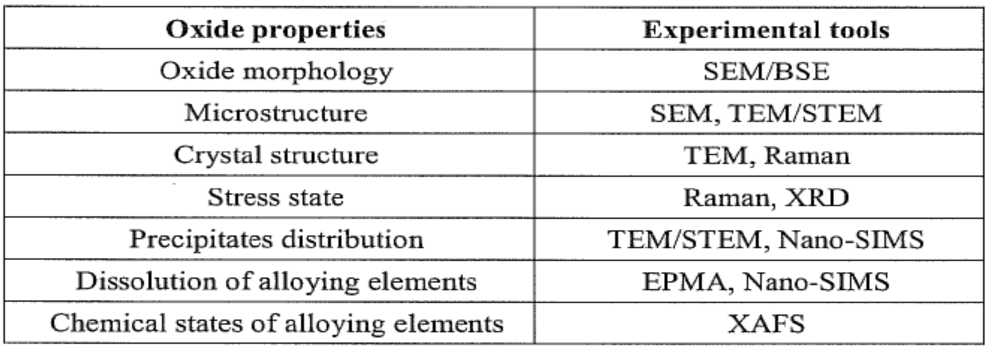


a) Low burnup b) High burnup

Garzarolli 認爲起因於金屬與緻密氧化層介面區域微結構差異，在高燃耗時，所有二次相析出物已經照射溶解，析出物成份元素全部固溶於鋯晶格結構內，但是鎳金屬可能偏析在緻密氧化層的晶界位置，這些晶界上的鎳具提供氫進入的窗口，如此可解釋無鎳成份的 Zircaloy-4 具較低的吸氫現象，此假設機制仍有待證實。

日本 NFD 參與此項研究工作，期能解決 BWR 廠燃料護套在高燃耗時的氫脆問題。NFD 使用所有解析微結構與局部微量成份分析的工具，如 SEM, TEM, Raman, EPMA, SIMS 等，用以探索金屬介面緻密氧化層(tetragonal ZrO_2)的氧化物形態、晶體結構、應力狀態等，以及二次相析出物種類、結構、成份、元素分佈等，如下表所示。

Table 1. Key experimental tools used in the studies



Oxide properties	Experimental tools
Oxide morphology	SEM/BSE
Microstructure	SEM, TEM/STEM
Crystal structure	TEM, Raman
Stress state	Raman, XRD
Precipitates distribution	TEM/STEM, Nano-SIMS
Dissolution of alloying elements	EPMA, Nano-SIMS
Chemical states of alloying elements	XAFS

各項研究仍在進行中，目前初步結論爲(1)氫的吸收速率控制步驟爲氫在緻密氧化層的擴散行爲/行徑，(2) 合金元素鐵與鈮會抑制氫在緻密氧化層的擴散，其解釋爲此二元素以三價電位固溶在氧化層晶格內，及界面高壓應力等之因素。待完成所有工作項目後，約在2015年，再提出真正的吸氫機制。

圖 3. 作者代表核研所發表論文一篇

最後作者代表核研所發表論文一篇(圖 3)，簡報資料如附錄二所示，題目是「Effect of Hydrogen on the Oxidation Kinetics of Zircaloy-4 Cladding at 650℃ in Air」。研究目標是探討用過核燃料鋯合金護套在空氣環境與水氣環境下，溫度在500~800℃區間之氧化行爲，主要模擬用過燃料儲存池發生喪失冷卻循環之情境，研究結果可用以評估用過燃料護套的完整性。由於用過燃料護套具有氫化之特性，因此實驗中準備氫化試片，氫含量在100ppm~1000ppm分佈範圍，探討在650℃時，上述氫含量在鋯合金內爲固溶狀態，研究固溶態氫對鋯合金之氧化行爲效應，此項之研究獲得日本NFD與JAEA人員之重視，特別與其交換研究心得。

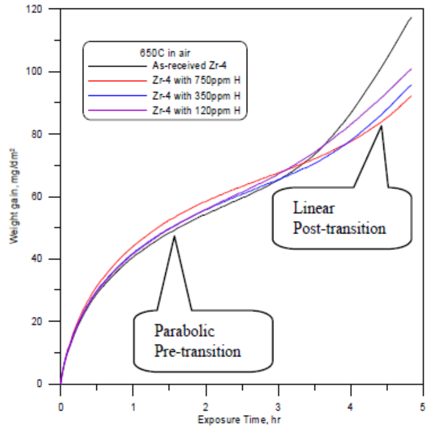
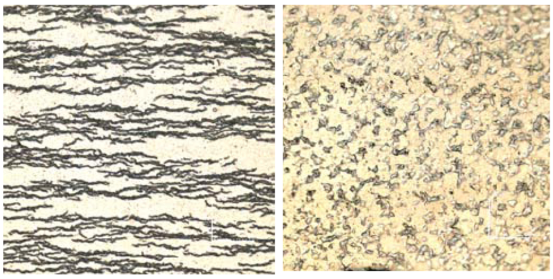


Figure 1. Weight gain against exposure time in 650℃ air for the hydrided Zircaloy-4 tube specimens.



(a) before oxidation (b) after oxidation

Figure 2. Hydride morphology: (a) before oxidation showing the circumferential hydrides, (b) after oxidation showing hydrides precipitated at grain boundary.

(四) 參觀鋯合金生產製造工廠

位於陝西省寶雞市的「國核寶鈦鋯業股份公司」成立於 2009 年，隸屬於大陸三大核電集團之一「國家核電」的一員。成立主要目標在整合現有鋯材生產資源，發展完整的核級鋯材產業體系，以滿足核電快速發展對核級鋯材的需要。

核級鋯材主要用於核燃料元件，是核電廠不可或缺的重要金屬材料。國核寶鈦鋯業生產線（圖 4）包括核級海綿鋯製造、鋯合金熔煉、管板帶材加工等，其生產目標爲年產 4000 噸海綿鋯、2000 噸鋯合金錠、1000 噸鋯材製品，西屋公司是其技術引進之合作對象。

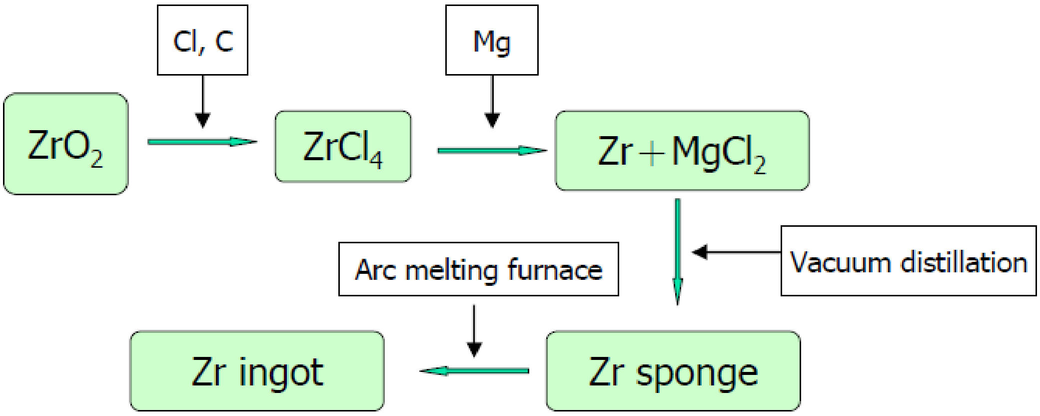
圖 4 滾軋設備

由於台灣本身沒有核燃料護套鋯合金生產工廠，此次能夠有機會現場觀看整個生產流程，實屬難得經驗，雖然禁止攝影拍照，仍然是印象深刻，茲將鋯合金生產製造重點彙整如下。

<u>鋯金屬提煉：Kroll製程</u>

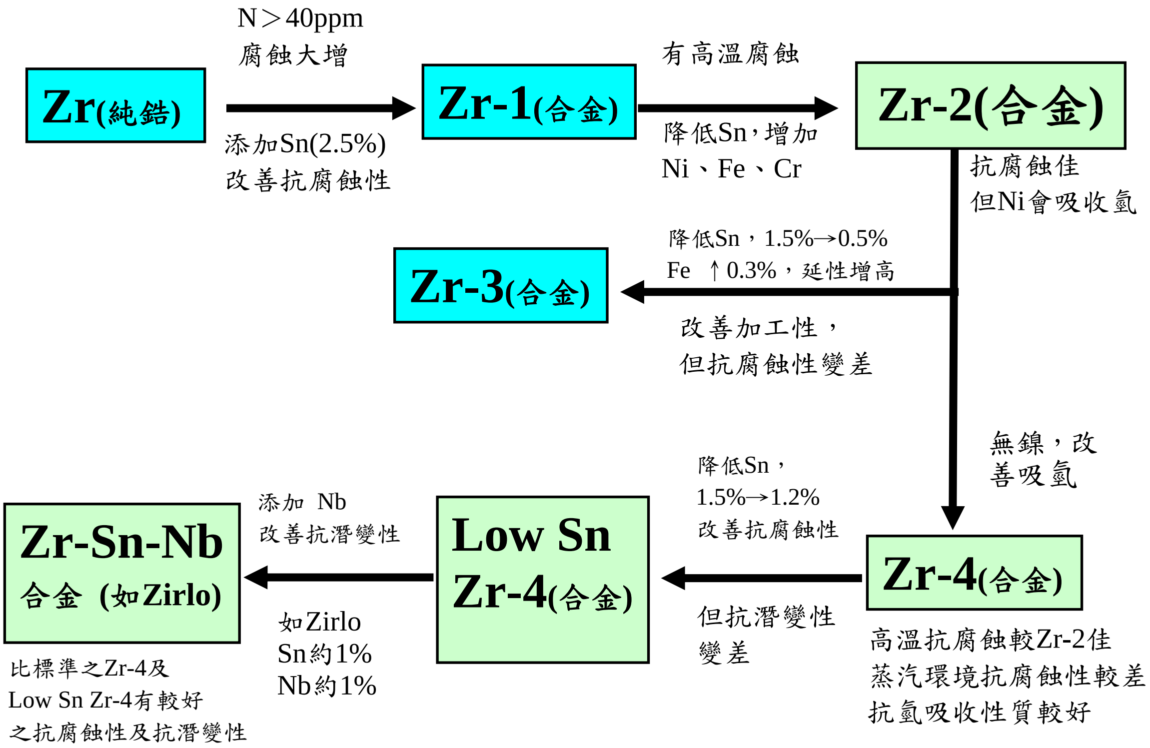
現今金屬鋯提煉製程是 1946 年美國 Oak Ridge 國家實驗室所發展。首先將含氧化鋯礦石製成 $ZrCl_4$，接著以鎂還原成海綿狀金屬鋯(Zr sponge)，最後將海綿鋯置入電弧熔煉爐(Arc-melting furnace)得到高純度之鋯鑄錠

(Zr-ingot)，其流程如下所示。



鋯合金演進：

早期發現在純鋯中添加適量錫(2.5% Sn)可以有效降低雜質元素，如氮、碳、氧、鋁等，大幅改善鋯的腐蝕抗性，因而發展出鋯一合金(Zircaloy-1)，接著適度添加鐵、鉻、鎳溶質元素與降低錫含量(1.5%)，以改善高溫腐蝕抗性，發展出鋯二合金(Zircaloy-2)，並成功應用於沸水式反應器(BWR)迄今。之後，曾爲了改進 300℃水中腐蝕狀態與改善加工性，進一步降低錫含量至 0.5%的鋯三合金(Zircaloy-3)，但是並未被廣泛接受採用。後來在壓水式反應器中爲改善吸氫量，因此無鎳與增加鐵含量的鋯四合金(Zircaloy-4)被發展出應用於壓水式反應器的燃料護套材料，其演進流程如下所示。



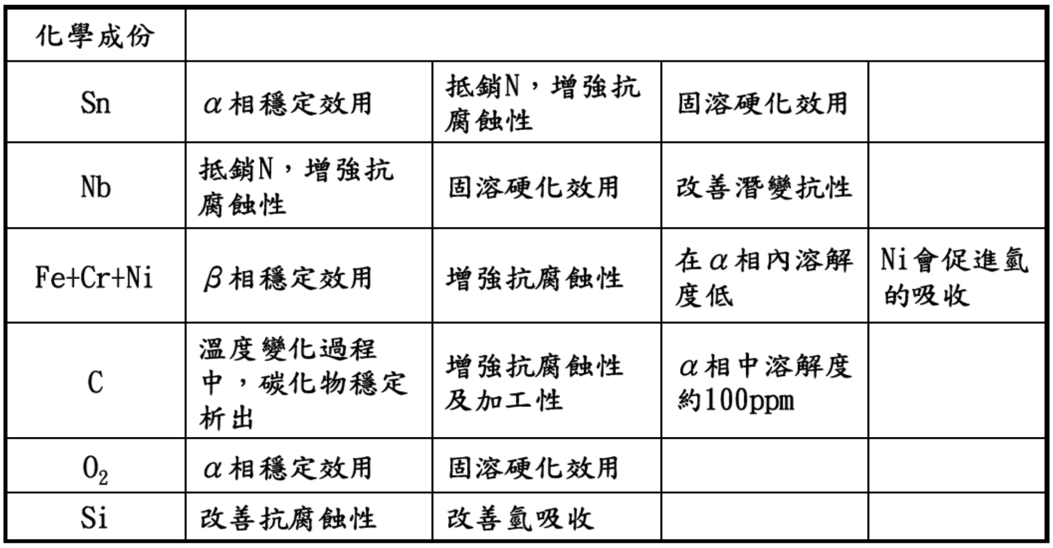
鋯合金的發展過程中，爲了繼續改善水中腐蝕抗性，採取進一步降低錫含量作法，因而有低錫鋯四合金(Low Sn Zircaloy-4)的出現，但伴隨抗潛變性變差之缺點。鋯合金演進的另一個重要的分歧點是鈮(Nb)元素的添加，其優點是具較佳機械強度，因而顯著地改善抗潛變性，其代表性合金如 Zirlo and M5 等，茲將重要鋯合金護套材料之成份規範示於表 1。

表 1 各種商用鋯合金成份規範(ASTM)

化學成份	**Zr-2**	**Zr-4**	**Low Sn Zr-4**	**ZIRLO**
Sn	**1.20 ~1.70**	**1.20 ~ 1.70**	**1.20 ~ 1.45**	**0.8 ~1.2**
Nb	—	—	—	**0.8 ~1.2**
Fe	**0.07 ~ 0.20**	**0.18 ~ 0.24**	**0.18 ~ 0.24**	**0.09 ~ 0.13**
Cr	**0.05 ~ 0.15**	**0.07 ~ 0.13**	**0.07 ~ 0.13**	—
Ni	**0.03 ~ 0.08**	—	—	—
Fe+Cr+Ni	**0.18 ~ 0.38**	—	—	—
Fe+Cr	—	**0.28 ~ 0.37**	**0.28 ~ 0.37**	—
O_2	**0.09 ~ 0.16**	**0.09 ~ 0.16**	**0.09 ~ 0.16**	**0.09 ~ 0.16**
Si	**0.005 ~ 0.012**	**0.005 ~ 0.012**	**0.005 ~ 0.012**	**0.005 ~ 0.012**

大陸發展的 SZA 與 N 系列合金，及韓國發展的 HANA 系列合金，皆是以 **Zr-Sn-Nb** 爲基礎，調整其它元素種類與含量，企圖發展自用的核燃料護套鋯合金規格，鋯合金各元素對冶金組織、機械性質、腐蝕抗性等的效用，請參考表 2 內容。

表 2 各種鋯合金成份之效用



化學成份				
Sn	α相穩定效用	抵銷N，增強抗腐蝕性	固溶硬化效用	
Nb	抵銷N，增強抗腐蝕性	固溶硬化效用	改善潛變抗性	
Fe+Cr+Ni	β相穩定效用	增強抗腐蝕性	在α相內溶解度低	Ni會促進氫的吸收
C	溫度變化過程中，碳化物穩定析出	增強抗腐蝕性及加工性	α相中溶解度約100ppm	
O_2	α相穩定效用	固溶硬化效用		
Si	改善抗腐蝕性	改善氫吸收		

鋯合金成品製造流程：

此工廠生產線從已完成的上游海綿鋯產品爲原料，進入電弧熔煉爐進行精煉獲得高純度鋯錠，接續爲合金元素添加，如鐵、錫、鎳、鉻等，熔煉出成份合乎規範要求之鋯合金錠。鋯合金鑄錠生產完成後，開始進入塑性加工程序，分別進行鍛造、熱冷軋、擠管、旋鍛等加工後，分別得到板材、帶材、棒材、管材等不同外觀型式產品，接著進行退火熱處理、表面清洗、檢驗等步驟後完成產品製造，其流程如圖 5 所示。

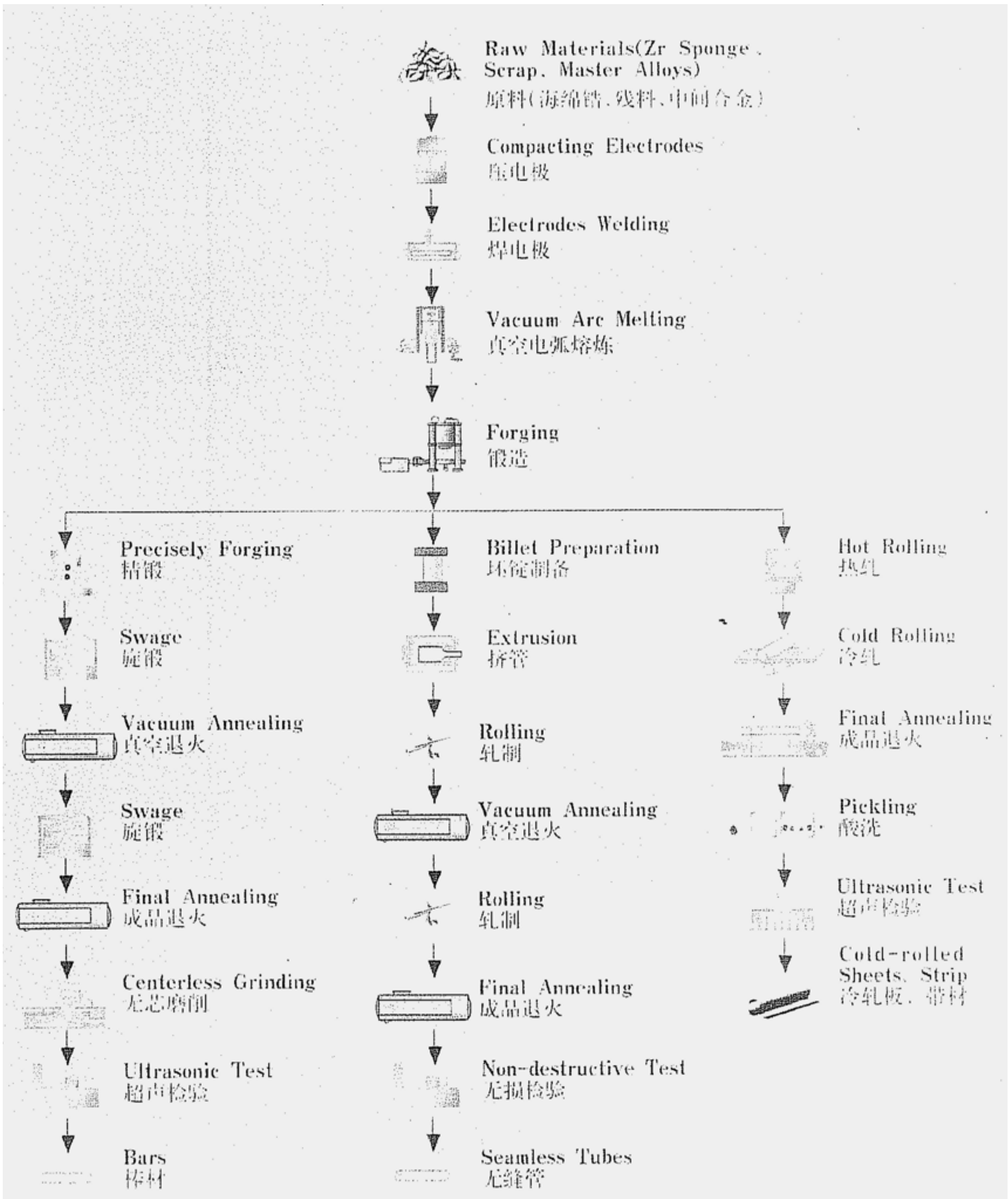


圖 5 各類鋯合金產品之加工與熱處理流程

三、心得

（一）鋯合金研討會

三天研討會期間總共發表 46 篇鋯合金相關研究成果，分別由主辦的中國大陸發表 26 篇、韓國 15 篇、日本 4 篇、台灣 1 篇，由發表數量與參與人數可知，中國大陸與南韓是主要參與者，日本與台灣成爲少數代表，此情況正也反映核工業在中國大陸與南韓的興盛，而在日本與台灣則呈現衰退情況。

參加此次研討會後，歸納各國所發表論文內重點如下：

大陸論文重點摘要：

由於大陸設立鋯合金生產製造工廠，因此有許多關於鋯合金在提煉製程、加工方法、熱處理條件等之相關研究。除此之外，因大陸採取自行發展鋯合金材料之計畫，如 N18, N36, SZA-6 等，因此投注許多人力與經費於合金設計、微組織、物理化學性質等基礎研究工作，亦針對新發展材料進行拉伸、碘應力腐蝕、360℃水中腐蝕、420℃水汽腐蝕等機械與腐蝕特性之測試，並與 Zircaloy-4 及 ZIRLO 等現有合金比較其在機械性質與腐蝕抗性之優劣，目前尚處於爐外條件之基本研發階段。

韓國論文重點摘要：

韓國發展的 HANA (High performance Alloy for Nuclear Application)合金則注重爐內環境的應用研究，如 LOCA (Loss of coolant accident)時的氧化行爲與 Burst Test 機械特性，並實際在挪威 Halden Reactor 進行爐內實驗，以獲得 HANA 鋯合金護套照射後的腐蝕與潛變特性，並進行熱室照射後檢驗(Post Irradiation Examination, PIE)，以掌握 HANA 合金應用性能。另在學術界有少量關於用過燃料乾式貯存可能遭遇的氫化鋯方位重排之研究。

日本論文重點摘要：

日本的 NFD (Nuclear Fuel Development), JAEA（Japan Atomic Energy Agency）, Osaka University（大阪大學）, Tohoku University（東北大學）等四單位各發表一篇論文。來自大學的二篇利用 XRD, TG-DTA, EBSD, TEM 等技術對氫化鋯(ZrH1.6)與 Zr-Nb 合金進行微結構之基礎探討。JAEA 則探討燃

料棒功率變化時，水中腐蝕對護套完整性之影響。NFD 則是研究合金元素對吸氫之效應，以了解鋯合金護套吸氫機制，期改善燃料護套氫脆化之現象。

台灣論文重點摘要：

本所對鋯合金研究工作重點是探討用過核燃料鋯合金護套在空氣環境與水氣環境下，溫度在 500~800℃區間之氧化行爲，主要模擬用過燃料儲存池發生喪失冷卻循環之情境，研究結果可用以評估用過燃料護套的完整性。

綜合而言，主辦會議的大陸核工業處於起步階段，因此偏向於新合金開發設計，例如中國大陸自行開發之 N18, N36, SZA 等，著重各項基礎冶金與微結構探討、機械性質與腐蝕測試，並與國際上標準的鋯四合金或 ZIRLO 合金進行比較，企圖發展自有的鋯合金成分規格，及期待有更優異的機械特性與抗腐蝕能力，綜合大陸所發表內容可歸屬爲基礎研究階段。其他來自韓國、日本、臺灣等國的研究則關注於運轉中遭遇之現象，或者用過燃料貯存相關問題，如護套氫化效應、水中腐蝕機制、LOCA 研究等，著重提昇運轉績效與燃料護套完整性的探討，屬於應用研究之領域。

另藉參與研討會，分別與各國單位代表性人物交換資訊與建立聯絡管道，例如日本 NFD 的主任研究員 Dr. Kan Sakamoto、韓國 KAERI 的 Director of Nuclear Materials development Division, Dr. Yong Hwan Jeong、大陸上海大學材料研究所的周邦新工程院士、及北京有色金屬研究總院的沈劍韻教授等人，對於掌握最新國際上鋯合金研究趨勢與資訊有所助益，並可加增進本與上述單位之交流。

（二）參觀鋯合金生產製造工廠

由於台灣本身沒有核燃料護套鋯合金生產工廠，此次能夠有機會現場觀看整個生產流程，實屬難得經驗，雖然禁止攝影拍照，仍憑著參觀印象與蒐集之資料，將鋯合金生產製造重點敘述於本公差報告內。

此次參觀鋯合金生產製造工廠後，了解從上游初始的海綿鋯，進入電弧熔煉爐精煉獲得高純度鋯錠，接續爲合金元素添加，如鐵、錫、鎳、鉻等，熔煉出成分合乎規範要求之鋯合金錠，之後爲各類塑性加工與熱處理程序，最後

得到棒材、管材、帶材與板材等各種鋯合金產品。此類參觀活動對於鋯合金護套材料有更深刻了解，對本所鋯合金材料相關研發工作多所助益。

北京有色金屬研究總院自 1957 年開始從事稀有金屬的研究工作，內容包括鈦之冶金與合金設計、鋯鉿分離、鉭鈮分離及製取鋰鈹等的研究，累積豐富的稀有金屬之研究成果。沈劍韻博士爲該單位資深研究人員，除擔任「金屬學報」編委，亦擔任「國核寶鈦鋯業股份公司」研發部門之顧問指導，是鋯合金與其它稀有金屬材料爲之重要學者專家，其所屬單位值得參訪了解，或能得到核能應用之外的稀有金屬材料領域資訊。

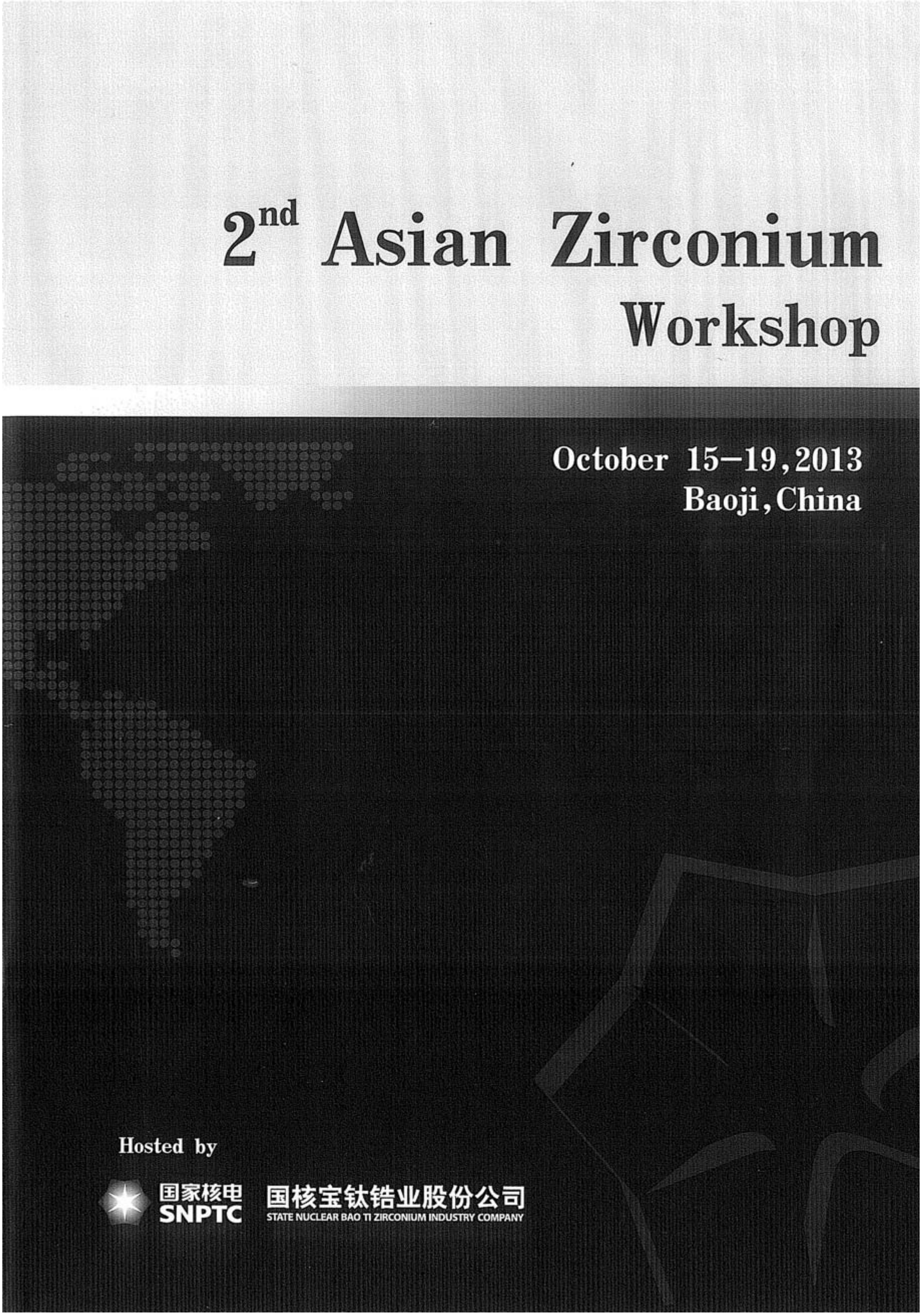
四、建議事項

（一）本次研討會已決定下屆研討會（第三屆）將於 2015 年在日本舉行，建議本所繼續參加此研討會，並鼓勵從事鋯合金相關研發工作同仁積極參與，以獲取專業資訊交流之機會，有助於提昇核能安全目標。

（二）本所進行兩岸核能交流以來，主要對象偏多於較早成立的「中核集團」與「中廣核」二者，對 2007 年才成立的「國家核電」集團，其單位主要位於大陸北方，且成立迄今時間較短，故較少接觸與獲得其相關訊息，建議進行兩岸核能交流時，適切增加對「國家核電」之參訪。

（三）鑑於核能發電在日本與臺灣所處情況類似，核燃料相關研究重點逐漸轉移至用過燃料在貯存期間可能的問題上進行探討，建議可加強與日方研究機構對用過燃料護套之研究計畫交流，俾有益於國內對用過燃料鋯合金護套相關的研究工作。

附錄一 第二屆亞洲鋯合金研討會論文摘要集



2nd Asian Zirconium Workshop

October 15–19, 2013
Baoji, China

Hosted by

国家核电 SNPTC

国核宝钛锆业股份公司
STATE NUCLEAR BAO TI ZIRCONIUM INDUSTRY COMPANY

Overview

2nd Asian Zirconium Workshop

Oct.15-19, 2013/ Joy International Hotel, Baoji, People Republic of China

Asian Zirconium Workshop is organized to exchange information on the research and development of zirconium alloys in the nuclear industry among Asian countries.

There are 46 research papers to be presented in the workshop. The workshop consists of four plenary talks and five sessions of Alloy Design & Basic Metallurgy, Corrosion, Post Irradiation Examination, Safety Issues & Hydriding, and Fabrication & Mechanical Properties. In addition, plant tour to SNZ (State Nuclear Baoti Zirconium Industry Company) is provided.

Hosted by State Nuclear Baoti Zirconium Industry Company

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- Wenjin Zhao (NPIC)
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- Shinsuke Yamanaka (Osaka Univ.)
- Yong Hwan Jeong (KAREI)

Abstracts

Effect of Niobium on the Anisotropic Growth of Oxide Layer Formed on Zirconium Alloys

Bang X. Zhou[1,2]*, Guo C. Sun[1,2], Mei Y. Yao[1,2], Qiang Li[1,2] and Jin L. Zhang[1,2]
1. Laboratory for Microstructures, Shanghai University, Shanghai 200444
2. Institute of Materials, Shanghai University, Shanghai 200072, P. R. China
*Corresponding author: zhoubx@shu.edu.cn

The corrosion resistance of zirconium alloys is improved by the addition of Nb in Zr-Sn alloys, such as ZIRLO, E635, N18 and X5A. Despite recent progress in the research work of Zr-Sn-Nb alloys, the mechanism of improving corrosion resistance by adding Nb in zirconium alloys remains to be elucidated. Zirconium alloys of a hexagonal close-packed crystal structure have prominent anisotropic characteristic in comparison with metals of a cubic structure. The anisotropic characteristic is bound to be reflected on the corrosion behavior of zirconium alloys, and a strong texture is produced in sheet or tubular materials during the fabrication process. In order to clarify the mechanism of improving corrosion resistance by adding Nb in zirconium alloys and investigate the effect of Nb on the anisotropic growth of oxide layer formed on zirconium alloys, Zircaloy-4, N18 and 3# alloy (which is similar to ZIRLO) with different contents of Nb were adopted for the experimental materials. All the plate specimens with 2 mm in thickness have a similar rolling texture. Corrosion tests were carried out by static autoclave at 360℃/18.6 MPa in lithiated water of 0.01 M LiOH and at 400℃/10.3 MPa in superheated steam. The corrosion resistance on different surfaces of the specimens, i. e. the surface perpendicular to the normal direction (S_N), the surface perpendicular to the rolling direction (S_R) and the surface perpendicular to the transverse direction (S_T) of the specimens, was evaluated by measuring the thickness of oxide layer respectively after corrosion tests. The microstructure of oxide was also examined by electron microscopy. The results show that the anisotropic growth of oxide layer on different surfaces of the specimens is more prominent for Zircaloy-4 than that for N18 and 3# alloy corroded at 360℃ in lithiated water. There is a marked transition for the oxide growth on S_N of Zircaloy-4 specimens at about exposure 80 days, and after transition the oxide growth rate increases to show a worse corrosion resistance. But the transition of oxide growth is not obvious on S_R and S_T, and the corrosion resistance is much better than that on S_N. For N18 and 3# alloy specimens corroded in lithiated water at 360℃, the anisotropic growth of oxide layer is restrained by the addition of Nb, and the oxide thickness on different surfaces of S_R, S_T and S_N is about the same. For three different alloy specimens corroded at 400 ℃ in superheated steam, the growth rate of oxide layer on S_N, S_R and S_T surfaces shows no difference for the same alloy specimen, but it increases with the increase of the Nb content. It is concluded that the improvement of corrosion resistance by adding Nb in Zr-Sn alloys is attributed to the restraint of anisotropic growth of the oxide layer. The corrosion resistance on S_N surface is remarkably improved when the specimens contained Nb are corroded in lithiated water. But the corrosion resistance on S_N surface for the specimens contained Nb is degraded in comparison with Zircaloy-4 specimens corroded at 400 ℃ in superheated steam due to the oxide growth rate increasing with the increase of Nb content. The phenomena of the restraint of anisotropic growth of oxide layer by adding Nb are discussed based on microstructural evolution of oxide layers affected by composition and water chemistry.

DEVELOPMENT OF HANA ALLOYS FOR ADVANCED FUEL CLADDINGS

Jeong-Yong Park[1*], Hyun-Gil Kim[1], Yang-Il Jung[1], Dong-Jun Park[1], Yang-Hyun Koo[1], Yong-Hwan Jeong[1], Jong-Sung Yoo[2], Yong-Kyoon Mok[2], Jung-Min Suh[2]

[1]KAERI, 989-111, Daedeok-daero, Yuseong, Daejeon 305-353, Republic of Korea
[2]KEPCO NF, 989-242, Daedeok-daero, Yuseong, Daejeon 305-353, Republic of Korea
**Tel:+82-42-868-8911, Fax:+82-42-862-0432, Email: parkjy@kaeri.re.kr*

High performance
Alloy for
Nuclear
Application

The development of the advanced nuclear fuel claddings with improved corrosion resistance has been widely carried out in many countries operating nuclear power plants. HANA alloys have been developed to increase the fuel rod discharge burn-up up to 70,000 MWD/tU mainly by improving the corrosion resistance. In the early stage of development, a basic research has been carried out using a great number of model alloys. The effects of alloying elements, precipitates and processing parameters on the corrosion behavior of Zr alloys have been studied to establish the database for developing HANA alloys. The candidate alloys to be manufactured into tubes were selected based on the results obtained from the basic research. We have carried out a variety of out-of-pile performance tests for the manufactured tubes. In particular, the out-of-pile corrosion behavior of HANA alloys were investigated in various corrosion environments including a PWR simulating loop condition. HANA alloys showed a much corrosion rate than Zirclaoy-4 irrespective of the alloy compositions as well as the corrosion environments. We have also performed in-pile performance tests for the HANA alloys in Halden research reactor, which showed that the corrosion resistance of HANA alloys was 30-50% higher than that of Zircaloy-4. HANA alloys also showed a superior creep resistance over Zircaloy-4 in the Halden test. One lead test rod program for the HANA claddings has completed three cycles of irradiation in the Westinghouse-type plant. The poolside examination of the lead test rods showed that the corrosion resistance of the HANA claddings was improved by 50% when compared to the reference Zr-Nb cladding after three cycles of irradiation. PIE for the irradiated HANA claddings is now ongoing in the hot laboratory in KAERI. Another lead test rod program and one lead test assembly program are now in progress in two different OPR1000 plants.

Zr-4

Halden
Reactor

ROLE OF ALLOYING ELEMENTS IN HYDROGEN PICKUP MECHANISM OF ZR-BASED ALLOYS

Kan Sakamoto[1*], Katsumi Une[1], Masaki Aomi[2], Kenichi Hashizume[3], Ikuji Takagi[4]

[1]*Nippon Nuclear Fuel Development, Co., Ltd., 2163 Narita-cho, Oarai-machi, Ibaraki-ken, 311-1313 Japan*
[2]*Global Nuclear Fuel Japan Co., Ltd., 3-1 Uchikawa 2-chome, Yokosuka-shi, Kanagawa-ken, 239-0836 Japan*
[3]*Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka-shi, Fukuoka-ken, 812-8581 Japan*
[4]*Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan*

**Corresponding author: Kan.Sakamoto@nfd.co.jp*

Understanding the mechanism of hydrogen pickup of Zr-based alloys is essential to reduce the risk of hydrogen embrittlement of fuel claddings. It is well know that the alloying elements, such as tin, iron, chromium, nickel and niobium, affect the hydrogen pickup property strongly, but its role in the hydrogen pickup mechanism has not been fully understood. By using many advanced experimental tools, the authors have conducted systematic experimental studies to obtain a better understanding of the role of the alloying elements. In the experiments, a special attention has been paid on the oxide layer since this oxide layer has a barrier effect against hydrogen pickup. Table 1 summarizes the key experimental tools used in the studies.

The systematic experimental studies revealed the following key findings by using three Zr-Sn-Fe-Cr-(Ni) alloys and one Zr-Nb alloy.

- Hydrogen pickup was rate-controlled by the hydrogen diffusion in the oxide layer
- Alloying elements (Fe and Nb) suppressed the hydrogen diffusion in the oxide layer by 1) the dissolution into zirconia matrix with valence of +3 or less and/or 2) the high compressive stress at the O/M boundary resulting from the delayed oxidation of precipitates.

In the presentation, the hydrogen pickup mechanism will be explained with some important experimental results obtained by the authors.

Table 1. Key experimental tools used in the studies

Oxide properties	Experimental tools
Oxide morphology	SEM/BSE
Microstructure	SEM, TEM/STEM
Crystal structure	TEM, Raman
Stress state	Raman, XRD
Precipitates distribution	TEM/STEM, Nano-SIMS
Dissolution of alloying elements	EPMA, Nano-SIMS
Chemical states of alloying elements	XAFS

EFFECT OF NB AND FE ON THE RECRYSTALLIZATION BEHAVIOR OF ZR-BASED ALLOYS

Il-Hyun Kim[1,2*], Hyun-Gil Kim[1*], Jeong-Yong Park[1], Seon-Jin Kim[2]

[1]LWR Fuel Technology Division, Korea Atomic Energy Research Institute
989 Daedeok-daero, Yuseong-gu, Daejeon, 305-353, Republic of Korea
[2]Department of Materials Sci. & Eng. Hanyang University,
Haengdang 1-dong, Seongdong-gu, Seoul, Korea

**Tel:+82 42 868 2522, Fax:+82 42 862 0432, Email:s-weat@hanmail.net*

The effect of high Nb and Fe addition of zirconium alloy on recrystallization behavior. The chemical composition of experimental alloys. The Nb content ranged from 1.0 to 2.0 wt% and the Fe content ranged from 0.2 to 0.4 wt% in the zirconium based alloys. The specimens to study recrystallization behavaior were performed on annealing at 400°C - 550°C for 1 to 8h after 80% cold-worked alloy. The recrystallization behavior for the annealed Zr-based alloys is evaluated by using the polarized light microscopy, microvickers hardness tester, and transmission electron microscope (TEM). The increased hardness at initial point is caused by the precipitate hardening in Zr-Nb alloy system because the Nb content in this work is higher than the Nb-solubility in Zr alloy. The hardness behavior of Fe-containing Zr-based ternary alloys is similar to the Nb-containing Zr binary alloys. After the recrystallization, the grain size is decreased with increasing Nb and Fe contents. The recrystallization temperature of the alloys increased with Nb,Fe content due to decrease of activation energy.

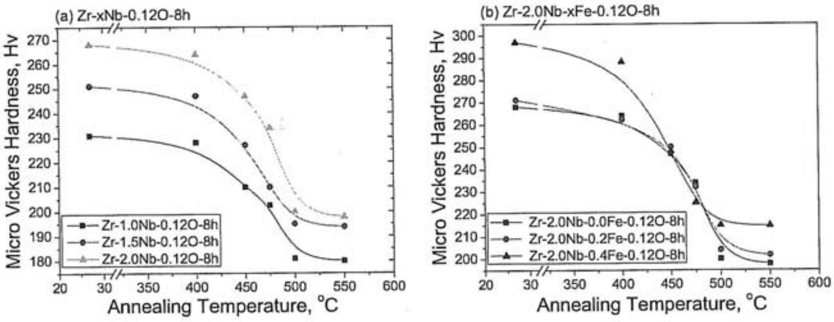

Fig. 1. Variation of Knoop hardness of the Zr-2Nb-xFe-0.12O alloys with Various annealing temperature for 8h

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Basic study on the Development of a Metal Cladding with Protective SiC Composites

Seonho Noh[a] , Kwangheon Park[a*]
[a]Department of Nuclear Engineering, Kyung Hee University, Kyunggi-do, 446-701
*Corresponding author: kpark@khu.ac.kr

Abstract

We have made an accident tolerant nuclear fuel, metal cladding that contains SiC composites as a protective layer. To make SiC composites, the current process needs high temperature (about 1100℃) for infiltration of fixing materials such as SiC. In this study, we had developed a low temperature process for making SiC composites on the metal layer, and we have made one kind(Cladding with protective SiC composites made by PCS) of specimens have been made, And corrosion test at 1200℃ in mixed steam and Ar atmosphere had been performed in these specimens. The corrosion test was successful, the coated layer on the specimen had been oxidized less than the metal layer. Coating on the metal cladding is very effective.

Figure 1.

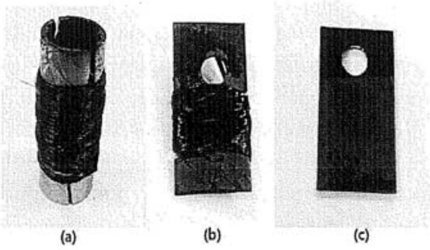

Figure 1. (a) Cladding with protective SiC composites made by PCS, (b) Cladding with protective SiC composites made by PVD. (c) Cladding with SiC coating using PCS

Figure 2,

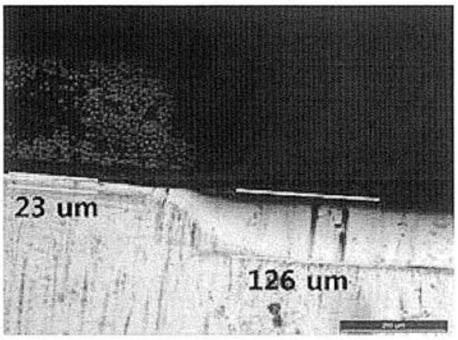

Figure 2. 1 line thickness specimen after corrosion

Suppression ratio = $\frac{\text{Metal layer oxide thickness}}{\text{Coated layer oxide thickness}}$	
1 line thickness	$\frac{24\ \mu m}{126\ \mu m} = 0.19$
4 line thickness	$\frac{27\ \mu m}{142\ \mu m} = 0.19$

Table 1. Suppression ratio of the specimen

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PROPERTIES EVALUATION OF REGROUND DIE AND DIE MATERIALS FOR INCREASING LIFE TIME OF PILGER DIE

Ki Bum Park , In Kyu Kim, Min Young Park, Jong Yeol Kahng, Hung Soon Chang

Korea Nuclear Fuel Co., Production & Technology Dept., 688, Gwanpyeong-dong, Yuseong-gu, Daejeon,305-509

Corresponding author : kibum@knfc.co.kr

The property of zirconium alloy tube is well known to be influenced by pilgering and its tooling; thus the control of its microstructure and mechanical property in the final tube product for nuclear fuel applications is a major concern of tube manufacture. It is obvious that the cold pilgering process is one of the key processes controlling the quality and the characteristics of the tubes manufactured, i.e. nuclear zirconium alloy tube in KEPCO NF. Cold pilgering is a rolling process for forming metal tubes in which diameter and wall thickness are reduced in a number of forming steps, using ring dies at outside of the tube and a curved mandrel at inside to reduce tube cross sections by up to 90 percent[1]. The OD size of tube is reduced by a pair of dies, and ID size and wall thickness is controlled simultaneously by mandrel. During the cold pilgering process, both tools are the critical components for providing qualified tube. The Development of our own pilger die and mandrel has been a significantly important in the zirconium tube manufacturing and a major goal of KEPCO NF.

The objective of this study is to evaluate the life time of reground pilger die for increasing life time of virgin pilger die through several times of regrinding and to evaluate the life time by pilger die materials during pilgering. Therefore, the comparison of the slip factor and mechanical properties of pilger die made of AISI 52100 material was made in this study and a comparison of the heat treatment and mechanical properties of AISI 52100 and AISI H13 materials was made in this study. It has been strongly demanded to improve a productivity and increase a life time of die in the cold pilgering. Recently, seamless tube manufacturing companies by cold pilgers are using AISI H13 materials with the intent to improve both ductility and hardness of the dies. So, this study handles with both the AISI 52100 and AISI H13 for better productivity and longer life time with chemical composition shown in Table1 and experimental condition for slip factor of reground pilger die shown in Table2.

Table 1 Chemical Composition(wt%) of Die Materials

Alloy	C	Mn	Si	Cr	Mo	V
AISI 52100	0.98 ~1.10	0.25 ~0.45	0.20 ~0.35	1.30 ~1.60	-	-
AISI H13	0.40	0.35	1.00	5.20	1.30	0.95

Table 2 Experimental Condition for Slip Factor(mm)

Die Dia.	OD Incoming	OD Final	Pinion Gear	Slip Factor
206.5	17.78	9.5	196.01	0.85
205.5	17.78	9.5	196.01	0.77
204.5	17.78	9.5	196.01	0.69
203.5	17.78	9.5	196.01	0.61

[1] Sandvik Special Metals, Zirconium Alloy Fuel Clad Tubing Engineering Guide, 1989, USA

COMPARISON CHARACTERISTICS OF HANA-4 TUBE SHELLS WITH MANUFACTURING PROCESS

M.Y. Choi, C. Y. Lee, Y. K. Mok, S. J. Lee, J. M. Suh

KEPCO Nuclear Fuel, 1047 Daedeokdaero, Yuseong-gu, Daejeon 305-353, Republic of Korea

**E-mail: mychoi@knfc.co.kr*

The characteristics of Zr-based alloy were determined by the performed manufacture process conditions. The manufactured process of HANA-4 tube shell consists of ingot melting, beta-forging, beta-quenching, extrusion, cold working, and annealing. Among the tube shell manufacturing processes, cold working process is different between two manufacturing processes; cold pilgering and cold forging, respectively.

HANA-4 tube shells with different manufactured process were characterized using optical metallography, crystal texture measurements, microstructural analysis using TEM, and micro hardness measurements.

ICP analysis revealed the requirements of chemical composition of the HANA-4 tube shell in specification are met. The microstructure was slightly different during the cold working stage, it has the same characteristics for the finished tube shell by the same final annealing. The hardness of the both tube shells is also decreased to the similar extent by the final annealing. The pilgered tube shells that were generated had higher kearns parameters than forging method. This result shows that the pilgering has an advantage of texture control.

ID GRIT BLASTING FOR TUBING

Sang Jin Han, Ju Pil Yoon, In Kyu Kim, Jong Yeol Kahng, Hung Soon Chang

KEPCO Nuclear Fuel Co.

Corresponding author: sjinhan@knfc.co.kr

Tube manufacturing process has been divided into three main processes such as forming process, finishing process and inspection. The cladding tubes must have the desired mechanical properties, corrosion resistance, dimension and surface condition and so on. Through the finishing process, tubes are becoming final products that meet all drawing and specification requirements. Finishing process consists of many following steps such as straightening, ID grit blasting, cut-to-length and finishing cell with LMS operation. Abrasive blasting is the operation of forcibly propelling a stream of abrasive material against a surface under high pressure. The primary purpose of ID grit blasting for cladding tubing is known to minimize the fluoride compound on the inner tube surface and enhance cleaning of the ID by removing stains, heat tint film and marks from the pilgering operation.

This study presents experiments that were accomplished to investigate the change of inner surface condition and chemical compound through the manufacturing process and the effect of abrasive on cladding tubing. The experiments were conducted using a localized ID grit blaster by TSA.

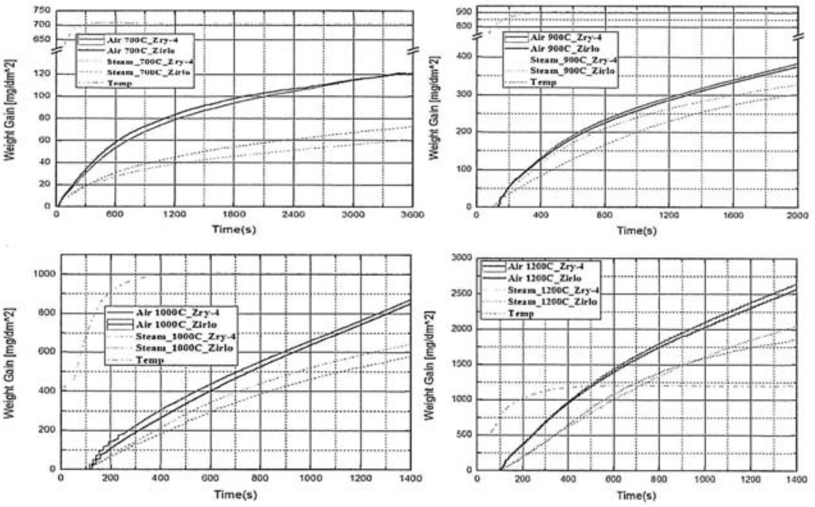
The High-temperature Oxidation Kinetics of Zr-alloys Claddings in Air Steam

Master [illegible] → Kyung Tae Kim[1] ✓, Kwangheon Park[1*] ← Professor [illegible]:

[1]*Department of Nuclear Engineering, Kyunghee University, Kyunggi-do, 446-701*

**Corresponding author: kpark@khu.ac.kr* ←

ABSTRACT: The characteristics of oxidation for the Zry-4 and Zirlo were measured in the temperature ranges of 700-1200℃ under air and steam conditions, using an apparatus for high temperature oxidation in the air and steam. Zry-4 and Zirlo follow a parabolic rate law at 700℃,900℃. And oxidation rates of Zry-4 at high temperatures are similar or slightly more than those of Zirlo under the steam. However, Zirlo oxidation rate is higher than Zry-4 at 700℃ under both atmosphere condition. The oxide scale seemed to be thicker layer under air conditions, because of the formation of nitrides in the metal layer.



oxidati
result

TGA
at
700°C

Figure 1. Oxidation behaviors of Zry-4 & Zirlo under Air, Steam at 700℃-1200℃

Weight change by the oxidation in air and steam for each specimen was measured by the microbalance at 700-1200℃. The weight gain per area for each specimen is shown in Fig. 1. At temperatures 700 and 800℃, both Zry-4 and Zirlo specimens show parabolic oxidation kinetics. However, initially a linear oxidation kinetic behavior was observed over 1000 and 1200℃ in air & steam. Zirlo seems more resistant to oxidatioin both in air and in steam at these temperatures at 900-1200℃ (Fig.1).

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Effect of Dissolved Oxygen in Water / Steam on the Corrosion Behavior of Zirconium Alloys

Wei Tianguo*, Long Chongsheng, Xiao Hongxing, Miao Zhi

Reactor Fuel and Material Key Laboratory, Nuclear Power Institute of China,
Chengdu, China, 610041
*Corresponding author, phone:+86-28-85903969, email: wtg05@163.com

Abstract

To increase the power rating, upcoming advanced nuclear reactors consider allowing partial boiling in the core, which is expected to increase the dissolved oxygen (DO) levels in the primary coolant. In present work, the effect of DO on the corrosion behavior of Zr-4, M5, N36, N18 and Zr-1.0Cr-0.4Fe alloys was investigated in two ways. In the first condition, corrosion test was carried out in 360 ℃ /18.6 MPa water in a static autoclave, to maintain a high DO level, no dearation practice was used in the test and the water was refreshed every 6 days. In the second one, corrosion test was carried out in 400 ℃ / 10.3 MPa steam in another autoclave attached to a recirculation loop, where DO was controlled at the level of about 100 ppb. In the static autoclave test, all the alloys showed uneven corrosion behavior and had rough oxide outside surface after long term exposure, even mildly minus weight gains was observed. Corrosion acceleration of the Nb-containing alloys was much more significant than that of Nb-free ones, after an exposure time of 75 days, average weight gains of M5 and N36 alloys had reached to about 90 mg/ dm^2, however, those of Zr-4 and Zr-1.0Cr-0.4Fe alloys was much lower, at the level less than 40 mg/dm^2. In the autoclave with recirculation loop test, as the condition in the static autoclave test, alloys with higher Nb content tended to had faster corrosion rate after long term exposure as well, even though they had lower weight gains than Zr-4 in the initial period of corrosion test. It was thought that Nb made corrosion behavior of zirconium alloy sensitive to DO, when DO in the water / steam reached to a certain level, oxidation of Nb containing particles in the oxide layer would change the oxide films to be less protective, so that the corrosion rate was increased.

Key words: Zirconium alloys; Corrosion; dissolved oxygen (DO)

Effect of the Manufacturing Process on the Composition and Size of Second Phase Particles in N36 Tubes

戴迅
Dai Xun*, Jiang Hongman, Wang Pengfei, Yang Zhongbo, Zhao Wenjin

Reactor Fuel and Material Key Laboratory, Nuclear Power Institute of China,
Chengdu, China, 610041

*Corresponding author, phone: +86-28-85903294，E-mail：164714098@qq.com

Abstract

The composition and size of second phase particles (SPPs) in N36 tubes for different manufacturing process were studied by SEM ,TEM, and EDS. The manufacturing processes included β-quenching, hot extrusion, cold rolling, intermediate annealing and final annealing. The analysis results showed that the average size of SPPs in the extruded tube was about 250nm, which were distributed along extruded direction and confirmed as β-Zr with a small quantity of β-Nb and the Zr-Nb-Fe type particles. After annealing during first cold rolling the average size of SPPs in the tubes would be decreased to about 120nm, and not be changed too much until final tube. Two types of SPPs in N36 final tubes were observed: one was mainly Zr-Nb-Fe particles with a few Cr，and other was a few of Zr-Nb particles. Nb/Fe ratio in the Zr-Nb-Fe particles would be changed from the range of 0.1 to 15 for extruded tube to about 2 for final tubes.

Keywords: N36 tube, SPPs, composition, size

The Effect of Heat Treatment and Reduction Process to the Second Phase Particles and the Texture

Gang Li[1]*, Sheng Peng, Tianguang Zhang, Zhouqiang Guo, Su Chen
State Nuclear Baoti Zirconium Industry Company , Baoji, Shaanxi, China 721013
*Corresponding author: llkkjj11@163.com

The SPPs strongly affect the corrosion-resistance property of the zirconium alloys. The transformation trend of SPPs remains to be elucidated in zirconium alloy manufacturing process. Zirlo cladding tubes were manufactured from Trex through three reductions in SNZ. After annealing process, the samples were picked up from TREX, Φ31.75mm tube, Φ17.78mm tube, and Φ9.5mm tube respectively. TEM and SEM are used to obtain the microstructures information; and EDX is used to analyze the composition of SPPs. The relationship between heat treatment & reduction process and SPPs was investigated from the Trex to the cladding tube.

A strong texture is produced during the fabrication process. The optimizing textures are useful to maintain good performance in the pile. The quantitative characterizations of textures are investigated to study the effect of reduction process and heat treatment. EBSD is used to analyze the texture factors.

SEM and TEM pictures are in Figure 1 and 2 respectively. The SPPs exhibit spherical or ellipsoidal shapes. The fine SPPs show random distribution in grain boundaries and internal grains. Few SPPs more than 300nm are observed in the samples. Zr-Fe-Nb and ß-Nb particles are identified by EDX. The average size of SPPs decreases due to heat treatment and reduction process. Both boundary migrations during recrystalization and Ostwald ripening process have a jointly effect on the distribution of SPPs.

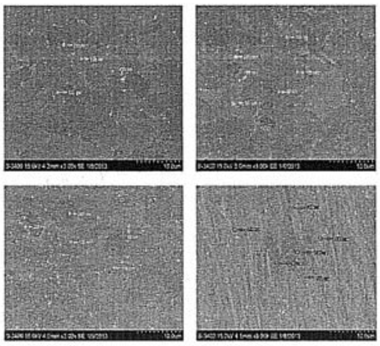


Figure 1 SEM Pictures

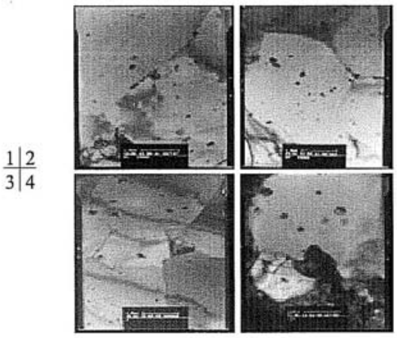


Figure 2 TEM Pictures

Only texture factors of three samples were analyzed in terms of EBSD in Figure 3. The texture factor of cladding tube is characterized by XRD due to residual stress. In the trend, the radial factor increases, the circumferential factor decreases and the rolling factor changes slightly in the Table 1. The XRD data is consistent with WEC data. Heat treatment makes the grain orientations randomly, but the reduction process drives the grain orientations orderly. Both heat treatment and reduction process jointly affect the texture factors, especially in normal and circumferential directions.

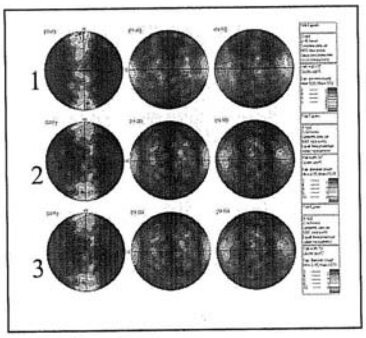


Figure 3 The Pole Figure

Table 1 Texture Factors

样品	F_{RD}	F_{TD}	F_{ND}
1	0.05	0.60	0.35
2	0.08	0.62	0.30
3	0.06	0.54	0.40
4	/	/	0.48

THE EFFECT OF ANNEALING PROCESS ON SURFACE RESIDUAL STRESS OF Zr ALLOY PLATE

SUN Ke-qiang*, PAN Qian-fu, YAO Sun-hong, LIU Chao-hong, WANG Lu-quan, CHEN Yong, PENG Xiao-ming
E-mail:abcsunke@163.com

Number 28, South 3 Duan, The First Ring Road, Chengdu City , Sichuan Province .

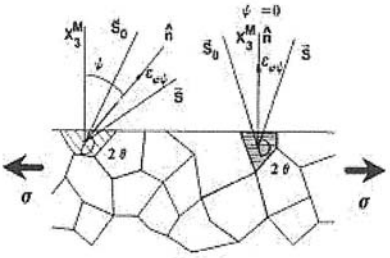
Abstract: The residual stress of Zr alloy plate can affect the stability of the plate shape. After annealing, the flatness of the plates were not satisfied with the accuracy requirement of the plate size. We put Zr alloy plates in the fixture for straightening in the annealing process. The straightening fixture continually applied force to the plates, while the stresses in plates are eliminated in annealing. This process is multiple productions. In this paper, the Zr alloy plates were put in the different annealing process, the condition of straightening, without straightening and different time of heat preservation are two parameters. After testing by Xstress-3000 analyzer, the surface residual stress value of the Zr alloy plates were obtained(3-6points were selected every plate).Comparing the surface residual stress values of the Zr alloy cold rolled plate and hot rolled plate, we draw the following conclusions:

1)After annealing, the surface residual stresses values of the Zr alloy plates are in ± 60MPa, The values decreased with the time of heat preservation.

2)When the time of heat preservation is 3hr. the surface residual stresses values of the Zr alloy plates approaches zero stress state, less than 65MPa of cold rolled plate and -135MPa of hot rolled plate.

3) The straightening of Zr alloy plates in annealing has no effect on the surface residual stress eliminating.

- Figures
  10 pt, bold, 1.0 line spacing. Each figure must have a caption that includes the figure number and a brief description, preferably one or two sentences. The caption should follow the format "Figure 1. Figure caption."



The main Stress direction

Fig. 1. The testing of X-ray diffraction diagram

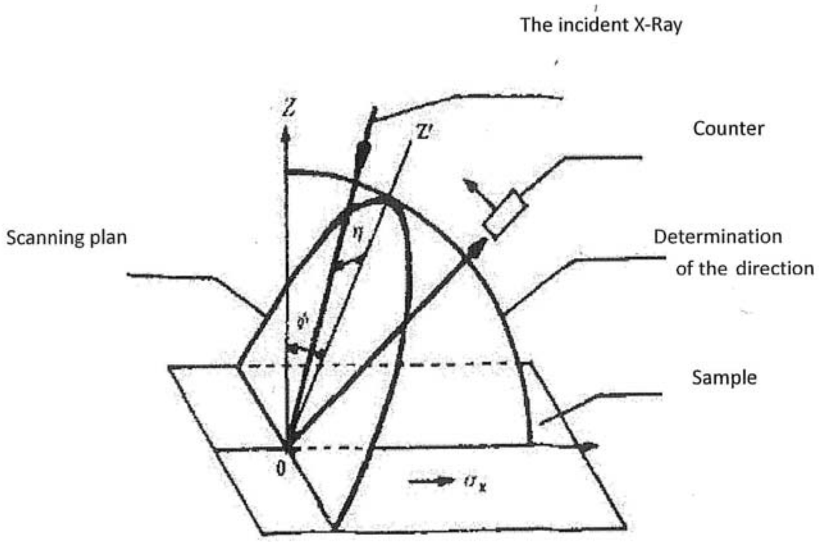


Fig.2 The method stress of X-ray diffraction testing

- Tables
- References

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Study of Second Phase Particles with Stripes in Zr-1Nb-0.1Fe Alloy

Lifeng Zhang[a,b], Hengfei Gu[a,b], Sheng Peng[c], Xiaoning Li[c], Songquan Wu[a,b], Lian Wang[c], Gaihua Yuan[c], Geping Li[a,*]

[a]*Institute of Metal Research, Chinese Academic of Sciences, 72 Wenhua Road, Shenyang 110016, China*
[b]*University of Chinese Academy of Sciences, Beijing 100039, China*
[c] *State Nuclear Bao Ti Zirconium Industry Company, Baoji 721000, China*
**Corresponding author: gpli@imr.ac.cn*

Abstract

It is well established that microstructure in Zr alloys is always composed of α-Zr matrix and inlaid second phase particles (SPP) while aging above the critical temperature. The SPP have a major influence on the corrosive, mechanical and irradiation behaviors. But the studies on the SPP above the critical point are rarely reported. The aim of this paper is to investigate the SPP with stripes of Zr-1Nb-0.1Fe alloy after heat treatment (aging at 700℃ above the critical temperature) by transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDAX). The results showed that the SPP with stripes was body-centred cubic (bcc) β-Zr in α-Zr matrix. Formation of stripes was due to moiré fringes and thickness fringes. The orientation relationship between β-Zr and α-Zr was $<111>_\beta // <11\bar{2}0>_\alpha$, $\{110\}_\beta // \{0001\}_\alpha$, and those β-Zr particles kept semi-coherent relationship with the α-Zr matrix.

Key words:
Zr alloys, second phase particles, stripes, moiré fringes

IRRADIATION PERFORMANCE OF HANA ALLOY TESTED IN HALDEN REACTOR

Hyun-Gil Kim[1*], Jeong-Yong Park[1], Yang-Hyun Koo[1], Yong-Hwan Jeong[1],
Jong-Sung Yoo[2], Yong-Kyoon Mok[2], Jung-Min Suh[2]

[1]LWR Fuel Technology Division, Korea Atomic Energy Research Institute
989 Daedeok-daero, Yuseong-gu, Daejeon, 305-353, Republic of Korea
[2]KEPCO Nuclear Fuel, 242, Daedeok-daero 989beon-gil,
Yuseong-gu, Daejeon, 305-353, Republic of Korea

**Tel:+82 42 868 2522, Fax:+82 42 862 0432, Email: hgkim@kaeri.re.kr*

HANA alloy was developed for application as fuel assembly component such as the fuel cladding, grid spacer, and guide tube in PWRs. After a long-term corrosion test and other performance tests in an out-of pile, it was revealed that HANA alloy has a better corrosion and creep resistance than reference Zircaloy-4 cladding [1]. Based on this result, the in-pile test was conducted in the Halden research reactor in Norway during 6.5 years (1148 FPD, 67 GWD/MTU). The main purpose of this test was to evaluate the in-reactor performances of HANA alloy claddings up to a high burn-up. Four alloy types of HANA claddings (HANA-3, HANA-4, HANA-5, and HANA-6) and reference cladding (Zircaloy-4) were prepared for irradiation testing. The irradiation conditions were controlled to simulate the commercial reactor operations in Korea. The test parameters of HANA cladding rods were the oxide thickness to evaluate corrosion behavior, dimensional changes to evaluate the creep behavior, hydrogen uptake, and tensile strength with the burn-ups.

The oxide thickness and diameter measurements of all test rods were conducted at approximately 200-day intervals. A hydrogen analysis, tensile test, and metallographic analysis were conducted for the discharged test rods. The oxide thickness, which was measured on the high heat flux region in the test rods using the ECT method, was ranged from 15 to 37 μm after the 1148 FPD, as shown in Fig. 1 [2].

All HANA claddings showed better corrosion resistance than Zircaloy-4 cladding. From the OM observation of the oxide layer, the oxide thickness of all HANA claddings was thinner than the Zircaloy-4 cladding, and the oxide thickness measurement result by OM was similar to the result by the ECT technique. The diameter measurement results, which were corrected for the oxide thickness, were changed with the irradiation burn-ups. Initially, the rod diameter was decreased up to about 20 GWD/MTU; however, the measured diameter was increased with an increase in the test burn-up, which was affected by the fuel swelling behavior after the fuel-clad interaction. Before the fuel-clad interaction region, all HANA claddings showed lower creep-down behavior than Zircaloy-4 cladding. The hydrogen content of HANA claddings ranged from 54 to 96 wppm at the high heat flux region of the test rods. These results were lower than the Zircaloy-4 cladding of 119 wppm. The tensile strength of HANA and Zircaloy-4 claddings was similarly increased when compared to the un-irradiated claddings owing to the radiation-induced hardening.

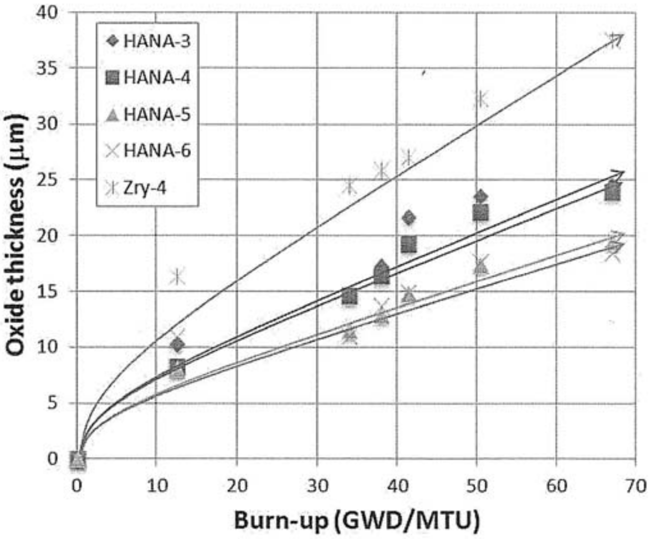

Fig. 1. Corrosion behavior of HANA and Zircaloy-4 claddings tested in the Halden research reactor [2]

References

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[2] H.G. Kim, J.Y. Park, Y.I. Jung, D.J. Park, Y.H. Koo, TopFuel 2012, Manchester, United Kingdom 2-6 September 2012.

Zr-4 : 30 ~ 50 GWD/MTU)

Oxide thickness 20 ~ 30 μm

Effect of Bi on the Corrosion Behavior of Zirconium Alloys

Mei Y. Yao[1,2*], Bang X. Zhou[1,2], Wei B. Zhang[1,2], Li Zhu[1,2], Ling H. Zou[1,2],
Jin L. Zhang[1,2], Jian C. Peng[1,2] and Qiang Li[1,2]

1. Laboratory for Microstructures, Shanghai University, Shanghai 200444
2. Institute of Materials, Shanghai University, Shanghai 200072, P. R. China

*Corresponding author: yaomeiyi@shu.edu.cn

Abstract: Optimizing composition or alloying with other elements is basic ways to develop advanced zirconium alloys with excellent corrosion resistance. In this study, the effect of Bi on the microstructure and corrosion resistance of zirconium alloys was investigated by TEM and autoclave corrosion tests in different water chemistries. Different zirconium-based alloys, including Zr-4 (Zr-1.2~1.5Sn-0.2Fe-0.1Cr, mass fraction, %), S5 (Zr-0.8Sn-0.35Nb-0.4Fe-0.1Cr) and T5 (Zr-0.7Sn-1.0Nb-0.3Fe-0.1Cr), were adopted to prepare the zirconium alloys containing Bi of 0.1%~0.5% in mass fraction. The corrosion results show that the effect of Bi addition on the corrosion behavior of different zirconium-based alloys is very complicated, depending on their compositions and corrosion conditions. (1) The addition of 0.1%~0.5% Bi is deleterious to the corrosion resistance of Zr-4 and the corrosion resistance of the alloys is markedly decreased with the increase of Bi contents whether in superheated steam at 400 ℃/10.3 MPa or in lithiated water with 0.01 M LiOH at 360℃/18.6 MPa. (2) The addition of 0.1%~0.5% Bi has a little beneficial effect on the corrosion resistance of S5 in lithiated water at 360℃; while it can improve the corrosion resistance in superheated steam at 400 ℃/10.3 MPa, but the improvement effect decreases with the increase of Bi content. (3) The addition of 0.1%~0.5% Bi is of a little benefit to the corrosion resistance in lithiated water at 360℃/18.6 MPa; While in superheated steam at 400℃/10.3 MPa, the addition of 0.3% Bi is of a little benefit to the corrosion resistance, but the addition of 0.5% Bi is deleterious to the corrosion resistance. Microstructure observation of the alloys shows that the addition of Bi promotes the precipitation of Sn as second phase particles, which is in solid solution in α-Zr matrix in Zr-4, S5 and T5 alloys. The Bi-containing SPPs can only be detected in the Zr-4+≧0.1Bi, S5+≧0.3Bi and T5+≧0.5Bi alloys. This indicates that the solid solution contents of Bi in α-Zr matrix increase with the increase of Nb in the alloys. Based on the results of microstructure and corrosion behavior, it is suggested that the solid solution of Bi in α-Zr matrix can improve the corrosion resistance, while the precipitation of the Bi-containing SPPs is harmful to the corrosion resistance.

Keywords: Zirconium alloy; alloying element Bi; corrosion; microstructure

Influence of Waterside Corrosion on Integrity of PWR Fuel under Power Transient

Kazuaki YANAGISAWA

Policy Planning and Administration Department, Japan Atomic Energy Agency
Watanuki-machi, Takasaki-shi, Gunma-ken

The integrity of the PWR fuel under the power transient was studied taking into consideration of the waterside corrosion and the rod pressurization as test variables. Concluding remarks are as follows;

(1) For the pressurized PWR fuel up to 3.1-3.6MPa, the waterside corrosion had no effect on the fuel failure, occurred by the ballooned/rupture mechanism. The failure threshold was the same as that observed in the standard fuel.

(2) For the unpressurized PWR fuel, the waterside corrosion had a significant effect to preventing the fuel from the failure, occurred by the melt/brittle mechanism. The corroded film tended to minimize the temperature gradient across the cladding. It also worked to prevent the additional oxide formation, where the hoop stress raised during the quench was tended to reduce. As a result, the failure threshold of the corroded fuel was higher than that of the standard fuel.

(3) The use of the ZrO_2 fuel under the unpressurized condition revealed that the magnitude of PCST, ΔT were suppressed and the time to quench was shortened when they compared with those of the standard fuel. For example, PCST was 1,748 deg. C for the standard fuel but 1,285 deg. C for the corroded fuel ($80\mu m$) at the energy deposition of 256cal/g·fuel. The PCST by 463 deg. C was suppressed to prevent from the failure.

(4) For the axial PCMI, the peak axial strain for the pressurized fuel increased with the increase of the ZrO_2 film; the maximum was 4% for the $40\mu m$ fuel. Hence, at the outermost rim the ZrO_2 film suppressed the cladding to balloon. By contrast, the peak axial strain for the unpressurized fuel was not exceeded 1% irrespective to the ZrO_2 film. This was due to the strong axial restriction occurred by the rapid radial movement of the hot fuel. For the radial PCMI, the residual diametral strain remained little in the fuel rod with ZrO_2 film.

A Study on the Microstructure and Corrosion Behavior of Zr-XSn-1Nb-0.3Fe Alloys

Yang Zhongbo*, Zhao Wenjin, Cheng Zhuqing Miao Zhi

Reactor Fuel and Material Key Laboratory, Nuclear Power Institute of China,
Chengdu, China, 610041
*Corresponding author, phone:+86-28-85903294, email: yangzhongb@mails.ucas.ac.cn

Abstract

To better understand the effect of tin on the corrosion behavior of Zr-Sn-Nb-Fe alloy, Zr-XSn-1Nb-0.3Fe（X=0-1.5wt%）sheets were prepared by thermomechanical processing and tested in static autoclave in 360℃/18.6MPa pure water, 360℃/18.6MPa/0.01mol/L LiOH aqueous solution and 400℃/10.3MPa superheat steam. The characteristics of the precipitates in the specimen were analyzed by TEM, the crystal structure of oxide film formed on the specimens during corrosion test were characterized by laser-Raman spectrometry. It was shown that the corrosion weight gain of specimens was decreased when tin content was reduced from 1.5wt% to 0.6wt%. As tin content was reduced from 0.6wt% to 0wt%, the corrosion weight gain was hardly changed in pure water and steam. However, it was found that the corrosion weight gain increased in LiOH aqueous solution. The microstructural characteristic indicated that the crystal structure and mean size of the precipitates in all tested specimen were almost the same even though the tin was considerably changed, but the area fraction of precipitates in the alloy was increasing with the tin content decreasing when all the samples were heat-treated in the same condition. It was observed that, the oxide film formed on the specimen during short term exposure was mostly consists of m-ZrO_2 and t-ZrO_2. With the prolongation of corrosion time, the t-ZrO_2 will transform to m-ZrO_2, The higher the transformation rate, the lower t-ZrO_2 content in oxide film and the higher corrosion rate of specimens. It was concluded that the solid solution content of tin in a-Zr will be responsible for the difference of corrosion resistance of Zr-Sn-Nb-Fe alloys.

Key words: Zirconium alloys; Corrosion; Microstructure; Oxide films

Investigation on Corrosion Properties of CZ1 and CZ2 New Zirconium Alloys

Liutao Chen[1], Jun Tan[1], Hong Zou[1], Rui Li[1], Dungu Wen[1], Lian Wang[2],
Bo Gao[2], Qiang Li[3], Jinlong Zhang[3], Meiyi Yao[3], Bangxin Zhou[3]
(1 China Nuclear Power Technology Research Institute, Shenzhen of Guangdong Prov.518026,China; 2 State Nuclear Baoti Zirconium Industry Company, Baoji of Shanxi Prov.721013, China; 3 Institute of Materials, Shanghai University, Shanghai.200072, China)

ABSTRACT: In order to increase the burnup of UO_2, two new zirconium alloys were developed by CGNPC, namely CZ1 (SZA-1)(Zr-0.85Sn-0.3Nb-0.3Fe-0.15Cr-Si-Cu) and CZ2(SZA-3)(Zr-1.0Nb-0.17Fe-Cu-O) alloys. Ingot of 1 ton for each alloy was melted, and was fabricated into fuel cladding tubes with different heat treatment processes. Corrosion resistance and microstructure of CZ1(SZA-1) and CZ2(SZA-3) alloys were investigated by autoclave tests and SEM /TEM observation, respectively. The autoclave tests were performed in four different water chemistry, which are 360℃ pure water, 360℃ water containing 70 ppm lithium(as LiOH), 360℃ water containing 3.5 ppm lithium(as LiOH) and 1000 ppm B(as H_3BO_3), as well as vapors at 400℃ and 10.3MPa. The experimental results showed that the corrosion resistance of cladding tubes fabricated in this study is better than that of low Tin Zr-4. Besides, Lower corrosion weight gain is obtained in the cladding tubes with decreasing annealing temperature, which correlates well with the smaller size of second phase particles.

Effect of Ge on the Corrosion Resistance of Zr-1Nb-0.7Sn-0.03Fe-*x*Ge Alloys Corroded in Lithiated Water

Jin L. Zhang[1,2*], Xing F Xie[1,2], Mei Y. Yao[1,2], Bang X. Zhou[1,2], and Jian C. Peng[1,2]

1. Laboratory for Microstructures, Shanghai University, Shanghai 200444

2. Institute of Materials, Shanghai University, Shanghai 200072, P. R. China

**Corresponding author: jlzhang@shu.edu.cn*

Abstract: It is well known that the corrosion resistance of zirconium alloys is controlled by chemical composition, characteristics of second phase particles (SPPs) and oxide evolution. The corrosion behavior of Zr-1Nb-0.7Sn-0.03Fe-*x*Ge (x=0, 0.05, 0.1 and 0.2, mass fraction, %) alloys was investigated by autoclave test in lithiated water with 0.01 mol/L LiOH at 360 ℃ under a pressure of 18.6 MPa. The microstructures of the alloys and oxide films on the corroded specimens were examined by TEM and SEM. The sample for the oxide microstructure observation was prepared by a HELIOS-600I focused ion beam. The results reveal that the corrosion resistance of Zr-1Nb-0.7Sn-0.03Fe-*x*Ge (x=0.05, 0.1 and 0.2) alloys was remarkably superior to that of the Zr-1Nb-0.7Sn-0.03Fe alloy. In addition to Zr-Nb-Fe-Cr second phase particles (SPPs) with a tetragonal (TET) structure and β-Nb SPPs with a body-centered cubic(BCC) structure, the Zr-Nb-Fe-Cr-Ge SPPs with a TET structure and Zr_3Ge SPPs with a TET structure were detected in Zr-1Nb-0.7Sn-0.03Fe-*x*Ge alloys. The oxidation of SPPs was slower than that of α-Zr matrix. There exist a few micro-cracks and more ZrO_2 columnar grains in the oxide film formed on Zr-1Nb-0.7Sn-0.03Fe-0.1Ge alloys corroded for 190 days. However, there exist more micro-cracks and ZrO_2 equiaxed grains in the oxide film formed on Zr-1Nb-0.7Sn-0.03Fe alloys corroded for 130 days. The addition of Ge can not only delay the developing process of the defects in oxide films to form micro-pores and micro-cracks, but also retard the microstructural evolution from columnar grains to equiaxed grains. Therefore, the addition of Ge can improve the corrosion resistance of the Zr-1Nb-0.7Sn-0.03Fe alloy.

Keywords: Zirconium alloy; Ge; Corrosion resistance; Oxide film; Microstructure

Iodine Induced Stress Corrosion Cracking of N36 Zirconium Cladding

Yan Meng

Reactor Fuel and Material Key Laboratory, Nuclear Power Institute of China,
Chengdu, China, 610041
Tel：（028）85903862，E-mail：yanmeng_spring@163.com

Abstract

Ring tension test was performed on N36 zirconium alloy tube ring specimen to study the Iodine induced stress corrosion cracking (I-SCC) behavior. In this test the slow tensile strain rate as 10^{-5}/s and iodine vapor partial pressure as 10^2Pa，10^3Pa，10^4Pa separately were adopted to be experiment condition. The Max tensile load, toughness were analyzed to evaluate I-SCC property. The results showed that: zirconium was susceptible to I-SCC in iodine vapor environment at 350℃. I-SCC cracks mainly affected necking process in tensile test after max load, but there was a little effect on elastic deformation and max load value. The toughness was dropped directly and proportional to the iodine content, which was 52% in 10^4Pa iodine condition comparing with non-iodine. Fracture appearance in iodine environment was different from cup-cup ductile fracture in Ar. The fracture surface after I-SCC was observed by scanning electron microscope (SEM). The results showed that the lateral cracks were parallel to fracture surface, IG occured at edge of lateral cracks, and TG cracks followed by IG cracks，with no clear boundary between them.

Keywords: zirconium cladding； ring tension； iodine vapor； I-SCC

High Temperature Creep Behavior of N36 Cladding Tube

Wang Pengfei* Zhao Wenjin

Reactor Fuel and Material Key Laboratory, Nuclear Power Institute of China,
Chengdu, China, 610041
*Corresponding author, phone:+86-28-85903294, email: wpf03082108@163.com

Abstract

Zirconium alloy cladding for nuclear fuel elements acts as a barrier between the coolant and the radioactive fuel pallets in light water reactors. Therefore the safety and reliability of fuel elements during reactor operation is closely related to the performance of fuel cladding. And the mechanical integrity of cladding tubes is very important. Creep property is one content of mechanical properties to examine the integrity. N36 zirconium alloy is China's advanced alloy which belongs to Zr-Sn-Nb ternary system alloy. In this work, the out-of-pile tensile creep behavior of N36 cladding tube was studied at temperature range from 593K to 723K and applied stress range from 60MPa to 160MPa. The stress exponent n and creep activation Q were calculated on the base of experimental data. The results showed that the steady-state creep rate was a nonlinear relationship with stress and the stress exponent n was divided into two sections at any given temperature range. The stress exponent n was about 3 in low stress regime and about 4-7 in high stress regime below 673K, respectively, the creep activation energy Q increased from 160kJ/mol to 180 kJ/mol as the applied stress increased from 60MPa to160MPa. When the temperature exceeds 673K, the stress exponent n exceeded 7 in high stress regime. The microstructure of the specimens before and after the creep test was analyzed by using the transmission electron microscope (TEM) to understand the creep mechanism. A variation of the crystal orientation with the creep deformation was investigated by using the electron back-scattered diffraction (EBSD) analysis. From the results of the TEM and EBSD observation, when the stress exponent n was about 3 the steady-state creep region was main controlled by glide of dislocations, and n was about 4-7 the creep was main controlled by climb of dislocations.

Key words: N36 Cladding Tube, High Temperature Creep, The stress exponent, creep activation Q, Microstructure evolution

Research on Tensile Property of New Zirconium Alloys Used in Fuel Cladding

Chen Le Liang Bo Yang Zhongbo
Reactor Fuel and Material Key Laboratory, Nuclear Power Institute of China,
Chengdu, China, 610041
*Corresponding author, phone:+86-28-85906033, email: jolin0102@126.com

Abstract

Tensile test is the fundamental method to study material mechanical properties. As an out-of-reactor basic data, it is important to design and determine related parameters for nuclear power plant. In this article, we mainly focused on the tensile property of two new zirconium alloys which were about to be used as the fuel cladding, namely SZA4(4#) and SZA6(6#). The tensile strength, yielding strength, elongation, work hardening and fracture morphology of the plate samples were studied by MTS 810 and scanning electron microscopy（SEM）at room temperature（RT） and high temperature（HT，380℃）. SZA-4 and SZA-6, which were two different composition alloys with the same heat treat processing, compared with Zr-4 plate at the rolling direction (RD) and transverse direction (TD). The results indicated that the properties of 3 parallel samples were similar at the same test condition, which showed the processing and test method was steady and repeatability. The strength of samples RD was higher than that of TD in RT and HT, and the 4# sample was higher than Zr-4 and 6# samples at RT, but no better than Zr-4 at HT. The elongation of RD was better than TD, and there was no difference between 4# and Zr-4 samples, although they were longer than 6#. The work hardening of SZA seemed more obvious than that of Zr-4. The fracture morphology of the new alloys were plastic feature with dimples，indicating that they both had excellent ductility.

Key Words: new zirconium alloys, tensile, work hardening, strength, elongation

? 375°c

No elongation ?

Radial Texture of SZA-1 Alloy Tube

Sheng Peng[1]*, Lian Wang [1], Gai H. Yuan [1], Xiao S. Li[1], Liutao Chen[2], Jun Tan[2], Hong Zou[2], Rui Li[2], Dungu Wen[2]

1. SNZ, Baoji, Shaanxi 721013, P. R. China

2. China Nuclear Power Technology Research Institute, Shenzhen of Guangdong Prov.518026,China

*Corresponding author: pengsheng@sn-zr.com

Four intermediate anneal （RXA） temperature (580℃-670℃) was used to produce SZA-1 alloy cladding, and the final recrystallization temperature 560℃. The radial texture factor(fr) of SZA-1 alloy cladding tubes was obtained by XRD inverse polar figure. The results show in the table 1: For the SZA-1 tube, With the OD was reducing from 31.75mm to 9.5mm, its fr increases from about 0.3mm to more than 0.5. For the same OD, compared with cold work (CW) tube, the recrystallization anneal process inceased fr by 0.04-0.1. Intermediate anneal temperature has less impact on the fr of final tube ,which mainly depends on the final anneal temperature. For the same final anneal (560℃), the fr of final tube is around 0.55.

Table1. Radial texture of SZA-1 alloy tube

OD (mm)	State	Intermediate anneal temperature			
		580℃	595℃	630℃	670℃
31.75	CW	0.32	0.32	0.32	0.32
31.75	RXA	0.38	0.39	0.34	0.40
17.78	CW	0.44	0.40	0.42	0.41
17.78	RXA	0.48	0.52	0.50	0.51
9.5	CW	0.58	0.51	0.54	0.45
9.5	RXA	0.57	0.53	0.54	0.53