INER-F0474 INER-F0474

出國報告（出國類別：其他）

參加第一屆亞洲鋯合金研討會出國公差報告

服務機關：核能研究所
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派赴國家：韓國
出國期間：100 年 6 月 7 日~100 年 6 月 11 日
報告日期：100 年 6 月 27 日

摘要

此次赴韓國公差之主要任務為參加第一屆亞洲鋯合金研討會(1st Asian Zirconium Workshop)，簡報本所在鋯合金材料之重要研究成果，並聽取大陸、日本和韓國在鋯合金材料上之研究發展及成果。

本次會議為期三天(2011 6/8-10)，在韓國東南部大田市(Daejeon)舉行，會議分為5 個議程，共有 39 篇報告：

1. Session 1: Alloy design & basic metallurgy
2. Session 2: Corrosion
3. Session 3: Post irradiation examination
4. Session 4: Safety issues & hydriding
5. Session 5: Fabrication & mechanical property

本所此次應邀與會發表兩篇論文：Enhanced corrosion of zirconium hydride on Zircaloy-4 cladding in 360℃ water、Fracture properties of hydride Zircaloy-4 cladding in recrystallized and stress-relieved conditions。會中並與各國學者在鋯合金燃料護套劣化行為和機制研究上互相交流心得。會議結束後，參觀韓國原子力研究所(Korea Atomic Energy Research Institute, KAERI)的 Hanaro 研究型反應器(Hanaro Research Reator)，以及隸屬於韓國電能公司(Korea Electric Power Corporation, KEPCO)之核燃料工廠(KECPO Nuclear Fuel, KNF)，了解目前韓國在核燃料工業的研究方向及發展現況。

關鍵詞：鋯合金，韓國原子力研究所(KAERI)、燃料護套

目　　錄

(頁碼)

一、目的

此次赴韓國公差之主要任務為參加第一屆亞洲鋯合金研討會(1st Asian Zirconium Workshop)，簡報本所在鋯合金燃料護套材料重要研究成果，並聽取大陸、日本和韓國各國學者在鋯合金材料上研究發展及成果；同時會後參訪 Hanaro 研究用反應器(Hanaro research reactor)、韓國電力公司(Korea Electric Power Corporation, KEPCO)燃料工廠(KECPO Nuclear Fuel, KNF)。

二、過程

100/6/7 ≀ 100/6/7	台北前往韓國大田市（Daejeon, Korea）旅途
100/6/8 ≀ 100/6/10	參加第一屆亞洲鋯合金研討會及參訪 Hanaro 研究用反應器、韓國燃料製造工廠(KepcoNF-TSA)
100/6/11 ≀ 100/6/11	韓國大田市返回台北旅途

(一)第一屆亞洲鋯合金研討會簡介

第一屆亞洲鋯合金研討會(1st Asian Zirconium Workshop)成立的宗旨為：在亞洲國家中，建立彼此在鋯合金研究開發的資訊交流平台。本次會議共有 39 篇研究報告，包含 5 大議題(附錄一)：

1. Session 1: Alloy design & basic metallurgy
2. Session 2: Corrosion
3. Session 3: Post irradiation examination
4. Session 4: Safety issues & hydriding
5. Session 5: Fabrication & mechanical property

核燃料護套的主要作用為固定內部燃料丸及防止核分裂產物溢出。目前大部分輕水式反應器均選用鋯合金（Zirconium Alloy）材料作為核燃料護套，因為鋯合金護套具有較低的中子吸收截面、良好的機械強度及耐腐蝕性等特性；一方面不會吸收中子抑制核燃料連鎖反應，一方面作為在護套內部燃料丸及分裂產物的屏蔽，使其不與爐水接觸。護套的完整性是影響核燃料

運轉實績和安全的重要因素。近年來，各國核電廠均致力於高燃耗運轉目標及延長燃料週期，因此燃料護套將遭受更嚴苛的操作環境與條件，許多以往燃料護套破損的臨界應變或極限應力，將由於腐蝕環境或氧化速率提升而下修，在無法符合高燃耗運轉的需求下，燃料廠家積極開發新的鋯合金燃料護套。

在亞洲地區，日本、韓國是核能工業較為蓬勃發展的國家，由於本身具有燃料製造相關產業，因應核能界未來高燃耗的運轉需求，均致力於鋯合金燃料護套新合金的材料改質及製程開發研究。例如韓國的 HANA4、HANA6 型鋯合金護套，相較於 ZIRLO 燃料護套，採用較低的錫含量及不同的熱處理強化材料強度。

本所應邀參加發表兩篇關於鋯合金護套腐蝕及氫脆研究報告：Enhanced corrosion of zirconium hydride on Zircaloy-4 cladding in 360^{o}C water、Fracture properties of hydride Zircaloy-4 cladding in recrystallized and stress-relieved conditions，報告摘要詳見附錄二、三。

研討會中，關於鋯合金腐蝕行為及安全問題相關議題相當受到重視。在鋯合金腐蝕行為的研究包含在高溫水蒸氣、氫氧化鋰(LiOH)水溶液的腐蝕氧化行為、以及鋯合金中微量合金元素對腐蝕氧化行為的影響；在安全相關議題則包含了高燃耗鋯合金護套在 LOCA 狀態下的行為評估、氫化鋯及碘蒸氣腐蝕對護套劣化行為的研究。另外，日、韓的核能研究機構也分享自有的熱室檢驗及照射後樣品的測試技術供各國專家學者參考。

下一屆的亞洲鋯合金研討會預計於兩年後(2013)在大陸寶雞市舉辦，由大陸上海大學及核動力研究設計院等單位聯合主辦，大陸代表也口頭邀請及歡迎本所人員參與。另外研討會中也簡介明年(2012)將於日本舉行新一代核燃料研討會，由日本 OSAKA 大學主辦。

(二) 參訪 Hanaro 研究用反應器(Hanaro research reactor)、韓國電力公司(Korea Electric Power Corporation, KEPCO)燃料工廠(KECPO Nuclear Fuel, KNF)

Hanaro 位於大田市郊的 KAERI 研究所中，為一 30MW 研究用反應器(圖一、二)，於 1985 年成立至 1996 年開始商轉，主要的用途為：中子照射應用研究、核燃料及材料照射樣品測試、同位素產品開發應用及研究開發下一代核能燃料。Hanaro 反應器廠房相當整齊清潔，門禁使用指紋辨識系統驗

證管制出入人員，控制室位於 4 樓制高處，運轉值班人員以 3 人一組實施 24 小時 3 班制；反應器的附近有部分材料測試系統，提供與爐水相同環境的材料測試條件。熱室位於 1 樓左側，提供照射過後樣品檢測及機械性質測試服務。

KNF 創立於 1982 年，從 2006 年起開始量產韓國核電廠所使用之 PLUS7 型燃料，目前也生產 ZIRLO 燃料及與 KAERI 研究所共同開發新一代的燃料，如 HANA4、6。KNF 的現階段工作以成為全球第三大燃料廠家為目標。KNF 分為燃料丸生產與燃料護套生產兩大部門：燃料護套生產工廠位於距 KAERI 將近 10 分鐘車程的大田市郊，與美國西屋公司技術合作之燃料護套生產工廠，主要生產 ZIRLO 與 Zircaloy-4 燃料護套。燃料護套成品將送往 KAERI 研究所進行燃料完裝填組裝。燃料丸生產工廠位於 KAERI 研究所內，並無開放參觀。

三、心得

近期適逢發生日本福島電廠意外事故，事故發生後，核燃料之安全為使用核能發電國家最緊要處理之問題，因此對以核燃料安全相關的研究議題更為重視。除此之外，日本、韓國目前均著力於高燃耗核燃料行為研究，除了繼續關注目前使用的燃料護套劣化行為研究外，更積極從事新一代核燃料護套的開發與研究，在不斷提升核能發電效率下，防範及降低核能事故的發生。

鋯合金護套是核燃料最主要的保護防線，本所以往參加 NFIR 相關研究計畫，在鋯合金護套的各項研究均有相當卓越的成果。雖然台灣並無核燃料製造相關產業，但宜針對日本福島電廠意外事故中用過燃料池喪失冷卻功能議題，及用過核燃料貯存議題，今後宜加強鋯合金護套在高溫水汽中氧化劣化行為之探討，並繼續關注燃料護套在中期乾式貯存期間各項材料行為變異及機械性質衰退的研究，並配合熱室檢驗加強照射過鋯合金護套劣化行為評估能力之建立，以應用於國內核燃料相關工作之需求。同時，為瞭解各國在核燃料護套的開發研究與相關安全評估，本所宜持續積極參與國際性核燃料相關之研討會。

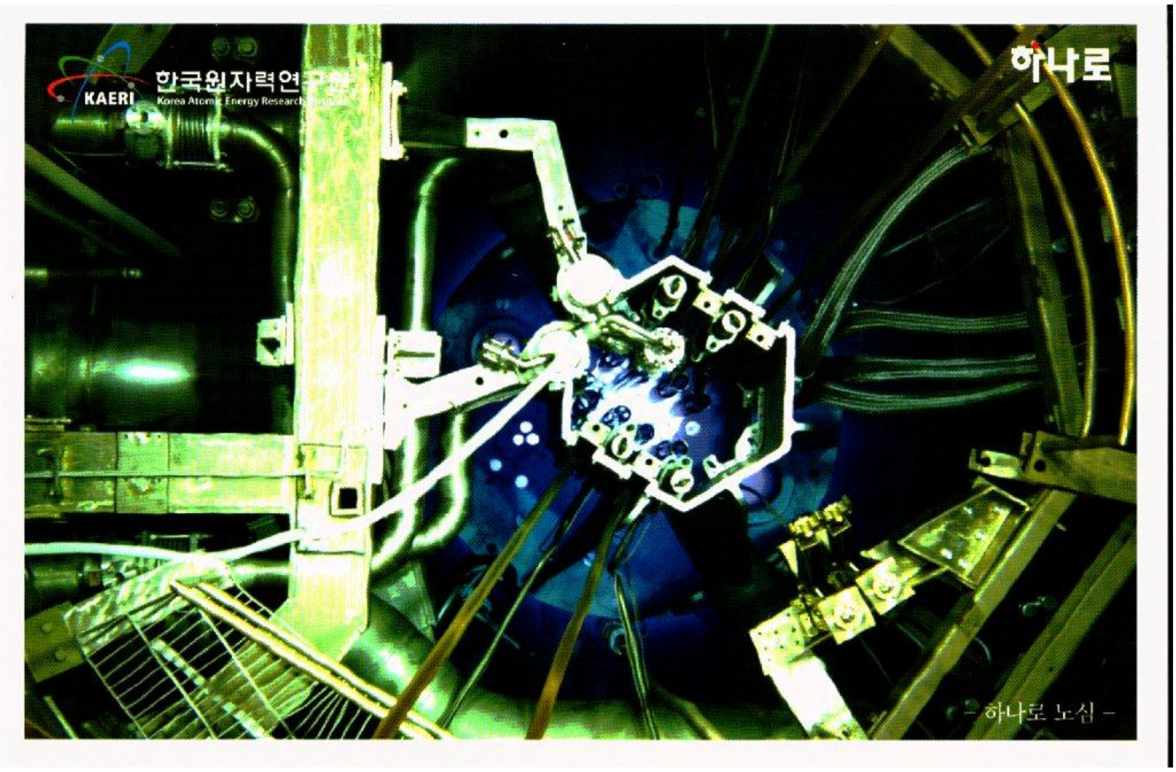
四、建議事項

雖然日本福島電廠的意外事故帶給國際上不少反核議題的爭論，從此次亞洲鋯合金研討會卻可看出日本、韓國及大陸仍對核能產業抱持積極樂觀的態度，持續投入核能相關產業的開發與人才的培育，尤以韓國為最。本所以往在核能電廠的運轉實績及相關安全評估皆有豐富的經驗及紮實的研究開發能力，今後將持續加強核燃料相關技術研發，以確保核電廠安全之政策目標。建議事項如下：

一、 持續參加核燃料相關國際會議或研討會，以獲取國際上最新資訊與技術。

二、 因應用過燃料池可能發生喪失冷卻功能之情境，宜加強鋯合金護套材料在水汽中高溫氧化劣化行為探討。

三、繼續關注燃料護套在中期乾式貯存期間各項材料行為變異及機械性質衰退的研究，以應用於用過燃料處置之需求。



圖一　　HANARO 反應器

圖二　　HANARO 反應器廠房

附錄一 亞洲鋯合金研討會會議程序

Workshop Program

1st Asian Zirconium Workshop

June 8–10, 2011
Hotel Spapia, Daejeon, South Korea

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 39 research papers to be presented in the inaugural workshop. The workshop consists of four plenary talks and five sessions of alloy design and basic metallurgy, corrosion, irradiation properties, safety issues, and fabrication and mechanical properties. In addition, technical tour to KepcoNF-TSA (Korean cladding manufacturer) and HANARO (Korean research reactor) is provided.

Program at a glance

	8 JUNE (WED)	9 JUNE (THU)	10 JUNE (FRI)
9:00		Session 2 Corrosion	Session 5 Fabrication & Mechanical Property
9:20			
9:40			
10:00			
10:20		Coffee break	Coffee break
10:40	Registration		
11:00		Corrosion	Fabrication & Mechanical Property
11:20			
11:40			
12:00			
12:20		Lunch	Closing Remarks
13:00			Lunch
13:30	Opening Remarks		
14:00	Plenary	Session 3 Post Irradiation Examination	Technical Tour (applicants only)
14:20	(1) K. Linga Murty		
14:40	(2) Bo Cheng		
15:00	(3) Bangxin Zhou		
15:20	(4) Fumihisa Nagase		
15:40		Coffee break	
16:00	Coffee break	Session 4 Safety Issues & Hydriding	
16:20	Session 1 Alloy Design & Basic Metallurgy		
16:40			
17:00			
17:20			
17:40			
18:00			
18:20			
19:00	Welcome Reception	Workshop Dinner	

Wednesday, 8 June 2011

Opening

13:30 - 13:40	**Opening Address** Yong-Hwan Jeong

PLENARY

Session Chairs: Yong-Hwan Jeong (KAERI)

13:40 - 14:10	**Creep Anisotropy and Transitions in Zircaloy Cladding** K. Linga Murty (NC State Univ.)
14:10 - 14:40	**Evolution of Zirconium Alloy Fuel Cladding to Meet Demanding Fuel Performance Requirements** Bo Cheng (EPRI)
14:40 - 15:10	**Study of the Oxide Films formed on Zircaloy-4** Bangxin Zhou (Shanghai Univ.), Q. Li, M.Y. Yao
15:10 - 15:40	**Failure Behavior of LWR Fuel Cladding under Accident Conditions: Key Observations from Fuel Safety Research Program at JAEA** Fumihisa Nagase (JAEA), T. Sugiyama, M. Amaya, Y. Udagawa, T. Fukuda, T. Mihara
15:40 - 16:00	*Coffee Break*

SESSION 1 **Alloy Design & Basic Metallurgy**

Session Chairs: Jeong-Yong Park (KAERI)
Fumihisa Nagase (JAEA)

16:00 - 16:20	**HANA Alloys for High Performance Fuel Components** Jeong-Yong Park (KAERI), Hyun-Gil Kim, Byung-Kwon Choi, Sang-Yoon Park, Yang-Il Jung, Dong-Jun Park, Yong Hwan Jeong
16:20 - 16:40	**Effect of Impurity Hafnium on the Physical Properties of Delta-phase Zirconium Hydrides** Ken Kurosaki (Osaka Univ.), H. Kimura, H. Muta, Y. Ohishi, K. Konashi, S. Yamanaka
16:40 - 17:00	**The Effect of Reprocessing on Microstructure Evolution of Zr-Sn-Nb Alloy Plates** Dai Xun (NPIC), Zhao Wenjin, Liu Hong, Jiang Hongman, Wang Ying
17:00 - 17:20	*Coffee Break*

17:20 - 17:40	**Effect of Microstructure on the Corrosion Behavior of Zr-Sn-Nb-Fe (Cr) Alloys** Meiyi Yao (Shanghai Univ.), B.X. Zhou, Q Li, J.C. Peng, W.Q. Liu
17:40 - 18:00	**Effect of Cooling Rates on the Microstructural Changes of Zr-0.85Sn-0.4Nb-0.4Fe-0.1Cr-0.05Cu Alloy during β→α Transformation** Linjiang Chai (Chongqing Univ.), Baifeng Luan, Jianwei Chen, Jun Zhou, Qing Liu
18:00 - 18:20	**Qualification of HANA Claddings for Commercialization** Sang Jin Han (KEPCO-NF), Seung Hwan Lee, In Kyu Kim, Jong Yeol Kahng
19:00 - 20:00	*Welcome Reception*

Thursday, 9 June 2011

SESSION 2	Corrosion
	Session Chairs: Kwangheon Park (Kyunghee Univ.) Wenjin Zhao (NPIC)
9:00 - 9:20	**Effect of Cu on the Corrosion Resistance of Zirconium Alloys in Superheated Steam at 500℃** Meiyi Yao (Shanghai Univ.), X. Zhang, S.L. Li, Q. Li, J.C. Peng, B.X. Zhou
9:20 - 9:40	**Enhanced Corrosion of Zirconium Hydride on Zircaloy-4 Cladding in 360℃ Water** Jen-Hung Chen (INER), Cheng-Chang Peng, Wen-Chen Liao
9:40 - 10:00	**Adsorbed LiOH Effects on the Oxidation of Zr-alloys in Air** Kwangheon Park (Kyunghee Univ.), Yeonseung Kim, Kwangil Ho
10:00 - 10:20	**High Temperature Oxidation Behavior of N18 Zirconium Alloy in Steam** Jun Qiu (NPIC), Wen-Jin Zhao, Xin Liu
10:20 - 10:40	*Coffee Break*
10:40 - 11:00	**Mechanism of LiOH Aqueous Solution Accelerating Corrosion Rate of Zircaloy-4** Wenqing Liu (Shanghai Univ.), Qiang Li, Meiyi Yao
11:00 - 11:20	**Electrochemical Characterization of Oxide Film of Zry4 and NDA in High Temperature Water** Kiyoko Takeda (Sumitomo Metal Industries)
11:20 - 11:40	**A New Manufacturing Process of Zr-Alloy Strips for Spacer Grids** Yang-Il Jung (KAERI), Byoung-Kwon Choi, Hyun-Gil Kim, Dong-Jun Park, Sang-Yoon Park, Jeong-Yong Park, Yong-Hwan Jeong

11:40 - 12:00 **Preliminary Performance Models of HANA Claddings**
Jae-Myung Choi (KEPCO-NF), J.S. Yoo, H.T. Han, H.K. Kim, B.J. Cho, J.I. Kim, K.L. Jeon, J.Y. Park, H.G. Kim, Y.H. Jeong

12:00 - 12:20 **Effect of Cu on the Corrosion Resistance of Zr-2.5Nb Alloys Corroded in SCW at 550℃/25 MPa**
Qiang Li (Shanghai Univ.), B.X. Zhou, M.Y. Yao, J.C. Peng, X. Liang

12:20 - 14:00 *Lunch*

SESSION 3 Post Irradiation Examination

Session Chairs: Jong Seong Yoo (KEPCO-NF)
Jen-Hung Chen (INER)

14:00 - 14:20 **Study on Mechanical Properties of PWR Fuel Cladding after Power Transient up to Burn-up of 42MWd/kgU**
Kazuaki Yanagisawa (JAEA)

14:20 - 14:40 **Microstructural Characteristics of HANA Claddings after Irradiated in Research Reactor**
Hyun-Gil Kim (KAERI), Byoung-Kwon Choi, Yang-Il Jung, Dong-Jun Park, Sang-Yoon Park, Jeong-Yong Park, Yong-Hwan Jeong

14:40 - 15:00 **Irradiation effect on Mechanical Properties of N18 Zircaloy Weld Joints**
Guoyun Li (NPIC), Haisheng Zhang, Juan Huang, Furong Li, Lili Liu

15:00 - 15:20 **Uniaxial Hoop Tensile Test Technique for a Nuclear Fuel Cladding in a Hot Cell**
Masafumi Nakatsuka (NFD), K. Sakamoto, S. Saito, M. Aita

15:20 - 15:40 **Post Irradiation Examination of High Burn-up ZIRLO Cladding at the Conformal Contact Shaped Spacer Grid Position**
Jeong-Nam Jang (KAERI), Duck-Kee Min, Hyung-Moon Kwon, Joo-Seong Kim, Yong-Bum Chun

15:40 - 16:00 *Coffee Break*

SESSION 4 Safety Issues & Hydriding

Session Chairs: Kyu Tae Kim (Dongguk Univ.)
Ken Kurosaki (Osaka Univ.)

16:00 - 16:20 **A Study on Fuel Rod Oxidation-Induced Fuel Failure**
Kyu Tae Kim (Dongguk Univ.), Myung Soo Kim

16:20 - 16:40	**Safety Evaluation of Simulated High Burn-up Fuel Cladding under LOCA Condition** Dong-Jun Park (KAERI), Yang-Il Jung, Byung-Kwon Choi, Hyun-Gil Kim, Sang Yoon Park, Jeong-Yong Park, Yong Hwan Jeong
16:40 - 17:00	**Analyses on Hydrogen Diffusion to a Crack Tip in Delayed Hydride Cracking of Zircaloy-2** Toshio Kubo (NFD), Y. Kobayashi, K. Sakamoto, T. Higuchi
17:00 - 17:20	*Coffee Break*
17:20 - 17:40	**Evaluation of an ISCC Mechanism and a PCI Resistance of HANA Cladding** Sang Yoon Park (KAERI), Jeong-Yong Park, Hyun-Gil Kim, Byung-Kwon Choi, Yang-Il Jung, Dong-Jun Park, Yong Hwan Jeong
17:40 - 18:00	**Fracture Properties of Hydrided Zircaloy-4 Cladding in Recrystallized and Stress-Relieved Conditions** Hsiao-Hung Hsu (INER), Wen-Chen Liao
18:00 - 18:20	**The Effects of Steam Pressure on the Oxidation of Zr-alloys at High Temperatures** Kwangheon Park (Kyunghee Univ.), Sungwoo Yang, Kwangil Ho
19:00 - 21:30	*Workshop Dinner*

Friday, 10 June 2011

SESSION 5	**Fabrication & Mechanical Property**
	Session Chairs: In Kyu Kim (KepcoNF-TSA) Meiyi Yao (Shanghai Univ.)
9:00 - 9:20	**Westinghouse Qualification to supply KEPCO NF's Tube** Nam Chan Cho (KepcoNF-TSA), Jung Suk Park, Jong Yeol Kahng
9:20 - 9:40	**ZIRLO® Cladding Tube Properties made by KEPCO NF** Yong Kyun Mok (KEPCO-NF), Y.H. Kim, S.J. Lee, J.I. Kim, K.L. Jeon, S.D. Kim
9:40 - 10:00	**The Compression Deformation Behavior of Zirconium Alloy with Different Grain Orientations at High Temperature** Shasha Gao (Chongqing Univ.), Baifeng Luan, Qing Liu
10:00 - 10:20	**Microstructural and Textural Developments during Tube Fabrication of Zr-Sn-Nb alloy** Dai Xun (NPIC), Zhao Wenjin, Liu Hong, Wang Pengfei, Dai Xun, Liu Hong, Jiang Hongman, Wang Ying, Zhao Wenjin

10:20 - 10:40	*Coffee Break*
10:40 - 11:00	**Development of Two Passes Cold Pilgering Technology for Dashpot Tube** Ki Bum Park (KepcoNF-TSA), In Kyu Kim, Yong shin Choi, Jong Yeol Kahng
11:00 - 11:20	**Effect of Initial Texture on Deformation Mechanisms and Texture Evolution of the Zr-Sn-Nb Sheets during Cold Rolling** Jianwei Chen (Chongqing Univ.), Baifeng Luan, Hongbing Yu, Qing Liu, Zhongkui Li
11:20 - 11:40	**Temperature Dependence of Deformation Anisotropy in Zircaloy-4 Fuel Cladding** Toshiya Kido (NDC), T. Kitagawa, K. Ogata
11:40 - 12:00	**Twinning Behavior of Pure Zr during Rolling at 77K** Baifeng Luan, Qing Ye (Chongqing Univ.), Yunchang Xin, Chongsheng Long, Qing Liu
12:00 - 12:20	**Status of Korean Zirconium Industry and Plan of Zirconium Extraction** Go-Gi Lee (RIST), Mi-Seon Choi, Sung-Koo Jo, Chang-Kyu Lee, Jae-Young Jung

Closing

12:20 - 12:30	**Closing Remarks** Yong-Hwan Jeong
12:30 - 14:00	*Lunch*

Technical Tour

14:00 - 16:00	**Technical Tour to KepcoNF-TSA and HANARO** (applicants only)

Committees

Organizing Committee (from Korea):

Yong Hwan JEONG (Chair, KAERI), Jeong-Yong PARK (KAERI)
Kyeong Lak JEON (Kepco-NF), Chan Hyun PARK (Kepco-NF)
Kyu Tae KIM (Dongguk Univ.), Kwangheon PARK (Kyunghee Univ.)

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附錄二 發表論文摘要與簡報內容

ENHANCED CORROSION OF ZIRCONIUM HYDRIDE ON ZIRCALOY-4 CLADDING IN 360℃ WATER

Jen-Hung Chen, Cheng-Chang Peng and Wen-Chen Liao

Institute of Nuclear Energy Research, Taiwan

Corresponding author: jhchen@iner.gov.tw

In order to investigate the role of zirconium hydride in the oxidation of fuel cladding at high burnups, a long term corrosion test of Zircaloy-4 cladding with different levels of hydrogen content was performed. Zircaloy-4 tube specimens were uniformly hydrided to 120ppm and 500ppm respectively by a gaseous thermal cycling process. Moreover, for the specimen with extremely high hydrogen concentration, an external hydride layer was formed on the external surface of Zircaloy-4 tube by a cathodic charging. Then four specimens with different hydrogen concentrations were tested in autoclave with 360℃ saturated water according to ASTM G2 specification. The weight gains were measured periodically during the exposure time of 300 days.

The results indicate that corrosion rate significantly increases with increasing hydrogen content, as shown in Fig. 1. The as-received specimen shows the lowest weight gain while compared to the other three hydrided specimens. The two uniformly hydrided specimens show similar increase of weight gain with the exposure time. However the specimen with external hydride layer shows the highest corrosion rate and demonstrates a linear relationship between weight gain and exposure time. The effect of enhanced corrosion with increasing hydrogen concentration is revealed in Fig.2. It is obvious that the weight gain for hydride-layered specimen is several times more than those for the other three specimens with low hydrogen content after 60-day exposure. The enhanced corrosion of hydride-layered specimen increases with the increasing exposure time until end of the test, 300 days. It can be concluded that zirconium hydrides in Zircaloy-4 cladding enhance the corrosion in water and the enhancement is more significant in long term exposure.

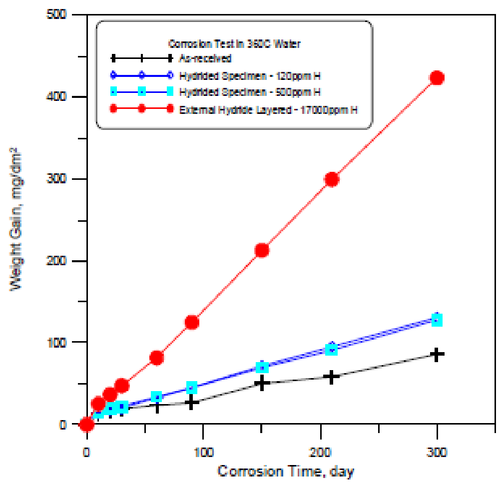


Figure 1: Weight gain against exposure time in 360℃ water for the hydrided Zircaloy-4 tube specimens.

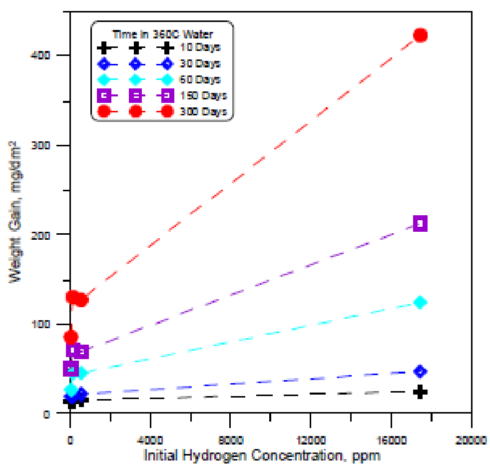


Figure 2: Effect of enhanced corrosion with increasing hydrogen concentration revealed by increasing exposure time.

Enhanced Corrosion of Zirconium Hydride on Zircaloy-4 Cladding in 360℃ Water

Presented at
1st Asian Zirconium Workshop
Hotel Spapia, Daejeon, South Korea
June 8 – 10, 2011

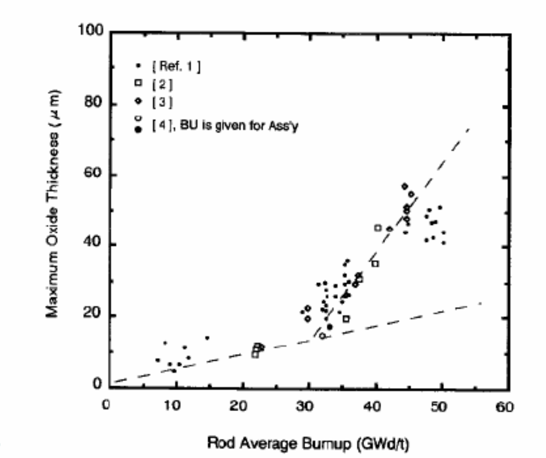
By
Jen-Hung Chen
Institute of Nuclear Energy Research

Outline

- Introduction and Objective
- Experimental
- Results
- Conclusions

Introduction

- The corrosion of Zircaloy-4 cladding is accelerated at high burnups in PWRs
- Hydride is one of the possible causes for the corrosion enhancement



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Objective

- To investigate the corrosion behaviour of Zircaloy-4 cladding with hydrogen in water
- To investigate the effect of hydrides on the corrosion of Zircaloy-4 cladding

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Experimental

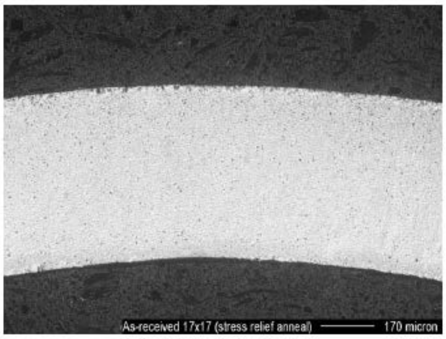
- Specimen Preparation
  - Zircaloy-4 tube with 3 cm long, 9.5mm outer diameter, and 8.375mm inner diameter
- Specimen Hydriding
  - As-received specimen with H $<$ 20 ppm
  - 120 ppm H and 500 ppm H by a gaseously thermal cycling process
  - 40 μm external hydride layer by a cathodic charging

Experimental

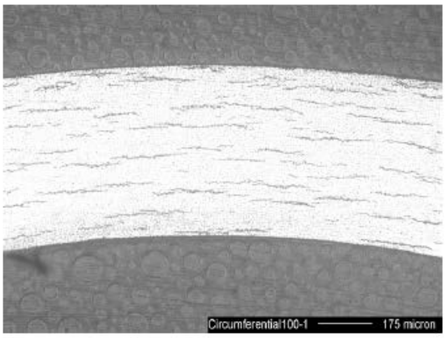
- Corrosion Test
  - Static autoclave test in 360℃ saturated water
    - ✓ According to ASTM G2 specification
  - Weight gain measured at 10, 20, 30, 60, 90,150, 210, and 300 days

Experimental

- Specimen micrographs before testing



As-received Zry-4 cladding



Zry-4 cladding with 120 ppm H

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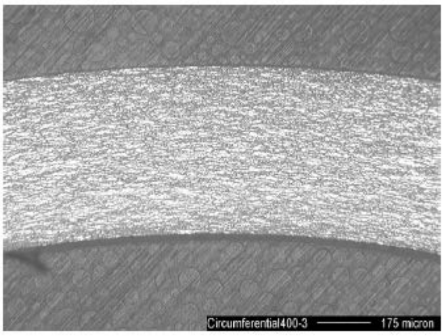
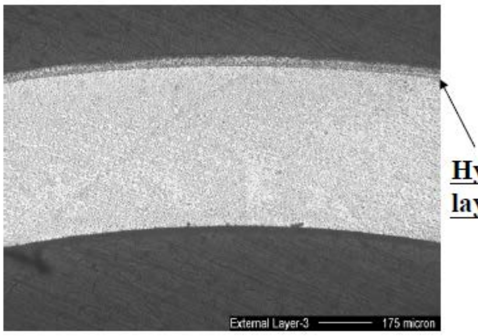
Experimental

- Specimen micrographs before testing



Zry-4 cladding with 500 ppm H



Hydride layer

Zry-4 cladding with 40 μm external hydride layer

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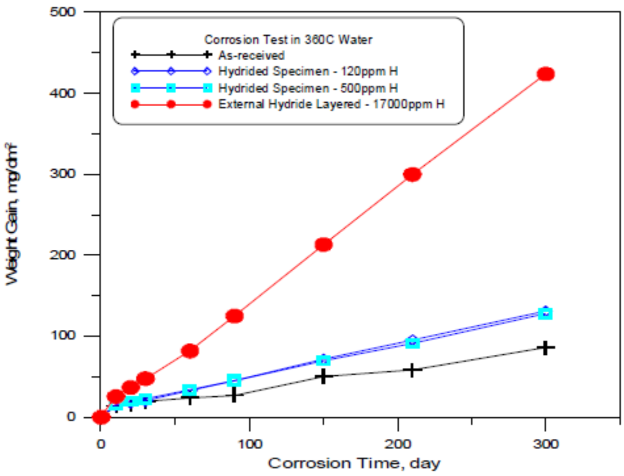
Results

- Weight gain
  - Linear rate law
  - Increases with increasing hydrogen

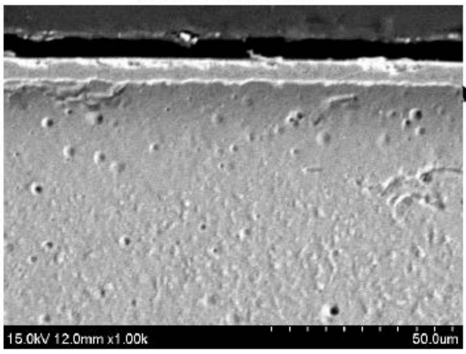


Weight gain against exposure time in 360℃ water for the hydrided Zircaloy-4 tube specimens.

Results

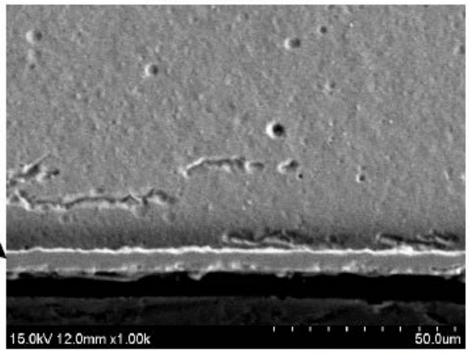
- Oxide layer after 300 days
  - As-received specimen
  - ~5 μm

Outer surface



oxide layer

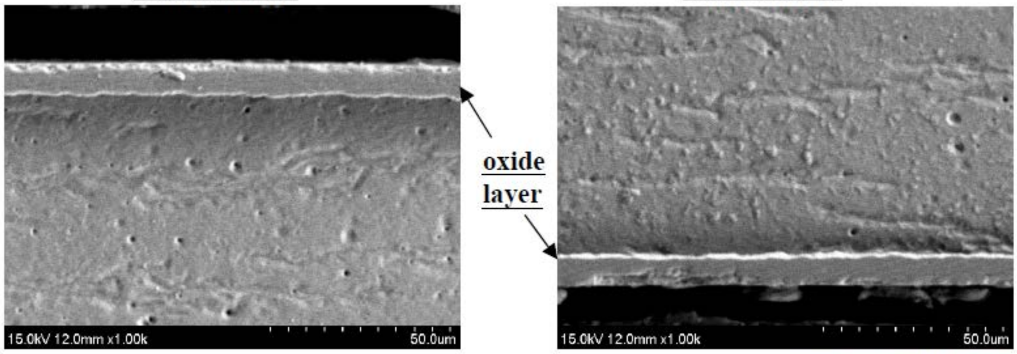
Inner surface



Results

- Oxide layer after 300 days
  - Specimen with 120 ppm H
  - ~10 μm

Outer surface　　Inner surface



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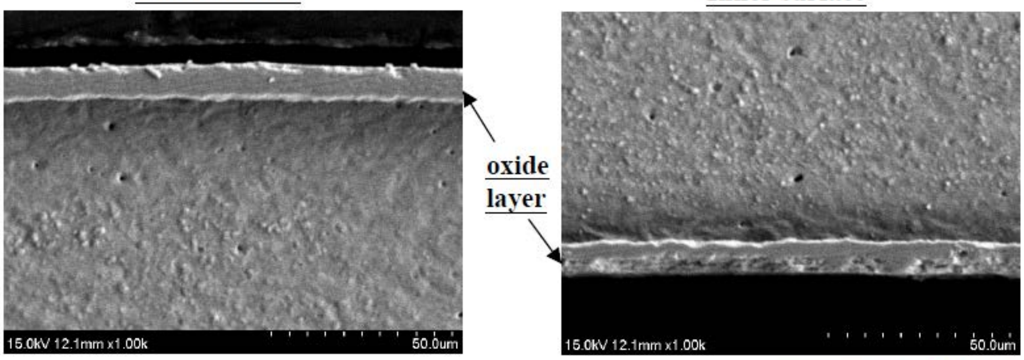
Results

- Oxide layer after 300 days
  - Specimen with 500 ppm H
  - ~10 μm

Outer surface　　Inner surface



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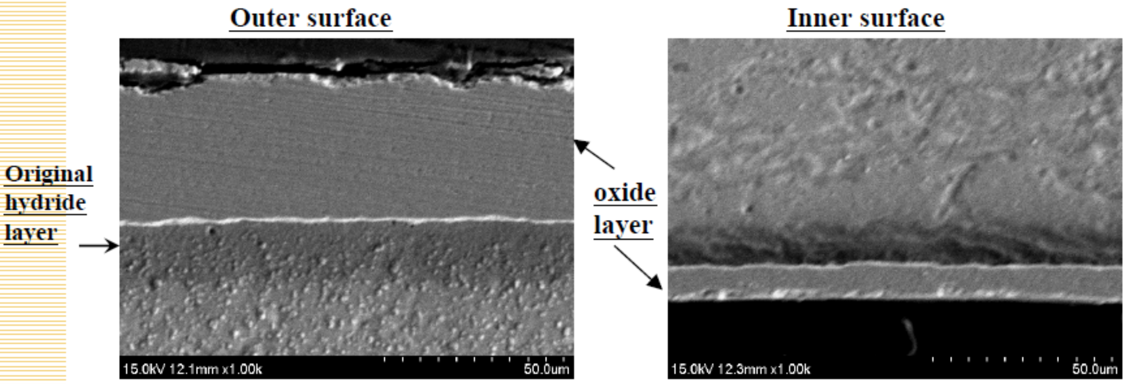
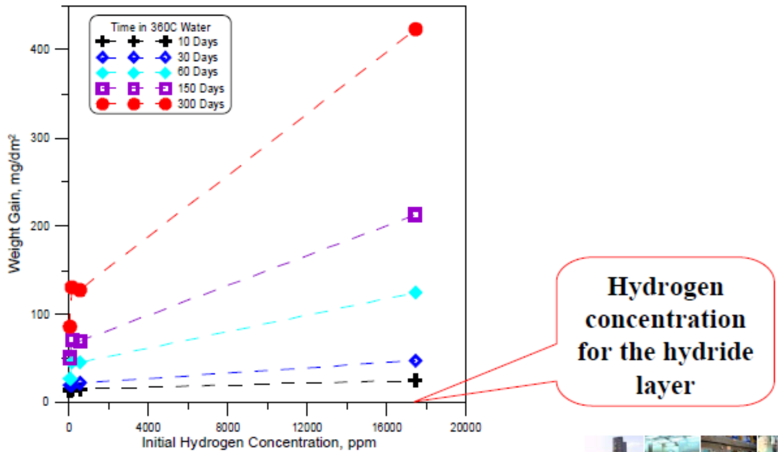
Results

- Oxide layer after 300 days
  - Specimen with external hydride layer
  - ~40 μm at outer surface, ~10 μm at inner surface



Results

- Effect of enhanced corrosion
  - Significant enhanced-corrosion at higher H content and longer exposure time



Conclusions

- Zircaloy-4 cladding corrosion rate in 360℃ water increases with increasing hydrogen content.
- Oxide layer thickness is consistent with the weight gain result
- Zirconium hydrides (layer) in Zircaloy-4 cladding significantly enhance the corrosion and the enhancement is revealed in long term exposure.

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附錄三 發表論文摘要與簡報內容

FRACTURE PROPERTIES OF HYDRIDED ZIRCALOY-4 CLADDING IN RECRYSTALLIZED AND STRESS-RELIEVED CONDITIONS

Hsiao-Hung Hsu, Wen-Chen Liao

Institute of Nuclear Energy Research (INER), Lungtan Township, Taoyuan County 325, Taiwan

Corresponding author: hhhsu@iner.gov.tw

Abstract

Hydrogen embrittlement occurs when there are sufficient hydrides to cause detrimental effects to mechanical properties, including tensile ductility and fracture toughness of Zircaloy (Zry) fuel cladding, at high burnups. In this study, the stress-relieved (SRA) and recrystallized (RXA) Zry-4 cladding tubes were hydrogen-charged to the 300 wppm and manufactured into X-specimens [1]. For comparison purpose, the *J*-integral values of Zry-4 cladding have been obtained to evaluate the susceptibility to hydrogen embrittlement. The *J*-integral values for both RXA and SRA Zry-4 x-specimens at room temperature decreased significantly as the hydrogen concentration increased, as shown in Fig. 1. The brittle zirconium hydrides formed could impact the fracture toughness of Zry-4 cladding. For Zry-4 cladding with the same level of 300-wppm hydrides, the *J*-integral values in RXA condition were higher than the ones in SRA condition. As shown in Fig. 2, the degradation of fracture toughness depends on the zirconium grain morphology and hydride distribution.

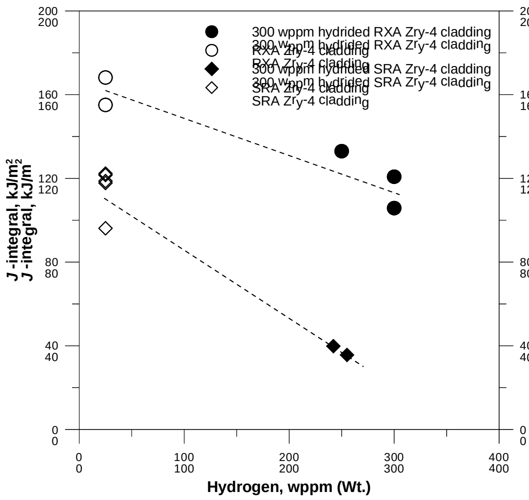
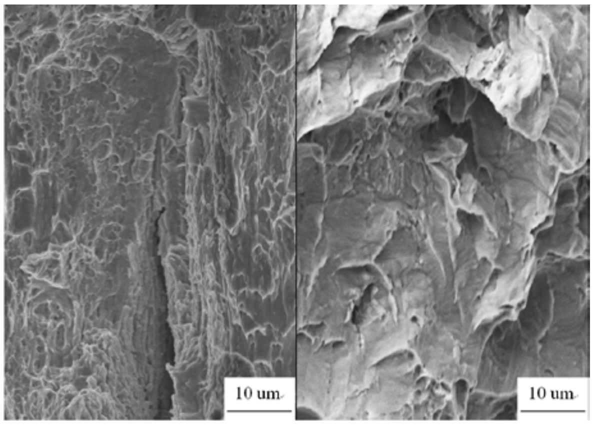


Figure 1: J-integral values against hydrogen content for Zry-4 cladding



(a) (b)

Figure 2: SEM Fractographs of 300-wppm hydrogen (a)SRA and (b) RXA Zry-4 cladding. (The crack propagation from top to bottom of the fractographs)

[1] H.H. Hsu, K.F. Chien, H.C. Chu, R.C. Kuo, P.K. Liaw, ASTM STP 1406, 2001, pp.214.

Fracture properties of hydrided Zircaloy-4 cladding with recrystallized and stress-relieved annealing conditions

Presented at
1st Asian Zirconium Workshop
Hotel Spapia, Daejeon, South Korea
June 8-10, 2011

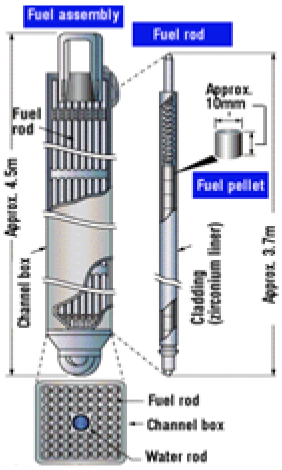
By
Hsiao-Hung Hsu
Institute of Nuclear Energy Research

Outline

- Introduction and Objective
- Experimental
- Results
- Conclusions

Introduction

- Zircaloy materials
  - neutron transparency
  - satisfied mechanical strength
  - corrosion resistance
- Design and criteria
  - More than 1 % plastic strain
  - BWR
    - recrystallized (RXA)
  - PWR
    - cold worked stress relief (SRA)



Introduction

- High burnup
  - Irradiation
  - Hydrogen embrittlement
  - PCI (pellet-cladding interation)
- Spent fuel dry storage
  - Creep
  - Delay hydride cracking
  - Stress corrosion cracking (SCC)

Objective

- Fracture behavior of thin-walled tube
- Hydrogen embrittlement of Zircaloy-4 cladding (Zry-4)
  - Recrystallized annealing (RXA)
  - Stress-relieved annealing (SRA)

Experimental

- Materials: Zry-4 cladding
  - SRA: archived
  - RXA: 650°C, 5 hrs in vacuum
- Hydrogen charging
  - Gaseously thermal cycling process: 300 wppm
- Fracture toughness testing
  - X-specimen test

Experimental

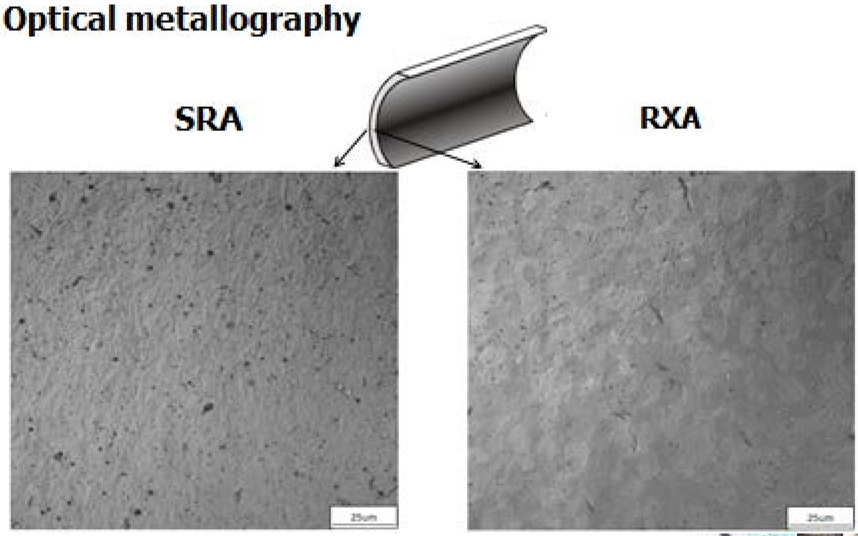
- **Chemical composition of Zry-4 cladding**

Chemical composition of Zry-4 cladding

Element	wt.%
Cr	0.11
Fe	0.21
O	0.12
Si	<0.01
Sn	1.2
Zr	Balance

Experimental

Optical metallography



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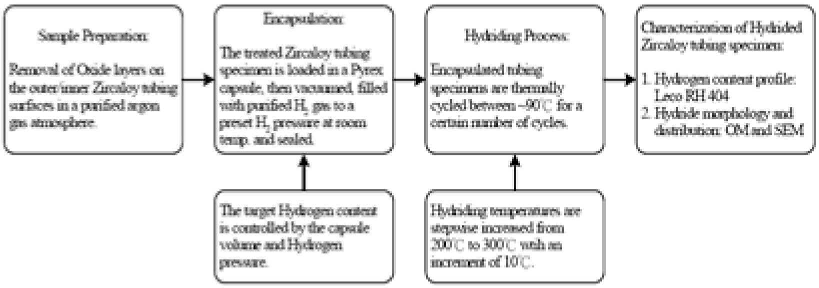
Experimental

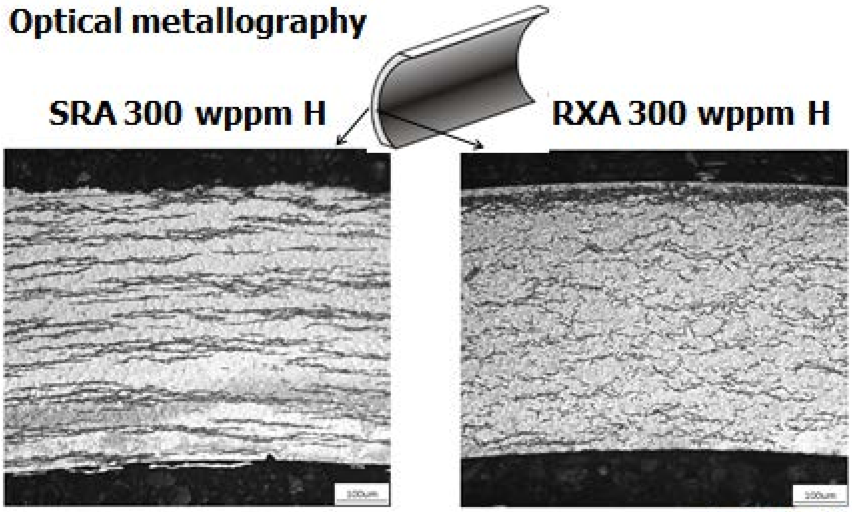
- **Hydrogen charging method**
  - Gaseously thermal cycling process



Experimental

Optical metallography

SRA 300 wppm H **RXA 300 wppm H**



Experimental

- **Considerations of Specimen Design**
  - An axial through-wall flaw
    - Loaded in the circumferential direction
    - Crack propagated along the cladding axis
  - Curved compact tension specimen
    - A similar test method as flat CT specimen
  - Bending effect
    - Simplifying the stress field around the crack-tip

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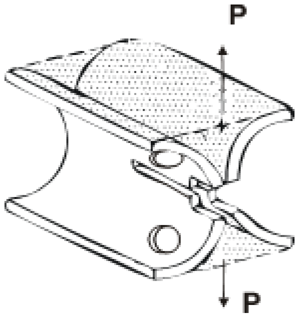
Experimental

- **Specimen Model**
  - Two curved CT specimens sampled from a hollow thin-wall tube section
  - Bond two specimens with epoxy adhesive to minimize the bending effect



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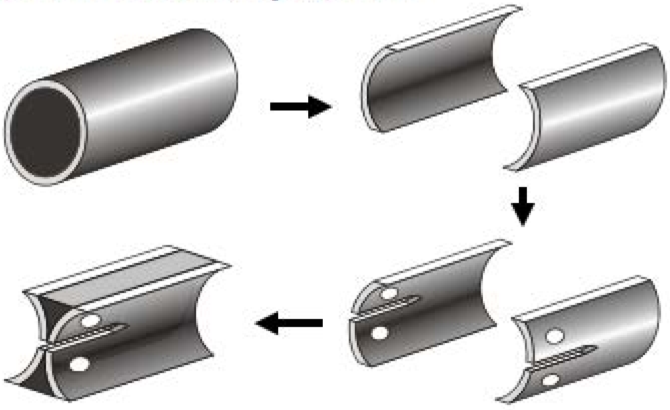
Experimental

- Flowchart for fabrication of Zry-4 cladding specimen into an X-specimen



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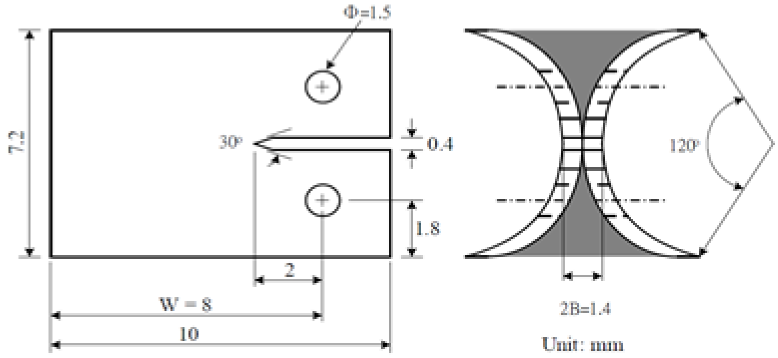
Experimental

- Configuration and dimensions of an X-specimen



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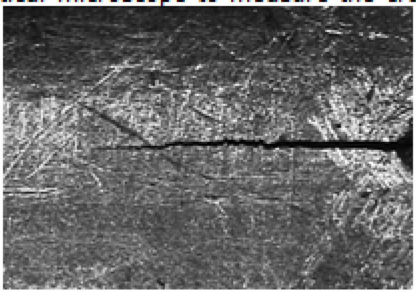
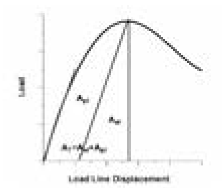
Experimental

- **X-specimen Testing**
  - Fatigue precrack to *a/W* =0.5~0.6
    - Frequency=1Hz
    - R=0.2
    - P_{max}=100 N
  - Using an optical microscope to measure the crack extension



Experimental

- **X-specimen Testing**
  - Simple tension
  - P-LLD curve



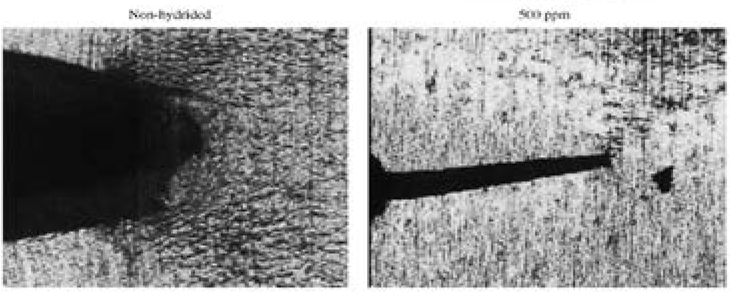
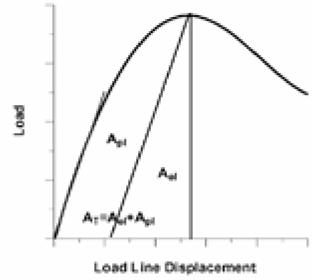


Fig. 8. The crack blunting of the crack tip on the inner surfaces of X-specimen with plastic deformation.

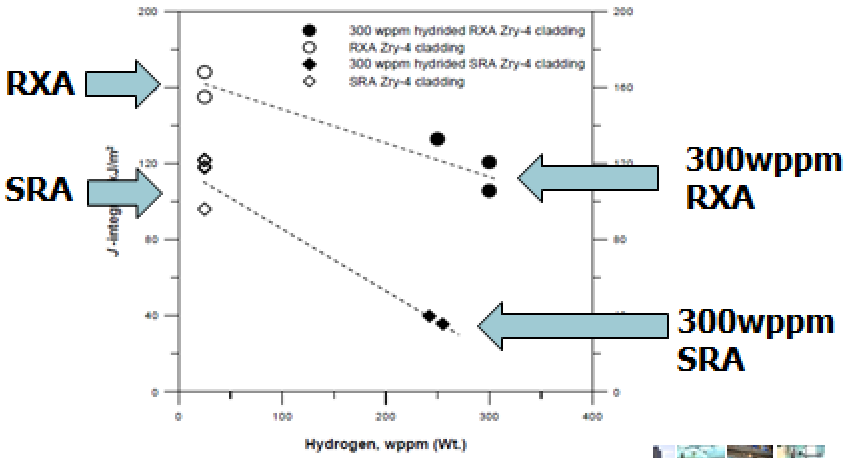
Results

- **Fracture Toughness Determination**
  - *J*-integral
    - $J = A_T / Bb_0$
    - A_T is the total area under the load versus load-line displacement curve, B is specimen thickness, and b_0 is the uncracked ligament length. The coefficient β depends on the ratio a_0/b_0, where is the initial crack length.



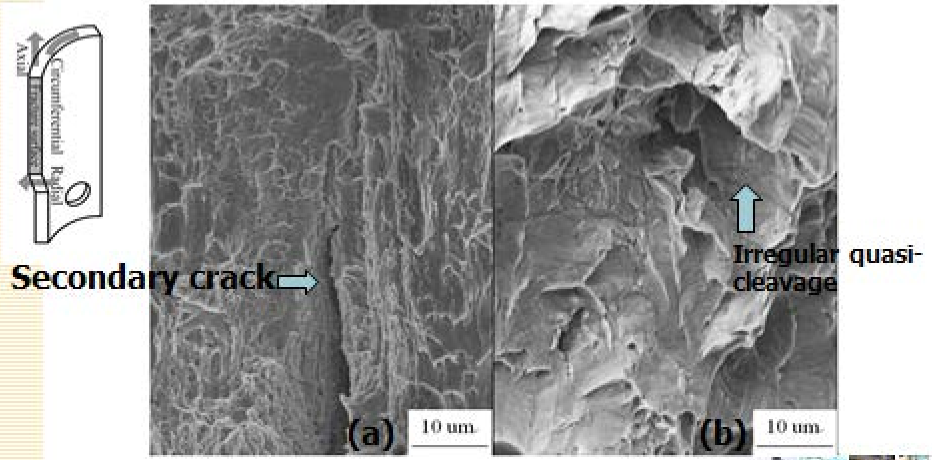
Results

- ***J*-integral**



Results

- 300-wppm hydrogen (a)SRA and (b) RXA Zry-4 cladding



Results

- A Comparison of Fracture Toughness Results Obtained by X-Specimen Tests

Fracture Toughness of Zry-4 cladding	SRA 300wppm circumferential hydrides	SRA 300wppm radial hydrides	RXA 300wppm hydrides
Unit: kJ/m^2	~40	~12	~115

Conclusions

- The *J*-integral values for both RXA and SRA Zry-4 x-specimens at room temperature decreased significantly as the hydrogen concentration increased.
- For Zry-4 cladding with the same level of 300-wppm hydrides, the *J*-integral values in RXA condition were higher than the ones in SRA condition.
- The degradation of fracture toughness depends on the zirconium grain morphology and hydride distribution.

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