HYDRIDE FORMATION IN ZIRCONIUM ALLOYS

by

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Dedicated to

My Parents Nimishakavi Venkata Visweswara Rao Nimishakavi Nagalakshmi

ABSTRACT

Zirconium alloys pickup hydrogen, during reactor operation. When the hydrogen content exceeds the solubility limit, the hydrides are formed. These hydrides have deleterious influence on the mechanical properties of the material. Therefore, it is important to improve our understanding of hydride morphology and behavior at different conditions approximating nuclear reactor environments.

Initial analysis was done on the hydrided, cold-worked and stressrelieved (CWSR) Zircaloy-4 sheet-samples. The hydrides have been identified as δ -ZrH_{1.5} phase. They were located within the grains and along the grain boundaries, but the grain boundary hydrides appeared to be dominant. The preferential orientation relationship of $(0001)\alpha$ -Zr//(111) δ -ZrH_{1.5} was observed between hydrides and the matrix at all locations. The changes in hydrogen concentration had no effect on the crystallographic orientation relationship of the hydrides.

Subsequently, the hydride behavior under hoop stress has been studied in detail. A range of hoop stresses were applied to the Zircaloy-4 cladding tube in a high pressure hydrogen gas furnace at a temperature of 350°C and a pressure of 20 MPa. Optical micrographs of the samples showed an increase in the number of hydrides oriented along radial direction at higher hoop stresses. Apart from radial hydrides, the hydrides which were inclined at an angle to circumferential and radial directions were also observed. Interestingly, the hydrides which were oriented perpendicular to the circumferential direction followed a $\{10\overline{1}1\}\alpha$ -Zr/ $\{111\}\delta$ -ZrH_{1.5}. relationship with the matrix grains. Habit planes of $\{10\overline{1}1\}$, $\{10\overline{1}7\}$, $\{10\overline{1}3\}$, $\{10\overline{1}0\}$ were observed for the hydrides which were inclined at an angle to the circumferential direction. This study helps in understanding the complex behavior of radial hydrides.

An attempt has been made to understand the superior resistance to corrosion and substantially lower hydrogen pickup of the Zr-1Nb alloy when compared with Zircaloy-4. Thus, Zircaloy-4, Zr-2.5Nb and Zr-1Nb (E110) alloys were hydrided in a high pressure hydrogen gas furnace. The hydrides in Zr-1Nb (E110) were short and thick, without any preferential orientation with respect to the sample reference direction. Heavy $\{10\bar{1}2\}$ twins were observed in the Zr-1Nb alloys, which were not seen in the Zircaloy-4 and Zr-2.5Nb alloys. Almost 50 % of hydrides in the Zr-1Nb (E110) alloy showed a new crystallographic relation of $(0001)\alpha$ -Zr// $\{100\}\delta$ -ZrH_{1.5}. This new orientation relationship in the Zr-1Nb alloy is attributed to the presence of twin boundaries.

In addition, the microstructural changes at the weld zone and its effects on the hydride behavior have been studied. The weld zone shows predominantly basket-weave structures, with very few colonies of parallel plate structures. Variant selection for α -phase formation inside prior

β-grains was identified at the weld center. As we move from the weld center to the as-received zone, the variant selection is found to be less probable. At the weld zone, a complete random orientation of hydrides was observed. Moreover, the δ-hydride platelets at the weld zone were always found to be growing perpendicular to the α-colonies, which had a misorientation of 60°, and followed a $(0001)\alpha$ -Zr//{111}δ-ZrH_{1.5} orientation relationship with the zirconium matrix. A proposed description of the complex distribution of hydrides and alloy microstructures, at the weld and heat affected zones, will contribute to a better understanding of the mechanisms of fuel cladding failure in various types of nuclear reactors.

Keywords: Zirconium, Zircaloy-4, Zr-2.5Nb, Zr-1Nb (E110), EBSD, crystallographic orientation, hydride reorientation, hoop stress

RÉSUMÉ

Les alliages de zirconium ramassent de l'hydrogène, au cours de l'opération de réacteur. Lorsque la teneur d'hydrogène dépasse la limite de solubilité, les hydrures sont formés. Ces hydrures ont un effet néfaste sur les propriétés mécaniques du matériel. Par conséquent, il est important d'améliorer notre compréhension de la morphologie des hydrures et leur comportement sur les conditions différentes rapprochant des environnements de réacteur nucléaire.

L'analyse initiale a été faite sur les hydrided hydrures, travaillés à froid et soulagés de contraintes du Zircaloy-4 (CWSR) feuille-échantillons. Les hydrures ont été identifiés comme phase δ -ZrH1.5. Ils sont trouvés dans les grains et le long des frontières de grains, mais les hydrures de limite de grain semblaient être dominants. La relation d'orientation préférentielle de (0001) α -Zr// (111) δ -ZrH_{1.5} a été observée entre hydrures et la matrice à tous les endroits. Les variations de concentration de l'hydrogène n'ont eu aucun effet sur la relation de l'orientation cristallographique des hydrures.

Par la suite, le comportement d'hydrure sous *hoop stress* a été étudié en détail. Une plage de *hoop stress* a été appliquée au tube de revêtement du Zircaloy-4 dans un four à gaz à haute pression d'hydrogène à une température de 350°C et sous une pression de 20 MPa. La microscopie

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optique des échantillons ont montré une augmentation du nombre des hydrures orientés le long de la direction radiale à des données de *hoop stress* plus élevées. Hormis les hydrures radiaux, les hydrures qui étaient enclins à un angle de circonférence et radiales des instructions ont aussi été observés. Fait intéressant, les hydrures qui étaient orientés perpendiculairement à la direction de circonférence suivent la relation de $\{10\bar{1}1\}\alpha$ -Zr// $\{111\}\delta$ -ZrH_{1.5} avec les grains de la matrice. Les plans d'habitude de $\{10\bar{1}1\}$, $\{10\bar{1}7\}$, $\{10\bar{1}3\}$, $\{10\bar{1}0\}$ ont été observés pour l'hydrure qui étaient enclins à un angle avec la direction de la circonférence. Cette étude permet de comprendre le comportement complexe des hydrures radiaux.

Une tentative à comprendre la résistance à la corrosion et à baisser substantiellement la ramasse de l'hydrogène de l'alliage Zr-1Nb comparativement à Zircaloy-4. Ainsi, Zircaloy-4, Zr-2.5Nb et alliages Zr-1Nb (E110) ont été hydrudés dans un four à gaz à haute pression de l'hydrogène. Les hydrures dans le Zr-1Nb (E110) étaient courts et épais, avec aucune orientation préférentielle par rapport à la direction des échantillons de référence. Des jumeaux lourds {1012} ont été observés dans les alliages de Zr-1Nb, qui n'étaient pas considérés dans la Zircaloy-4 et Zr-alliages 2.5Nb. Près de 50 % des hydrures dans l'alliage Zr-1Nb (E110) ont montrés une nouvelle relation cristallographique de

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 $(0001)\alpha$ -Zr//{100} δ -ZrH1.5 Cette nouvelle relation d'orientation dans l'alliage Zr-1Nb est attribuée à la présence des limites des jumeaux.

En outre, les changements des microstructures à la zone de soudure et ses effets sur le comportement d'hydrure ont été étudiés. La zone de soudure montre surtout des structures nattées, avec très peu de colonies ayant des structures de plaques parallèles. La sélection variante pour la formation de α -phase à l'intérieur de grains de β préalables a été identifiée au centre de la soudure. Alors que nous déplacons du centre de soudure à la zone reçu, la sélection de la variante est jugée moins probable. Dans la zone de soudure, une orientation aléatoire complète des hydrures a été observée. En outre, les plaquettes δ -hydrure dans la zone de soudure ont toujours été croissante perpendiculaire aux α colonies, qui avaient une différence angulaire de 60° et qui suivent une $(0001)\alpha$ -Zr//{111} δ -ZrH1.5 relation d'orientation avec la matrice de zirconium. Une description proposée de la distribution complexe des hydrures et alliage microstructures, à la soudure et la chaleur des zones touchées, contribuent à une meilleure compréhension des mécanismes de rupture de revêtement de carburant dans divers types de réacteurs nucléaires.

Mots clés: Zirconium, Zircaloy-4, Zr-2.5Nb, Zr-1Nb (E110), EBSD, orientation cristallographique, réorientation hydrure, cerceau stress

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Co-Authorship

Contributions of the Co-authors in Chapters 3 - 6

This dissertation is presented in a manuscript format, with each chapter based on either published or submitted journal articles. The full bibliographic citations of the papers presented in the dissertation are as follows:

Chapter 3:

N.A.P. Kiran Kumar, J.A. Szpunar, and Z.He, Preferential precipitation of hydrides in textured Zircaloy-4 sheets, Journal of Nuclear Materials, (2010), 403, 101-107.

Chapter 4:

N.A.P. Kiran Kumar, and J.A.Szpunar, Hydride formation under hoop stress in Zircaloy-4 cladding, Journal of Nuclear Materials, (Submitted for publication).

Chapter 5:

N.A.P. Kiran Kumar, and J.A Szpunar, EBSD studies on microstructural and crystallographic orientation of δ -hydrides in Zircaloy-4, Zr-1%Nb and Zr-2.5 %Nb, Materials Science and Engineering A, (2011), 528, 6366-6374.

Chapter 6:

N.A.P. Kiran Kumar, and J.A Szpunar, Microstructural studies and crystallographic orientation of different zones and δ -hydrides in resistance welded Zircaloy-4 sheets, Journal of Nuclear Materials, (2011), 414, 341-351.

I, N.A.P. Kiran Kumar, carried out all the research and wrote the papers. My co-author, Professor Jerzy Szpunar, was my thesis supervisor. My other co-author, Dr. Zhang.He, Section Head at Atomic Energy Canada Limited (AECL), provided hydrided Zircaloy-4 sheets for analysis. Additionally, both provided invaluable comments and suggestions, and reviewed the papers before submission.

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1.0 Introduction

1.1 General background

Zirconium alloys are heavily used in the nuclear industry due to their unique combination of properties such as strength, ductility, corrosion resistance in boiling water, and its low cross-section to neutron absorption. Pure zirconium has a rather low resistance to corrosion, thus, in commercial nuclear reactors, zirconium alloys Zircaloy-2, Zircaloy-4, and Zr-1Nb (E110), are used as fuel cladding materials, while Zr-2.5Nb is the material used as pressure tubes in CANDU reactors. However, the life expectancy of zirconium alloys is limited due to oxidation, hydriding and irradiation damages. Hydrogen has a destructive influence on the mechanical properties of the zirconium alloys; zirconium oxide acts as a protective barrier to hydrogen ingress.

Hydrides, which form when the concentration of hydrogen in an alloy exceeds the solubility limit, are fracture initiation sites [1, 2]. The uniform distribution of hydrides in the form of a rim or layer has a significant influence on the tensile ductility of the zirconium [3, 4, 5]. Therefore, it is important to minimize the probability of the formation of

Chapter1

hydrides with a chain-like structure (hydride rims). Despite the numerous studies conducted in past 60 years, knowledge of the mechanism of hydride orientation and hydride growth are still not complete. In terms of orientation, it is known that hydrides that are oriented along the radial direction of the tube are more damaging to the latter's mechanical properties than circumferential hydrides [6, 7]. In general, hydrides tend to orient perpendicular to tensile stresses and parallel to compressive stresses. Therefore, during manufacturing, sufficient compressive strain is applied to ensure the formation of circumferential hydrides [8]. However, radial hydrides are formed due to the hoop stress generated during reactor operation and are still of great concern to the nuclear industry.

Weld joints are known for their low tolerance to hydrogen-assisted cracking [9]. However, defects, such as insufficient fusion, undercut, porosity, and short cracks have presently been minimized. Despite these minimizations, weld zones are often prone to failure [10]. Such failures are particularly damaging to the core of nuclear reactor, where the uranium fuel pellets are surrounded by Zircaloy-4 cladding, and both ends of the cladding are sealed by resistance welding, with end plates. When the fuel bundle is exposed to a temperature of approximately 350°C [11], any failure at that point (which, when it happens, is often the

result of cracking at the weld zone) can lead to fuel leaking. Researchers have commonly attributed this weld failure to the high residual stress generated at the weld zone, as well as the brittleness of the hydride platelets. However, very little effort has been made to describe and analyze these failures [12, 13, 14]. Therefore, it is important to address these issues and try to understand the mechanism of hydride formation in the weld area.

1.2 Objectives

The current research aims to improve our understanding of hydride formation, reorientation, and behavior, which can enhance the service performance of Zircaloy-4, E110 (Zr-1Nb) and Zr-2.5 Nb alloys, used in the core of nuclear reactors. The objectives of this research are listed below:

- To evaluate the role of grain boundaries, grain orientations and micro-textures on the shape and orientation of hydrides and to identify the hydride preferential grain boundaries;
- To propose a fundamental, microstructure-based understanding of the behavior of hydrides under the presence of both hoop stress and a high pressure hydrogen atmosphere;

- To determine the microstructural differences between E110 and Zircaloy-4, and to identify factors which influence the hydride structure;
- 4) To investigate the influence of microstructural changes due to welding on texture, hydride distribution and orientation in zirconium alloys.

1.3 Dissertation format

The research done in this dissertation has been published, or accepted, in peer-reviewed scientific journals.

Chapter 1 covers the basic information and the modes of failure of zirconium alloys used in the nuclear industry. As each chapter contains an introduction, the introduction of Chapter 1 is intentionally kept short.

Chapter 2 gives an extensive review of existing literature. The intension of the literature review is to provide information on the current state of knowledge on corrosion and failure of zirconium alloys. The literature review is followed by four chapters (3-6) containing journal articles (three published and one submitted)

Chapter 3 contains the first paper as published in the Journal of Nuclear Materials, titled "Preferential precipitation of hydrides in textured

Zircaloy-4 sheets." This paper analyzes the role of grain orientations and structure in the formation of inter-granular hydrides.

Chapter 4 contains the second paper as submitted to the Journal of Nuclear Materials, titled "Hydride formation under hoop stress in Zircaloy-4 cladding." This paper proposes a new mechanism to explain hydride formation under hoop stress. It also illustrates the influence of grain boundaries, along the radial direction of the tube, on the orientation of hydrides.

Chapter 5 contains the third paper as published in *Material Science* and Engineering A, under the title "EBSD studies on microstructural and crystallographic orientation of δ -hydrides in Zircaloy-4, Zr-1%Nb and Zr-2.5 %Nb." This paper illustrates the microstructural difference between the aforementioned three alloys and explores the influence of twins on the hydride structure.

Chapter 6 contains the fourth paper as published in the Journal of Nuclear Materials, titled "Microstructural studies and crystallographic orientation of different zones and δ -hydrides in resistance welded Zircaloy-4 sheets." In this chapter, the microstructural changes at the weld and heat affected zones, and their influence on hydride structure and texture inhomogeneity, are discussed. Chapter 7 & 8 include the conclusions of this work and the contribution to knowledge, respectively.

In addition, three appendices have been attached which describe the following: (I) the hydrogen charging procedure employed for hydriding our samples; (II) fundamentals of texture analysis; (III) fundamentals of EBSD and orientation imaging.

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2.0 Literature review

This chapter summarizes the relevant studies on zirconium alloys which lead to the current research. The critical review of the literature is presented in four subsections: 1) Zirconium and its alloys, which deals with the history of, and basic information on, zirconium; 2) Zirconium hydrides, which briefly describes the formation and growth of zirconium hydrides; 3) Welding of zirconium alloys, which deals with the structural changes in the weld region, and the behavior of the hydrides in the weld zone; 4) Texture of zirconium alloys, which describes the influence of texture on the mechanical properties of zirconium alloys and zirconium hydrides.

2.1 Zirconium and its alloys

Zirconium at low temperature has a hexagonal closed-packed (HCP) structure with a stable α phase, and at high temperature has body centered cubic (BCC) β phase structure. The allotropy transformation takes place at 865°C, and the melting point of zirconium is 1865°C. Sixty years after its discovery, an application for zirconium was finally found in the nuclear industry. Since then, all research on zirconium alloys has focused mainly on increasing its corrosion resistance in

boiling water and steam. Before zirconium, a thin stainless steel tube was used as a cladding material in commercial reactors, but sever longitudinal intergranular cracking at high burnups had limiting its use [1]. Later, the CANDU nuclear reactor developed by Canadian scientists significantly increased the use of zirconium alloys. Thus, from the 1960s, zirconium alloys replaced stainless steel as the main cladding material. Initially, Zircaloy-2 was used as a fuel cladding as well as a material for pressure tubes. Later, it was replaced by Zr-2.5 % Nb, which has higher strength and more corrosion resistance than Zircaloy-2, in CANDU and Russian reactors.

In the early 1970s, a significant cracking of fuel claddings had occurred due to the stresses generated during the mechanical interaction between the fuel pellet and the cladding, well known as a "Pellet Cladding Interaction" (PCI) defect [2]. Armijo et al. [3], found that a thin zirconium liner on the inner side of the cladding significantly decreases the probability of failure from the PCI defect. But, corrosion of zirconium liners in boiling water has again led to the severe degradation of claddings.

In the 1980s, importance was given to improving the corrosion resistance of Zircaloy-4, so that high burnups can be achieved. Several investigations [4, 5, 6, 7, 8] have been carried out with the aim of finding

the optimum Zircaloy-4 composition. Based on these investigations, optimized Zircaloy-4 was developed that is still in use in present day nuclear reactors. Table 2.1 shows the composition of the zirconium alloys which are at present considered standard materials. However, apart from Zircaloy-2, Zircaloy-4, Zr-2.5Nb, and Zr-1Nb, many new alloys [9, 10, 11] have been developed as alternatives, and research aimed at developing high corrosion resistant material for generation IV reactors is ongoing.

Table 2.1:	Composition	of zirc	onium	alloys
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Alloy	Zircaloy-2	Zircaloy-4	Zr-1Nb (E110)	Zr-2.5 Nb	Zirlo	М5	Excel
Sn (wt.%)	1.2-1.7	1.2-1.7			1		3.5
Fe (wt.%)	0.07-0.02	0.18-0.24	0.014	<0.15	0.03- 0.05	0.015- 0.06	
Cr (wt.%)	0.05-0.15	0.07-0.13	<0.003				
Ni (wt.%)	0.03-0.08	<35 ppm	0.0035				
Nb (wt.%)			0.9-1.1	2.4-2.8	1	0.8-1.2	0.8
Mo (wt.%)							0.8
O (wt.%)	0.1-0.14	0.1-0.14	0.05- 0.07	0.09- 0.13	0.1-0.14	0.09-0.12	
Zr	Bal	Bal	Bal	Bal	Bal	Bal	Bal
Typical Appilcation	Fuel Cladding/ Calandria Tubes	Fuel Cladding	Fuel Cladding	Pressure Tubes	Fuel Cladding	Fuel Cladding	Possible Generation 4 Candidate

2.1.1 Significance of alloying elements

The choice and relative proportion of alloying elements plays a major role on the properties of the resulting zirconium alloy. The main objective of adding an alloying element in zirconium is to improve the latter's mechanical and corrosion properties. According to Wagner-Hauffe's theory [12], foreign ions can dissolve substitutionally in anion deficient oxide, forming metals like zirconium, so higher-valency alloying elements whose oxides are soluble in zirconium oxide have the possibility of increasing the corrosion resistance of zirconium. Tin(Sn) is a α -Zr stabilizer, whereas alloying elements like Nb, Ta, Cr, Fe, Co, V, Ni, Cu are β -Zr stabilizers. A brief overview of the main alloying elements is given below.

Niobium (Nb):

- Provides reasonable oxidation resistance at high temperatures;
- Improves the strength and formability of zirconium;
- Decreases the hydrogen pickup rate.

Tin (Sn):

- Improves corrosion resistance against steam at higher temperatures;
- Counteracts the adverse effect of nitrogen absorbed during reactor corrosion.

Chromium (Cr):

- Increases the corrosion resistance of zirconium at concentrations of 0 to 1.6 wt.%;
- Decreases corrosion resistance at concentrations greater than 1.6 wt.% [13].

Iron (Fe):

• Decreases the corrosion rate of zirconium.

The increase in corrosion resistance due alloying elements Cr & Fe is attributed to the cathodic nature of intermetallic particles which form an anodically-polarized layer on the zirconium surface, thus slowing down the migration of hydrogen into zirconium oxide film [14].

Nickel (Ni):

- Improves oxidation resistance in superheated steam environments;
- Enhances the hydrogen pickup, and therefore opposes the action of the intermetallics formed by Cr & Fe.

Nitrogen is one of the major impurities in zirconium that accelerates the corrosion rate over a period of time [15]. Even with a concentration as low as 0.5 wt.% Ni, Zr will exhibit a high affinity towards hydrogen [16]. However, other major impurities such as Al, Ti, Si, Cu, and O_2 will also
significantly influence the corrosion behavior of zirconium [17]. With this in mind, the following limits (see Table 2.2) for the content of impurities have been recommended [18].

Table 2.2: Effect of impurity elements on the corrosion resistance of zirconium, in high temperature water and steam [18].

Impurity	Effect	Concentration at which the effect is noted, wt.%	Nominal composition (wt.%) in arc-melted iodide Zr	
Nitrogen	Harmful	0.004	0.002	
Carbon	Harmful	0.04	0.01	
Titanium	Harmful	0.1-5	0.002	
Aluminum	Harmful	0.1	0.003	
Magnesium	Harmful	Uncertain	0.002	
Fluoride	Harmful	0.002	0.001	
Lead	Harmful	0.01	0.003	
Oxygen	Slight	0.05	0.04	
Hydrogen	Slight	0.05	0.002	

2.2 Zirconium hydrides

2.2.1 Hydrogen solubility in zirconium

 α -Zirconium alone can dissolve up to 6 at.% of hydrogen in a solid solution at temperatures above 500°C, but solubility decreases rapidly with decrease in temperature to 0.7 at.% at 300°C and 10⁻⁴ at.% at room temperature [19]. The rapid decrease in solid solubility of hydrogen with

temperature results in the formation of hydride precipitates at reactor working temperatures. The operational performance of zirconium cladding materials is affected by problems associated with hydrogen ingress. The Zr-H phase diagram (see Figure 2.1) reported in the literature has gained lot of attention due to the severity of hydride-related problems in zirconium alloys [20, 21, 22].

The terminal solid solubility (TSS) of hydrogen was initially studied on Zircaloy-2 in 1957 [23] and later modified in 1965 [24]. These TSS values were considered as standards until Kearns in 1967 [25] revised the TSS data on zirconium, Zircaloy-2 and Zircaloy-4. Based on the experimental investigations, Kearns provided a best-fit curve on the data (often termed as the "Kearns line"), and this result is now considered as the standard TSS values for the material. Earlier, Erickson and Hardie [26] had addressed the effect of alloy addition on TSS in zirconium, and the difference in TSS between the different alloys was found to be small. Therefore, the Kearns line can reasonably be applied to all Zr alloys. The addition of oxygen has been reported to increase the TSS of hydrogen in Zr alloys. This can be due to either matrix strengthening or hydrogen trapping by the solute atom [27]. Below 500°C, the solubility of hydrogen decreases with higher oxygen concentrations, but for the temperatures above 500°C, the solubility of hydrogen is found to increase with increase of oxygen concentration [28, 29].



Figure 2.1: Zirconium-Hydrogen binary phase diagram showing α -, β -Zr and δ -, γ -, ϵ -hydride phases [22,30].

As shown in the zirconium-hydrogen phase diagram, below the eutectic temperature of 550°C, three hydride phases (γ , δ and ϵ), were extensively studied in last four decades. The crystal structures of the hydrides are given here [31]:

- (i) γ hydride; ZrH; FCT, a=4.596 A°; c=4.969 A°.
- (ii) δ hydride; ZrH_{1.6}; FCC, a= 4.778 A°.
- (iii) ε- hydride; ZrH₂; FCT, a=4.980 A°; c=4.445 A°.

It is generally accepted that two of the phases, δ (FCC) and ϵ (FCT), exist in the region ZrH_{1.6} to ZrH_{2.0}. However, on the basis of X-ray diffraction, hardness tests, and metallographic examination, researchers have reported that the true Zr-H binary system does not contain this twophase region [32].

The literature on γ -hydride (FCT) gives rather contradictory results, with two review articles reporting it as metastable [33, 34] and others considering it to be in an equilibrium phase below 250°C [30, 35]. On the other hand, δ -hydride (FCC) is considered to be a stable phase that is formed during slow cooling, while ϵ -hydride (FCT) is formed at higher hydrogen concentrations (>63 at.%) [33]. In general, slower cooling rates and higher hydrogen content, as well as mixed mode and pure diffusional transformations, favors δ -hydride formation [31, 36, 37]. Although, it is well known that the δ -hydride phase is most often formed in the material during irradiation in the reactor, the discussion on the formation mechanism of δ -hydrides is very limited [38, 39].

2.2.2 Hydrogen uptake mechanism

In order to understand the hydrogen uptake mechanism, it is important to list the main sources of hydrogen in the core of the reactor:

- 1) The coolant used in CANDU (CANada Deuterium Uranium) reactors is heavy water (D₂O), which is maintained at a ph of 10.3 using LiOD [40]. Part of the deuterium liberated during the oxidation reaction, $Zr + 2D_2O \rightarrow ZrO_2 + 4D$, is absorbed by zirconium.
- 2) About 3-10 cm³ H₂/kg of coolant is added to mop up the oxygen produced during the radiolytic decomposition of D₂O [41], which may lead to the liberation of the deuterium.
- 3) N₂ and CO₂ are used as dry annulus gases in the core of the reactor. The hydrogen bearing impurity present in these gases acts as source of hydrogen.

Shah et al [42], in his detailed study on hydrogen uptake, concluded that dissolved hydrogen will not be picked up by the zirconium. It is hydrogen in free radical form or atomic form which ingresses into zirconium.

Different hypothetical mechanisms have been proposed to explain the hydrogen uptake process. Schematically, the hydrogen ingress can be described using the following reaction:

$$2 H_2O + Zr \rightarrow ZrO_2 + 4H \dots (2.1)$$

 $4 H + 2 Zr \rightarrow 2 ZrH_2$(2.2)

Hillner [43], developed a model to explained the hydrogen absorption mechanism. This model assumes that the transportation of hydrogen is mainly dependent on the anion vacancy diffusion created by the oxygen atoms. The anion vacancy mainly occurs at the oxide/metal interface during the oxide film growth process. Since zirconium has a high affinity towards oxygen, oxygen ions jump to interstitial positions of metal, creating the vacancy gradient in the oxide as illustrated in Figure 2.2.

Water molecule on dissociation gives oxygen with two protons

$$H_2O \rightarrow 2H^+ + O^2$$
.....(2.3)

Hydrogen ions will be neutralized by electrons

$$H^+ + e^- \rightarrow H^0$$
.....(2.4)

The hydrogen atoms may recombine to form molecular hydrogen (H_2) or may enter the oxide in the atomic form. The hydrogen atom at the anion vacancy diffuses through the oxide to the metal by jumping from one anion vacancy to another.



Figure 2.2: Schematic representation of hydrogen ingress in Zircaloy [43]

Hatano [44] and Cox [45] proposed that the intermetallic precipitates present in the oxide will act as ingress routes for hydrogen uptake. Therefore, the hydrogen uptake increases with increase in intermetallic precipitate size.

In addition, Cox [46, 47] also proposed that hydrogen accumulates at the pores or small cracks within the oxide layer and when the oxide breaks, hydrogen enters the metal. According to Cox, ZrO₂ further reacts with H₂O and forms ZrOH and OH⁻ on the surface of the metal. Further, this OH⁻ accumulates at oxide defects and the hydrogen from the OH⁻ will diffuse to the metal-oxide interface.

$$ZrO_2 + nH_2O \rightarrow (ZrOH)n + OH^-$$
.....(2.5)

In summary, many hydrogen uptake mechanisms have been suggested by different authors. However, all these mechanisms suggest the presence of a defect-free oxide layer, or a better alloy composition, can serve to minimize the hydrogen pickup. Oxidation and hydrogen absorption in zirconium alloys are interlinked and it is hard to control the oxidation process due to the fact that during the corrosion process, oxygen is released from water. Therefore, it is difficult to completely eliminate hydrogen uptake, and the formation of hydride platelets, in zirconium alloys.

2.2.3 Hydride formation and growth

As discussed earlier in section 2.21, the solubility of hydrogen drastically decreases with decreasing temperature in zirconium alloys. In addition, zirconium is an exothermic absorber of hydrogen, where hydrogen is more stable as a solution in α -Zr than as a gas [48]. When hydrogen concentration exceeds the solubility limit in the zirconium, the hydrides form. The hydrogen ingress is mainly driven to areas of higher stress and lower hydrogen concentration. In general, hydrides can be seen with an optical microscope, appearing as single platelets or as a cluster of platelets, as shown in Figure 2.3. However, it is well known that long hydrides form by aggregation of small hydride platelets; the stress

generated by long hydride platelets facilitates the formation of smaller hydrides. Long hydride chains in the form of layers have influence on the ductility of zirconium [19, 49]. Therefore, it is important to minimize the formation of chain-like structures of hydrides.



Figure 2.3: - Zircaloy-2 sample with 500 ppm hydrogen [50].

The metal lattice of zirconium has a c/a ratio of 1.593, which is lower than the ideal c/a ratio of 1.633 for HCP metals. In addition, the c/a ratio of the di-hydride tetrahedral phase is 0.889, which is also lower than the regular c/a of 1 [51]. So, hydrogen occupying tetrahedral sites in a α -Zr solid solution leads to a distortion of the crystallographic lattice [52]. Because of this, hydrogen always segregates at high stress regions, where the lattice is distorted due to elastic stress, and the dislocations are accumulated in the vicinity of the hydrides (see Figure 2.4) [53].



Figure 2.4: Dislocation loops created by the hydrides (A, B dislocation have different Burger vectors) [53].

The partial molar volume of hydrogen in the α -Zr solution and in the form of hydride is the same, so the hydride formation from the solution involves no net volume expansion [48]. Therefore, it is important to note that the lattice distortion that takes place during the intake of hydrogen plays an important role in the nucleation of hydride precipitates.

However, as mentioned earlier, literature about the formation of different hydride phases is contradictory. One study claims that the γ -hydride is formed at a cooling rate greater than 10°C/min [54], whereas another study reported a decrease in the amount of γ -hydride with increase in cooling rate [55]. In contrast, it was also reported that γ -hydride is stable

at temperatures below around 250°C [30]. But later, Roots et al. [35] demonstrated that upon ageing the hydrided sample for many days at around 180°C, the $\delta \rightarrow \gamma$ transformation takes place. These contradictory results have led to extensive research on hydride phase stability. Most recent research [34, 56, 57] has shown that rapid quenching at higher hydrogen concentration preferentially produces γ -hydrides, whereas slow cooling promotes δ -hydride formation.

Carpenter [58] has suggested that the mechanism responsible for the growth of hydrides in the shear mechanism, where the co-operative motion of hydrogen atoms by diffusion, and zirconium atoms by shear, may lead to the formation of zirconium hydride. According to him, the glide of $a/3 < 10\overline{10}$ Shockley partial dislocation on alternate basal planes can cause a shear transformation which catalyses the formation γ -hydride in zirconium. The growth of the hydride takes place by repeated formation of partial dislocations on the basal plane. This mechanism was supported by Shinohara et al. [59] with an in-situ observation of the growth process of zirconium hydride using transmission electron microscopy. The growth mechanism is illustrated in Figure 2.5.





Hydride nucleation is not homogeneous in zirconium alloys. Grain boundaries are in general considered as preferential sites for hydrides. Daniel [24] has reported that cooling rate plays an important role in hydride nucleation and at slower cooling rates, nucleation occurs mainly at grain boundaries.

Apart from hydride formation at grain boundaries, several researchers have also observed hydrides within the grains themselves. In the late 1950s, Langeron et al. [60] proposed the prism plane $\{10\overline{1}1\}$ as the habit plane of the hydrides. Later, Kunz et al. [61] found the twinning planes $(\{10\overline{1}2\}, \{11\overline{2}1\}, \{10\overline{2}2\})$ to be the habit planes of hydride platelets. The habit planes $\{10\overline{1}0\}, \{10\overline{1}1\}, \{10\overline{1}2\}, \{10\overline{1}3\}, \{10\overline{1}5\}, \{11\overline{2}1\}, \{11\overline{2}2\}$ and (0002) have been found on Zircaloy-2 [62, 63].

Westlake [64, 65] tried to reassess the variable habit planes proposed in the previous studies by repeating the experiments on the previous authors' samples. He reported that hydride platelets in both unstressed Zircaloy-2 and Zircaloy-4 exhibited $\{10\overline{1}7\}$ habit planes, and proposed that there is a need for an in-depth study on factors like solution treatment, cooling, impurity, hydrogen concentration and stress, which can affect the hydride habit plane. The schematic hydride orientation on the $\{10\overline{1}7\}$ habit plane is illustrated schematically in Figure 2.6.



Figure 2.6: Schematic illustration of hydride formation on habit planes

[66].

Perovic et al. [67] reported that hydrides in two phase zirconium alloys nucleate at the α/β interface, but always grow on the α -Zr phase. He found two orientation relationships that described the growth of the hydrides on α -zirconium phase, $(111)\delta/(\overline{2}021)\alpha$ and $(001)\delta/(0001)\alpha$. However, the habit plane and the morphology of the final hydride precipitates are reported to be mainly dependent on relative contribution of the elastic strain energy and the interface energy, where the transgranular hydrides are formed at areas where elastic strain energy was high and the high interfacial energy contributes to the formation of intergranular hydrides. [36].

More recently, Une et al. [68, 69] used EBSD as an independent and effective tool for determining the crystallographic orientations of zirconium and zirconium hydride grains with sufficient spatial and angular resolution. The orientation of each crystal is represented with the pole figure, where the orientation relationship is obtained by observing the coincidence of crystallographic orientations of δ -hydride and α -Zr grains. Une et al. observed a higher number of grain boundary hydrides than hydrides within the grains. Hydrides with both $\{111\}\delta/(0001)\alpha$ and $\{111\}\delta/(10\overline{17})\alpha$ were reported.

Mani Krishna et al. [70] proposed hydride-resistant grain boundaries in an attempt to explain the inhomogeneous presence of hydrides at

different cross-sections of a Zircaloy tube. Low CSL boundaries, and the boundaries surrounded by elastically harder grains, were reported to be hydride resistant grain boundaries. However, the proposed CSL hydride resistant grain boundary theory was not able to explain the reason behind the strong orientation of hydrides in the circumferential direction, and not all hydride-resistant boundaries were classified.

In summary, contradictory results on hydride precipitation and phases are reported in the literature. Therefore, this thesis attempts to clarify some of the unresolved issues, using the orientation imaging microscopy (OIM) method.

2.2.4 Radial hydrides

The presence of hydrides oriented towards radial direction adversely affects the mechanical properties of the fuel cladding. Factors such as temperature gradient, stress gradient, texture and the fabrication method used, play a vital role in the formation of radial hydrides in Zircaloys [71, 72]. The radial hydride formation is believed to be driven by hoop stress, which acts as a tensile stress along the circumferential direction [73] (see Figure 2.7). The significance of the stress-reoriented hydrides became apparent with the failure of an in-reactor fuel element [66]. It was demonstrated that even a sample with 40 ppm of hydrogen can experience brittle failure, if the hydrides platelets are precipitated

perpendicular to the tensile stress direction [74]. In this regard, Marshall [71, 72] has shown that hydride reorientation in an unstressed sample is mainly due to the strain developed during the fabrication process. Marshall further proposed that hydride reorientation can be controlled by applying compressive strain along the radial direction. Furthermore, J.J. Kearns [75] has related the stress-reorientation process with fundamental metallurgical parameters and concluded that reorientation can be minimized through the control of texture, grain size and cold work.

It was made clear by these works that stress plays a major role in hydride reorientation. Therefore, a critical stress also known as the lowest threshold stress, under which the reorientation takes place, has been defined [76].



Figure 2.7: Micrographs showing: a) circumferential hydrides; b) reoriented hydrides after 8 cycles of thermal treatment [77].

In recent years, hydride reorientation has undergone a recrudescence due to the high burnup operations which also generate high hoop stress on the fuel claddings [78]. The mechanism of hydride reorientation involves dissolution of circumferential hydrides and the formation of radial hydrides [67, 79]. As discussed in section 2.2.3, hydride precipitation is affected by many factors including stress, hydrogen concentration, temperature, cooling rate etc. So, in order to understand the process, it is often necessary to consider the role of these factors separately when characterizing the reorientation behavior of hydride precipitates. Early reorientation experiments were conducted on flattened samples prepared from Zr-2.5Nb tubes and tested using a universal tensile testing machine. However, since the samples were flattened and then exposed to stress, it is possible that the results produced by these experiments may not be applicable for claddings [80]. Recent investigations were performed on the cladding tube with hoop stress applied by internal pressure and deformation induced by cylindrical wedges [77, 81]. But, one must keep in mind that in reality, during high burnups, a combination of hoop stress, corrosive environment and temperature influence the formation of radial hydrides.

In summary, despite knowing deleterious influence of radial hydrides, very little information is available on crystallographic orientation and the behavior of reoriented hydrides. As mentioned earlier, the reduction of

the fraction of radial hydrides, and formation of chains of circumferential hydrides, can improve the resistance to failure. Therefore, systematic investigations are needed to evaluate the hydrides behavior under different conditions.

2.3 Welding of zirconium alloys

Welding is considered as one of the most critical processes for manufacturing various elements for nuclear reactors from zirconium alloys. Even a small absorption of oxygen, nitrogen or hydrogen from the atmosphere during welding can drastically accelerate the corrosion process, resulting in embrittlement of welds. Therefore, proper shielding and cleanliness are important factors in making defect-free welds of zirconium alloys.

2.3.1 Welding techniques used for zirconium



Figure 2.8: Overview of different welding techniques [2].

Component	Tungsten Inert Gas Welding (TIG)	Electron Beam Welding (EB)	Laser Welding (LW)	Resistance Welding (US)	Resistance Spot Welding
Fuel rod End plate			\checkmark	\checkmark	
Grid/guide tube Spacer/water rod					\checkmark
Grid		\checkmark			
Fuel channel	\checkmark				

Table 2.3: - The welding techniques used for manufacturing different fuelassembly components [2].

Only some of the listed welding techniques are used in the present nuclear industry. The weld, weld root, and adjacent hot metal should be protected using inert gas shielding until the weld temperature cools below 315°C [2].

Welding of the end plate is an important step in the fabrication of nuclear fuel bundles. Three welding methods are used most often for the end plate welding of commercial fuel bundles (see Table 2.3); 1) tungsten inert gas welding (TIG), 2) resistance welding (RW), 3) laser beam welding (LB), where TIG and LB are fusion welding methods, in which joining is done by melting the welded materials. Resistance welding is classified as solid state welding in which joining is done in solid state without creating the molten zone region. This is a much faster process, which takes less

than 1 sec with a heating and cooling rate of order of 10³°Csec⁻¹ [82]. Resistance welding is preferred, since the welding time is short, resulting in a very small heat affected zone (HAZ). The fundamentals of this process are described in the literature [83].

2.3.2 Microstructural changes at the weld zone.

During welding, apart from the fusion zone, the sample area which undergoes microstructural changes is called the heat affected zone (HAZ). This is the area adjacent to the weld zone, where the temperature is below the melting point, but high enough to change the grain structure. The volume of the HAZ mainly depends on the working temperature during welding and the weld area. The microstructural changes at the HAZ severely influence the corrosion and mechanical properties of the weld [2].

Zirconium has two allotropic forms, α (HCP), stable at room temperature, and β (BCC), stable at temperatures above 863°C. Phase transformation of cold worked and stress relieved (CWSR) Zircaloy-4 sheet-material during heating ($\alpha \rightarrow \alpha + \beta \rightarrow \beta$), and cooling ($\beta \rightarrow \alpha + \beta \rightarrow \alpha$), gained importance because it involves both texture and microstructure changes [84, 85, 86] in the material and it takes place during the assembly-welding process. The $\beta \rightarrow \alpha$ phase transformation is reported to follow the Burger relation

 $\{110\}_{\beta}//\{0002\}_{\alpha}$ and $<111>_{\beta}//<1\overline{2}10>_{\alpha}$ [87]. If this relation is followed, then because of crystal symmetry, six β -phase orientations may arise during the $\alpha \rightarrow \beta$ transformation, and twelve inherent α orientations may arise during the cooling (i.e., the $\beta \rightarrow \alpha$ transformation). If all these orientations were selected during the transformation, the resulting texture of the α matrix will be very weak. However, recent studies on zirconium and titanium have suggested that variant selection takes place, and some preferred orientations of the α -phase are strengthened while others are suppressed [88, 89 and 90]. If the variant selection occurs during phase transformation, the crystallographic arrangement of grains in the weld zone may affect the precipitation of the hydrides. At present, this has not yet been studied in detail. However, such information is important for assessing the mechanical strength of the welds.

2.4 Texture of zirconium alloys

Due to the limited number of slip planes, hexagonal close-packed metals like zirconium, show anisotropic behavior. Therefore, zirconium alloys develop texture during deformation processes like sheet rolling and wire drawing, as well as during tube fabrication process [91]. The texture of zirconium alloys is usually represented as a stereographic projection of the distribution of poles of crystallographic planes in the reference frame

of the specimen, (see Appendix II for more details) [75]. During tube manufacturing, the decrease in cross-section can be obtained through a reduction in wall thickness (R_w), a reduction in diameter (R_D), or a combination of both (R_w) and (R_D). The reduction in the wall thickness will result in high compressive forces in the tangential direction of the tube [92]. In general, the basal planes of HCP metals orient parallel to the elongation direction. Therefore, the reduction ratio of the tube thickness influences the texture of the Zircaloy tubes. Tenckhoff [92, 93, 94] has investigated the effect of reduction parameters such as R_w and R_D on texture. Three examples of tube reduction at different R_w/R_D are shown in Figure 2.9.

For Case 1 ($R_w/R_D > 1$), where the reduction of thickness is higher than the reduction of the diameter, the compressive forces along the radial direction will be higher than in the tangential direction. This results in an orientation of basal planes close to the radial direction, as shown in figure 2.9 a1. For Case 2 ($R_w/R_D = 1$), the reduction in wall thickness is equal to a reduction in the diameter. The strain ellipse should produce a fiber texture with basal planes distributed in the radial-tangential plane (see Figure 2.9 a2). However, for Case 3 ($Rw/R_D < 1$), the reduction in the wall thickness is smaller than the reduction of the diameter of the tube. The high compressive forces in the tangential direction are responsible

for titling the strain ellipse by 90°, and the maxima of basal poles are moved towards the radial direction (see Figure 2.9 a3).



Figure 2.9: The basal and prism pole figures of deformed zirconium derived for different reduction values (AD = Axial direction, RD = Radial Direction and TD = Tangential Direction) [92]

The sheet rolling texture is identical to the tube in Case 1 ($R_w/R_D > 1$), as the dimensional change in the transverse direction is smaller than the dimensional change in the rolling direction (see Figure 2.9 b). However, in the case of the wire drawing, the material is compressed concentrically, resulting in a deformation with $R_w/R_D = 1$ (see Figure 2.9 c). Thus, the reduction ratio R_w/R_D controls the texture of zirconium alloys. Therefore, by changing the effective compressive forces, it is possible to control the texture of said alloys.

As discussed earlier, texture has a strong influence on the orientation of zirconium hydrides, and a great deal of work was done in order to understand the effect of texture on the mechanical properties, and failure of, zirconium alloys. In 1972, Wood [95] demonstrated that texture has little effect on stress corrosion cracking of Zircaloy in an iodide atmosphere. Further, Peesh et al. [96] demonstrated that there is more cracks when the applied stress is perpendicular to the basal plane. Schuster et al. [97] concluded that, for the stress corrosion cracking, texture plays more important a role than composition in Zircaloy. Later, many studies [98, 99,100,101] on the stress corrosion cracking have concluded that texture has a major influence on both the nucleation and the growth of cracks. On the other hand, dimensional stability of zirconium alloys during irradiation is also reported to be dependent on texture of zirconium alloys [102,103].

In summary, texture is an important parameter that influences many physical and mechanical properties of zirconium cladding and pressure

tubes. Continued work on zirconium texture is needed for better understanding and control of the mechanism of failure.

2.4.1 Kearns f parameter

Kearns f parameter is used to quantify degree of anisotropy [104]. It gives a fraction of projections of basal poles on the three principal directions i.e., circumferential, axial and radial (f_{CD} , f_{AD} , f_{RD}) of zirconium and other HCP tubes or sheets. Theoretically, the sum of the fraction of the basal pole projections in all three directions should be equal to 1.0 (see equation 2.6), but in general, the linear variation of diffraction intensities at different tilt angles can lead to slight errors.

$$f_{\rm CD} + f_{\rm AD} + f_{\rm RD} = 1.0....(2.6)$$

The value of f for any reference direction can be obtained by summation of the volume fractions (V_i) of crystals having basal poles inclined at angle (Φ_i) with respect to the reference direction, multiplied by $\cos^2 \Phi_i$, as shown in equation (2.7)

$$f = \sum_{\phi=0}^{\phi=\frac{\pi}{2}} (V_i) \cos^2 \Phi_i.....(2.7)$$

Nagai et al. [105] obtained an equation which is used to predict the basal plane orientation of CWSR Zircaloy tubes based on the reduction ratio.

$$f_{\rm RD} = 0.5 + 0.078 \ln (Q)$$
.....(2.8)

Where,
$$Q = \frac{\ln(\frac{t_f}{t_0})}{\ln(\frac{D_f}{D_0})}$$
 and $RA = \frac{R_w}{R_D}$

Later, a similar relation was obtained by Konishi et al. [106] for pilgered tubes (see Equation 2.9),

$$f_{\rm RD} = 0.94 + 0.05 \ln (Q) - 0.005 (RA) \dots (2.9)$$

Where f_{RD} is the fraction of basal planes in the radial direction, t is the thickness of the tube at initial and final passes, subscripts f and o refer to the final and initial values, respectively, R_w is the wall thickness, and R_D is the wall diameter reductions. This clearly demonstrates that the texture of zirconium, as defined by Kearns parameters, can be predicted knowing the reduction ratios that characterize the deformation process.

2.4.2 Texture inhomogeneity

Texture inhomogeneity can become an important problem when dealing with present-day nuclear materials. This inhomogeneity can be due to many factors, such as geometry of plastic forming, coefficient of friction between the tool and the deformed metal, deformation rate, temperature of deformation, and localized heating [107]. Although some studies have been conducted on the effect of texture inhomogeneity on various mechanical properties [103, 108, 109, 110], it is still not clear how texture inhomogeneity may influence the failure of Zr alloy tubes in nuclear reactors.



a)



Figure 2.10: a) Angular distribution of basal poles along TD-RD axis; b) Layer by layer change in Kearns parameter (TD – Transverse direction, RD – Rolling direction, ND – Normal direction) of a Zr-2.5Nb sheet. A and B correspond to different procession routes)[103].

Perlovich et al. [103] have investigated the layer-by-layer inhomogeneity in rolled zirconium sheets. A significant difference in pole density and Kearns parameter was reported along layers of the sheet (see Figure 2.10b). Based on this observation, it was concluded that, during hot rolling, the deformation-induced $\alpha \rightarrow \beta$ transformation is primarily responsible for the texture inhomogeneity. Also, the dependence of thermal expansion coefficient of zirconium alloys on preferred orientation has been clearly demonstrated [111]. In conclusion, the texture inhomogeneity in zirconium alloys creates differences in thermal expansion of different layers of the materials and is responsible for internal stresses that may contribute to failure of Zr alloy tubes.

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3.0 Preferential Precipitation of Hydrides in Textured Zircaloy-4 Sheets

Preface

The preferential sites of hydrides nucleation and growth has been identified and analyzed. Hydrided Zircaloy-4 sheets with different hydrogen concentrations were examined. The results presented and discussion offer novel understanding of hydride behavior in zirconium alloys. The paper presented in this chapter has been published in the *Journal of Nuclear Materials [Vol. 403 (2010), 101 – 107].* This article has been listed in the Top 25 Hottest Articles' list of 'Science Direct' in Energy – JNM, July-September, October-December (2010) and January-March (2011) segments.

Abstract

Cold-worked and stress relieved (CWSR) Zircaloy-4 sheet-samples were charged with 45–247 wt. ppm of hydrogen using an electrolytic technique. Morphology and orientation of hydrides was examined with the help of optical microscopy (OM) and electron backscatter diffraction (EBSD) technique. The hydrides identified as δ -ZrH1.5 phase by EBSD analysis, were located both within the grains and along the grain boundaries, but the grain boundary hydrides appeared to be dominant. The hydrides and the matrix have the $(0001)\alpha$ -Zr//(111) δ -ZrH1.5 orientation relationship at all locations. Three types of grain boundary hydrides were observed. A closer look on the grain boundary hydrides shows that the grain boundary hydrides are not exactly on the grain boundary; but very near the grain boundaries that follow the crystallographic relation $(0001)\alpha$ -Zr//(111) δ -ZrH1.5, only very few exceptions were recorded. The preferential sites for the grain boundary hydrides were basal planes of zirconium matrix located close to grain boundaries. Also, the hydrides show strong {111} texture with maxima located at the same angle on the pole figure as the maxima of basal plane of α -zirconium matrix. The reproducibility of the results was verified using samples with different hydrogen concentrations.

Keywords: Zircaloy-4, EBSD, Texture, Crystallographic relation

3.1 Introduction

Zircaloy-4 is widely used as a key structural material (e.g., cladding material) of CANDU^{®1} fuel-bundles. Hydrogen pick-up during fuel-bundle irradiation leads to formation of hydrides, often in the form of platelets in the material. These hydrides have a deleterious impact on the mechanical properties of the material. Thus an in-depth understanding of the hydriding process and the hydride orientation relative to the α -zirconium matrix should contribute to improvement in fuel-manufacturing technologies and may increase the safety margin.

It is well known that the hydrogen solubility in a-zirconium decreases rapidly from 6 at.% at 550°C, to 0.7 at.% at 300°C, and 10⁻⁴ at.% at room temperature [1] and that excess hydrogen is precipitated from the matrix in the form of zirconium hydrides. Three types of hydride phases were reported earlier and which one is formed depends on the cooling rate and hydrogen concentration. Among the hydrides, the literature about γ hydride (FCT) is contradictory with two review articles reporting it as metastable [2, 3] and others reported it as equilibrium phase below 250°C [4,5], δ -hydride (FCC) is considered to be a stable phase that is formed during slow cooling and ϵ -hydride (FCT) is formed at higher hydrogen concentration (63 at.%) [2]. It is well known that the δ -hydride

 $^1\mbox{CANDU}^{\mbox{\tiny (B)}}$ is a registered trademark of Atomic Energy of Canada Limited (AECL).

phase is most often formed in the material during bundle irradiation; however, there has been little discussions on formation mechanism of δ hydrides [6, 7].

It has been proposed that, in unstressed sample, hydrides would grow into grains along particular habit planes of the matrix [8, 9]. Various habit planes have been suggested to date, like the prism plane of $\{10\overline{1}0\}$ [10,11], pyramidal plane of $\{10\overline{1}1\}[12,13]$, basal plane (0001), $\{10\overline{1}7\}$, [9,14] and twinning planes of $\{10\overline{1}2\}$, $\{11\overline{2}1\}$ and $\{11\overline{2}2\}$ [15] of the HCP matrix. Insufficient evidence has been presented to support these assignments however, and the facts that many habit planes have been suggested make it difficult to understand the crystallographic relationship between the hydride and the matrix. A few researchers reported that the hydride preferential sites are grain boundaries (intergranular hydrides) but could not come up with rationalized notations [16]. Few papers reported the crystallographic relation of inter-granular hydrides in Zircaloy-2 [6, 17, 18, and 19]. Zircaloy-4 that has slightly higher iron content and almost no nickel is showing better resistance to hydrogen pickup than Zircaloy-2 [20, 21]. However, the amount of hydrogen pick up in the material increases with fuel irradiation time; and therefore a thorough understanding of hydride precipitation behavior in

Zircaloy-4 is needed for further improvement of fuel irradiation performance.

Zirconium hydrides at macroscopic level can be identified and tracked by neutron and X-ray diffraction techniques [22,23]. However for microscopic levels, where high spatial resolution characterization is needed, TEM and EBSD are used. For the present work EBSD was used over TEM, as it gives more statistically reliable data and allows obtaining information from larger areas [24]. (See Appendix III for more details).

The objective of the present investigation was to determine the crystallographic relationship between δ -hydrides and the matrix in Zircaloy-4 CWSR sheet. Because Zircaloy-4 sheet and tubing materials are both used for fabrication of CANDU fuel-bundles, and they have very similar texture and hydrogen pick-up behavior, the results of this investigation are also applicable to the tubing material.

3.2 Experimental

The chemical composition of the Zircaloy-4 sheet-material is given in Table 3.1. The samples, provided by Atomic Energy of Canada Limited (AECL), were electrolytically hydrided in 0.125 M H_2SO_4 solution at AECL Chalk River Laboratories. The current density was 150 mA/cm², and the solution temperature was controlled at 70 ± 5°C. Hydrogen

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content in the samples was varied from 45 wt. ppm to 247 wt. ppm by adjusting the operation time for the hydrogen-charge process. After the charging, the samples were homogenized by heating them in flowing argon at 375°C for 3h, and then furnace cooling to room temperature. The hydrogen concentrations in the samples were determined by hot vacuum extraction mass spectrometry.

Table 3.1: Alloy composition of Zircaloy-4

	Sn (wt.%)	Fe (wt.%)	Cr (wt.%)	Ni (wt.%)	O (wt.%)	Zr (wt.%)
Zircaloy-4	1.52	0.21	0.11	<35 ppm	0.125	bal

The samples for EBSD analysis were prepared by etching them in a solution of 45% HNO₃, 45% H₂O and 10% HF, followed by colloidal silica polishing. The EBSD measurements were carried out with an orientation imaging microscopy (OIM) system, installed on a FEG XL30 scanning electron microscope (SEM). The EBSD patterns were obtained and analyzed by means of the TSL OIM software.

3.2.1 The reference frame for electron backscatter pattern (EBSP) analysis

The Zircaloy-4 sheet directions represented in the present optical, EBSD and texture analyses are RD, TD and ND. Where RD is the rolling

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direction of the sheet, TD is the transverse direction of the sheet and ND is the normal direction.

3.3 Results and discussions

3.3.1 Optical microscopy







Figure 3.1: Typical optical micrographs of the samples with ~247 ppm of hydrogen. Note the hydrides (arrow) are along the TD direction in ND-TD planes; along RD direction in ND-RD planes and along RD direction in RD-TD planes.

Optical examination of the hydrided samples revealed the presence of hydride platelets. Many hydride platelets found to be precipitated in the direction perpendicular to applied stress in ND–TD, ND–RD, RD–TD planes in the form of long chains as shown in Figure 3.1.The grains and grain boundaries are however not discernable optically, and thus, we cannot obtain any detailed information regarding location of the hydrides with respect to the grains and grain boundaries. However, this information is crucial for understanding the mechanical behavior of the material, for example, fracture mechanism of it under load.

3.3.2 Hydride crystallographic orientation

The EBSD technique not only identifies the hydride phase by indexing their characteristic diffraction patterns, but also determines their crystallographic orientations with respect to Zircaloy-4 matrix. Kikuchi patterns indexed with EBSD system show the presence of α -zirconium (HCP) and δ -hydrides (FCC), with negligible amount of γ -hydride. Figure 3.2 shows the grain map of un-hydrided and hydrided samples where each grain is mapped with different color code based on the crystal orientation. As shown in Figure 3.2 (a), the matrix has the characteristic CWSR microstructure characterized by the presence of elongated grains along the rolling direction (RD). Figure 3.2 (b) shows the typical microstructure of hydrided sample. For better contrast, the hydrides are marked with red color.



Color Coded Map Type: Crystal Orientation

				Total	Partition
		Min	Max	Fraction	Fraction
	Zirconium (Alpha)	0°	30°	0.081	0.081
	Zirconium (Alpha)	30°	60°	0.637	0.637
	Zirconium (Alpha)	60°	90°	0.267	0.267



Color Coded Map Type: Phase Total Partition Fraction Fraction Phase

i naoc	ridenon	Thatta
Zirconium (Alpha)	0.944	0.944
Zirconium Hydride (Delta)	0.052	0.052
Zirconium hydride (Gamma)	0.004	0.004

(b)

Figure 3.2: EBSD grain and phase map of a) Un-hydrided b) Hydrided Zircaloy-4 samples (247 wt.ppm).

The α -zirconium (HCP) matrix and δ -Zr-H_{1.5} (FCC) hydrides are indentified using the standard Kikuchi patterns of zirconium (JCPDS 00-005-0665) and zirconium Hydride (JCPDS- 00-008-0218), respectively. As shown in Figure 3.3, the hydrides have precipitated both inside the grains and along the grain boundaries. EBSD was also recorded at lower magnification as shown in Figure 3, in-order to obtain good statistical data about the hydride precipitation sites.



Figure 3.3: EBSD grain map of hydrided sample at lower magnification (247

wt.ppm)

Out of 150 analyzed locations 97 were observed to be grain boundary hydrides, where as 53 were intra-granular (within the grains) hydrides. So the ratio of intra-granular hydrides to inter-granular hydrides is about 1.8 which indicates that hydride precipitation along the grain boundaries is predominant. However, the ratio of inter-/intra-granular hydrides varies based on the cooling rate and initial sample condition [17, 25, 26].

3.3.2.1 Intra- and inter-granular hydrides

In the literature [27, 28] different habit planes were suggested for intragranular hydrides. To determine the habit plane for the present samples, the crystallographic relationship between the hydrides and the α -Zirconium matrix was analyzed using pole figure method. The hydrides were observed within the grains, although they are in contact with the grain boundaries along its length. At all points intra- and inter-granular hydrides were found following (0001) α -Zr//(111) δ -ZrH_{1.5} relationship as illustrated in Figure 3.4. This observation supports the interpretation of hydride formation proposed by K. Une et al. [13,29] for Zircaloy-2 samples and such orientation relationship exists in the alpha component of Zr-2.5wt.%Nb alloy as well [18]. Root et al. [4] have also shown by neutron diffraction that such orientation relationship exists for both δ and γ hydrides.



Figure 3.4: Zirconium hydrides precipitated within grains and at grain

boundaries

3.3.2.2 Hydride at grain boundaries

Three types of grain boundary hydrides were observed in the stress relieved Zircaloy-4 samples.

- Hydride initiated at the grain boundary, but growing on both sides of the grain as shown in Figure 3.5 (I)
- Hydride along the grain boundary; On both sides of the grain boundary as shown in Figure 3.5 (II)
- 3) Hydride near the grain boundary as shown in Figure 3.5 (III).

These three types of grain boundary hydrides look like precipitates on the grain boundary at lower magnification in EBSD and optical micrographs. But this observation can be misleading. Let us look at the grain boundary hydrides at higher magnification in-order to get a clear picture on the hydride orientation relation with the zirconium matrix.

1) <u>Hydride growing on both sides of the grain boundary</u>

In this case the hydride on the grain "a" is found to be following the $(0001)\alpha$ -Zr//(111) δ -ZrH_{1.5} orientation relation with the grain "a" and the hydride on grain "b" is found to be following the $(0001)\alpha$ -Zr//(111) δ -ZrH_{1.5} orientation relation with the grain "b"



Figure 3.5 (I)

2) <u>Hydride on the grain boundary.</u>

In this case hydride precipitated at the grain boundary. But even here the hydride near to the grain boundary on the grain "a" is showing $(0001)\alpha$ -Zr//(111) δ -ZrH_{1.5} orientation relationship and the hydride on the grain "b" near the grain boundary is again following $(0001)\alpha$ -Zr//(111) δ -ZrH_{1.5} orientation relationship with the zirconium matrix.



Figure 3.5 (II)

3) <u>Hydride near the grain boundary</u>

This is the most interesting case; unlike in the above two cases, the hydride is growing within a single grain without spreading onto other grains, however also in this case $(0001)\alpha$ -Zr//(111) δ -ZrH_{1.5} orientation relationship is clearly observed



Figure 3.5 (III)

Figure 3.5: Three different grain boundary hydride. Hydrides growingI) on both sides of the grain boundary, II) on the grain boundary andIII) near the grain boundary.

A closer look at the grain boundary hydrides shows that the hydrides are very close to the grain boundaries following $(0001)\alpha$ -Zr//(111) δ -ZrH_{1.5} orientation relationship.

The hydride, during the fast cooling, may precipitate at random grain boundaries, but in the case of δ -hydrides which forms at slow cooling rates and also mainly observed during nuclear reactor operation are found to be showing crystallographic relation with the zirconium matrix. The hydride precipitation is reported to be associated with micro stresses which arise from cold working [30]. But this is ruled out in the present case as the sample is stress relieved. Perhaps the most revealing part of the present analysis is that, in-order to follow (0001) α -Zr//(111) δ -ZrH_{1.5} orientation relationship with zirconium matrix, the hydrides are precipitating on the grains whose basal planes is oriented close to the grain boundary. In this way, the elastic strain energy and interferential energy and at the same time grain boundary energy can be minimized. Singh et al. using strain energy minimization technique, have reported that δ -hydride can minimize its strain energy by precipitating on basal plane (0001) of α -zirconium [31]. This preferential behaviour of δ -hydrides can be a reason for inhomogeneous precipitation of hydrides at different parts of the sample.

3.3.3 Sample with low hydrogen concentration

Experiments were performed on the sample with 117 wt. ppm hydrogen. Figure 3.6 shows a typical EBSD pattern of sample. A lower number of small hydride platelets is recorded however even in this case the hydrides still followed the $(0001)\alpha$ -Zr//(111) δ -ZrH_{1.5} orientation relation, irrespective of the hydride location.



RD Figure 3.6: EBSD of sample with 117 wt. ppm hydrogen concentration

3.4 Texture

The micro and macro texture data were obtained from X-ray diffraction (XRD) and EBSD techniques, respectively. Both shows strong (0002) basal plane texture, a typical texture of CWSR Zircaloy-4 material as shown in Figure 3.7



Figure 3.7: (0002) basal plane texture of Zircaloy-4 sheet a) macro texture determined by XRD b) micro texture determined by EBSD



b)

Figure 3.8:- Texture of Zirconium hydride (δ -ZrH_{1.5}) a) macro texture b) micro

texture

Interestingly, both the micro and macro texture analyses of the hydride phase show that the zirconium hydride has a strong {111} texture and if we compare the results presented in the pole figures of Figures 3.7 and 3.8, we can find that, the peak of basal plane of zirconium and the {111} plane of zirconium hydride are at the same location (i.e., the areas color-coded in red in the pole figures). This implies that {111} plane of zirconium hydrides always prefer to orient parallel to the (0002) basal plane of the matrix.

The present study provides the detailed evidence about grain boundary hydrides and documents the orientation relationship of hydrides with the zirconium matrix in CWSR Zircaloy-4 samples.

3.5 Conclusions

The Crystallographic orientation between the hydrides and a CWSR Zircaloy-4 matrix was examined using the EBSD technique. The following conclusions can be derived based on the results of this investigation:

 Statistical data on hydrided sample (247 wt.ppm) shows more inter-granular hydrides than intra-granular hydrides in CWSR Zircaloy-4 sheet.

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- 2. Both inter-granular and intra-granular hydride are found to follow the $(0001)\alpha$ -Zr// $(111)\delta$ -ZrH_{1.5} orientation relationship with the zirconium matrix.
- 3. Three types of grain boundary hydrides were observed. EBSD at higher magnification shows that hydrides are very close to the grain boundaries following $(0001)\alpha$ -Zr// $(111)\delta$ -ZrH_{1.5} orientation relationship.
- 4. Hydride preferential sites are the grains that have basal plane close to the grain boundaries and decreasing hydrogen concentration has no effect on the $(0001)\alpha$ -Zr// $(111)\delta$ -ZrH_{1.5} orientation relationship.

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4.0 Hydride Formation under Hoop Stress in Zircaloy-4 Cladding

Preface

In this study, hydride behavior under different hoop stress has been investigated. A high pressure hydrogen gas furnace has been designed for these experiments. Details of the hydrogen charging procedure are provided in appendix I. Novel experimental data has allowed for a detailed description of a role of stress in the process of radial hydrides formation to be presented. The paper presented in this chapter has been submitted to the *Journal of Nuclear Materials*.

Abstract

Zircaloy-4 cladding was hydrided in high pressure hydrogen gas furnace at a temperature and pressure of 350°C and 20 MPa respectively. During hydriding, range of hoop stresses were applied on the cladding tube using copper rod. The effect of different hoop stresses on the orientation of hydride platelets was studied using optical microscopy (OM) and diffraction electron backscattered (EBSD) techniques. Optical micrographs, showed the increase in number of hydrides oriented along the radial direction with the hoop stress. Apart from radial hydrides, the hydrides which are inclined at an angle in-between circumferential and radial direction are also observed. The hydrides formed without hoop found to follow $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} orientation stress are relationship. Interestingly, the hydrides which are oriented perpendicular to the circumferential direction are following $\{10\overline{1}1\}\alpha$ -Zr// $\{111\}\delta$ -ZrH_{1.5}. relationship with the matrix grains. In addition, habit planes such as {10 $\{10\overline{1}0\}$ are observed for the hydride which are $\overline{1}1$ }, {10 $\overline{1}7$ }, {10 $\overline{1}3$ }, inclined at an angle to the circumferential direction. Present paper helps in better understanding the process of hydrides reorientation under hoop stresses.

Keywords: Zirconium, EBSD, Zirconium hydride, Reorientation, Hoop stress

4.1 Introduction

Zirconium alloys have gained a lot of importance due to their extensive application in nuclear industry. The low coefficient of neutrons absorption and a high corrosion resistance made them an important material in nuclear reactors. During reactor operation, zirconium alloys absorb hydrogen atoms due to the corrosion between the cladding and the coolant. However, an unalloyed zirconium can dissolve up to 450 wt.ppm of hydrogen at a temperature of 500°C, but the solubility drastically decreases to 65 wt.ppm at 300°C and it further decreases to 0.05 wt.ppm at room temperature [1]. The low solubility of the hydrogen with temperature leads to formation of brittle hydride platelets.

In general, the formation of hydride platelets affect the mechanical properties of the fuel cladding. Some of the main failure mechanisms of zirconium alloys are: delayed hydride cracking [2], corrosion assisted hydride cracking [3] and hydrogen assisted localized shear [4]. In all these mentioned mechanisms, hydride orientation plays a significant role. In addition, extensive studies on the orientation of hydrides showed that the presence of hydrides oriented towards radial direction play a major role on the functional behavior of the zirconium alloys [5, 6, 7, 8, 9]. Factors such as temperature gradient, stress gradient, texture and

the fabrication method used, play a vital role in the formation of radial hydrides in Zircaloy [10, 11]. It has been reported that Zircaloy tubes having radial hydrides show less strength and ductility than the tubes with circumferentially oriented hydrides [12, 13]. Therefore, all commercial tubes are manufactured using the pilgering process which generates high compressive stresses along radial-circumferential plane, so that the circumferential hydrides are formed [10, 11, 14]. However, during reactor operation, the hoop stress is generated due to fuel expansion during shuffling, temperature variation and during dry storage, which leads to formation of radial hydrides [15].

The precipitation of δ -hydrides in the α -phase of zirconium alloys has been extensively studied during last six decades. Zirconium hydrides are observed at both grain and grain boundaries. Many habit planes of the hexagonal matrix have been suggested for the hydrides formed in grains, like the prism plane of $\{10\overline{1}0\}$ [16,17], pyramidal plane of $\{10\overline{1}1\}$ [18,19], basal planes $\{0001\}$, $\{10\overline{1}7\}$, [20,21] and twinning planes of $\{10\overline{1}2\}$, $\{11\overline{2}1\}$ and $\{11\overline{2}2\}$ [22]. Insufficient evidence has been presented to support these crystallographic relationships, and the facts that so many habit planes have been suggested make it difficult to understand what factors affect the relationship between the hydride and the matrix. Recently
using EBSD technique, Une et al. [23] have shown that hydrides mainly follow $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} orientation relationship with only a few hydrides showing orientation relationship of $\{10\overline{1}7\}\alpha$ -Zr//{111} δ -ZrH_{1.5}. In our previous analysis we showed that under stress relieved condition, hydrides always precipitate on the basal plane and hydride preferential sites are the grains with basal planes closer to grain boundaries [24]. However, the preferential habit planes of re-oriented hydrides formed due to hoop stress has never been clearly established.

Zirconium hydrides at macroscopic level can be identified, and also tracked by neutron and X-ray diffraction techniques [25] and [26]. However for microscopic observations, where high spatial resolution is needed, TEM and EBSD are used. In the present work EBSD was used, as it gives statistically reliable data, allows obtaining information from larger areas and makes possible to identify habit planes for hydride formation [27].

Many researchers have studied the effect of reoriented hydrides on the mechanical properties of the hydrides. But, the mechanism behind the hydride reorientation process is still unknown. In the present study, the cladding is hydrided under different hoop stresses and the effect of hoop stress on hydride orientation and crystallographic relation with the zirconium matrix has been studied in details.

4.2 Experimental

Zircaloy-4 cladding tubes received from GE-Hitachi were employed in this study. A cylindrical tube of length 31 mm with 12.23 mm in diameter and 0.705 mm thickness was cut from the as received cladding. The chemical composition of the cladding is given in Table 4.1.

Table 4.1: Alloy composition of Zircaloy-4

	Sn (wt.%)	Fe (wt.%)	Cr (wt.%)	Ni(wtppm)	O (wt.%)	Zr (wt.%)
Zircaloy-4	1.52	0.21	0.11	<35	0.125	bal

The Zircaloy-4 cladding reference frame, used in EBSD analyses, is defined by CD, RD and AD directions. Where CD is the circumferential direction, RD is the radial direction and AD is the axial direction of the cladding.

Gaseous hydriding was done on the samples using high pressure hydrogen gas furnace. Initially, the sample chamber was evacuated using mechanical pump. Then, the chamber is flushed with argon gas. After that, the chamber is filled with hydrogen gas and a pressure of 20 MPa was maintained. Thermal cycling was done on the samples at temperatures from 350°C to room temperature. This process is repeated 10 times with 5h soaking time at 350°C per each cycle, followed by furnace cooling (see Appendix I for more details).

Samples for EBSD measurement were prepared by etching in the solution of 45 % HNO_3 , 45 % H_2O and 10 % HF, followed by colloidal silica polishing. The EBSD measurements were carried out using TSL-OIM system, installed on a FE-XL30 scanning electron microscope (SEM). The EBSD patterns were analyzed by TSL OIM software.

4.2.1 Hoop stress

In-order to achieve close approximation to reactor working conditions, the hydriding was done at 350°C; simultaneously hoop stress was applied on the cylindrical sample using a solid copper rod of diameter 12.18 mm. The hoop stress was generated due to the resistance offered by cladding to the thermal expansion of copper at 350°C. A cylindrical copper rod having a taper of 15 μ m (see Figure 4.1) from the initial diameter was made using high precision machining.



Figure 4.1: Schematic view of a) Method of applying hoop stress using copper rod, b) Copper rod was tapered off differently at different areas of the sample.

Shape of the copper rod near the sample area is designed in such a way that after thermal expansion, a different stress will be applied at every 8 mm interval of the cladding tube. Shape of the copper rod placed inside the Zircaloy-4 cladding tube is shown in Figure 4.1 (b). The sample area is divided into four stress gradient zone of 8 mm each. In each zone different pressure is exerted on the cladding tube. For simplification of the calculations of the hoop stress applied on the cladding, the following assumptions were made: 1) the structure of the copper rod used is isotropic; 2) the stress generated by the thermal expansion of copper rod was approximated as an internal pressure. Based on these assumptions hoop stress applied on thin-walled Zircaloy-4 cladding was calculated using Equation 4.1.

Where σ_{Φ} is hoop stress, P is the internal pressure generated due to thermal expansion of copper, r is an internal radius of the cladding tube, and t is the cladding wall thickness.

The hoop stresses applied on the cladding at areas of four different copper rod diameters, calculated using Equation 4.1, are 1) 47 MPa, 2) 272 MPa , 3) 497 MPa and 4) 780 MPa respectively. After the high temperature gaseous hydriding at 350°C, the samples of 4 mm each were cut from the cladding tube in such a way that the intersection areas between different stress zones were eliminated. However, the stress

values reported in this paper are based on the mathematical calculations of resistance to thermal expansion of the copper rod. But, knowing that copper is soft at 350°C [28], one can assume that in reality, the hoop stress exerted by the copper rod before deforming itself along the longitudinal direction can be much lower than the estimated stress values. Nevertheless, the objective of the present paper is to qualitatively assess the change of habit plane of the hydrides with the change of hoop stress. While quantitative information on the specific hoop stress magnitude might be of interest, but it is beyond the scope of the present paper, and left for the future

4.3. Results

4.3.1 Optical analysis

Figure 4.2 shows the optical images of the hydrided samples which were subjected to different levels of hoop stress. The hydrides are orienting towards the radial direction with increase in hoop stress.



Figure 4.2: Optical micrographs of sample at hoop stress of a) no stress, b) 47 MPa, c) 272 MPa, d) 497 MPa and e) 780 MPa

The hydrides formed under hoop stress, are oriented at different angle of inclinations with respect to the circumferential direction. At an initial hoop stress of 47 MPa, only few radial hydride platelets (i.e. hydrides oriented parallel to the radial direction) are found (see marked areas of Figure 4.2 (b)). Interestingly the hydrides which were not completely oriented towards radial direction but inclined at an angle to the circumferential direction are also observed (see areas marked in Figure 4.2 (b)). At 47 MPa, about 25 % of hydrides are oriented at an angle to the circumferential direction, and with the increase in hoop stress, the number of hydrides oriented at an angle to the circumferential direction has increased to about 90% at 780 MPa. Apart from the radial hydrides, the hydrides inclined at an angle to the circumferential direction are observed in all hoop stresses. In our earlier experiments on unstressed samples, the orientation of hydrides is found to follow $(0001)\alpha$ - $Zr/({111}\delta-ZrH_{1.5})$ relation with the zirconium matrix [24]. If the stress is applied the question is to be asked whether this crystallographic relationship is still important or other habit planes are introduced. This information is crucial for understanding the hydride reorientation process under stress and the mechanism of cladding failure.

Hoop Stress (Mpa)	Average circumferential hydride length (µm)	Average length of hydrides under stress	Number of analyzed locations	No of circumferential hydrides	No of hydrides oriented at an angle w.r.t circumferential direction	Percent of hydrides oriented at an angle w.r.t circumferential direction
		(µm)				
No	47.07±19	N/A	100	100	0	0
stress						
47	33.03±13	16.60±6	100	74	26	26.00%
272	25.58±8	15.81±5	109	67	42	40.36 %
497	19.04±6	16.81±4	140	41	99	70.71 %
780	16.23±3	15.58±4	131	13	118	90.08%

Table 4.2: Statistics illustrating hydride distribution for different hoop stresses

*N/A = Not available

Table 4.2 shows the length of hydrides, and the percent of the hydrides inclined at an angle to the circumferential direction at different hoop stresses. Generally the length of the hydride platelets depends on hydrogen concentration, where small stacks of hydrides merge together to form a long chain. Assuming that hydrogen concentration is constant, since the whole cladding is hydrided in a closed furnace at uniform hydrogen pressure of 20 MPa, the decrease in the length of hydrides formed under hoop stress can be attributed to the increase in number of hydride nucleation sites.

4.3.2 Orientation imaging of hydride formation under stress

Electron backscattered diffraction technique was used in-order to examine the hydride formation under stress and hydride orientation with respect to the matrix. The raw data obtained from TSL data collection software contains few wrongly indexed patterns. Cleanup was performed on the raw data by removing the data points having confidence index (CI) lower than 0.1. The grain tolerance angle of 5° was used. The hydrides at the radial-circumferential plane were examined. Figure 4.3 shows a typical EBSD phase map of unstressed Zircaloy-4 cladding, where long hydrides are orientated along the circumferential direction. EBSD study confirms the presence of δ - hydride platelets.



Figure 4.3: Typical EBSD phase map of unstressed hydrided Zircaloy-4

The orientation relationship is obtained by observing the coincidence of crystallographic orientations of δ -hydride and α -zirconium grains, where coincidence is judged with an angle difference of $<\pm5^{\circ}$ [23, 29]. As reported earlier [24], the hydrides in unstressed condition were observed to be following the (0001) $-Zr//\{111\}\delta$ -ZrH_{1.5} orientation relationship with zirconium matrix (see Figure 4.4 (I)). Interestingly, this orientation relationship was no longer observed for the hydrides which formed under stress. Hydrides with different angle of inclinations were analyzed using EBSD images of stressed samples. These hydrides are mainly found to be

growing on $\{10\overline{1}1\}$ plane following $\{10\overline{1}1\}\alpha$ -Zr// $\{111\}\delta$ -ZrH_{1.5} relation (see Figure 4.4 (V)). Although the $\{10\overline{1}1\}$ plane, which is pyramidal plane of the hexagonal structure, is predominantly observed as main habit plane for hydrides formed under stress, other habit planes are also observed for the stressed samples (see Figure 4.4 (II), (III) (IV)). Few hydrides that are inclined at an angle close to the circumferential direction are formed on $\{10\overline{1}7\}$ following $\{10\overline{1}7\}\alpha$ -Zr/ $\{111\}\delta$ -ZrH_{1.5} orientation relation and the habit planes of $\{10\overline{1}3\}$ and $\{10\overline{1}0\}$ were also observed for the hydrides, which were aligned close to the radial direction and followed $\{10\overline{1}3\}\alpha$ -Zr// $\{111\}\delta$ -ZrH_{1.5}, $\{10\overline{1}0\}\alpha$ -Zr// $\{111\}\delta$ -ZrH_{1.5} orientation relationships. In addition, under hoop stress, some hydrides that are parallel to circumferential direction are still following $(0001)\alpha$ -Zr//{111} δ - $ZrH_{1.5}$, and the hydrides oriented at an angle parallel to the radial direction (radial hydrides) of the cladding are always found to be following the orientation relationship of $\{10\overline{1}1\}\alpha$ -Zr// $\{111\}\delta$ -ZrH_{1.5} with the zirconium matrix. The statistics illustrating hydride habit planes at different stresses is given in Table 4.3.







(IV)



(VI)



CD

Figure 4.4: EBSD Phase map with orientations of hydrides of samples subjected to following hoop stresses I) no stress, II) 47 MPa, III) 247 MPa, IV) 497 MPa, V) 780 MPa, VI) 780 MPa (a, b are pole figure locations on EBSD phase map, where " a) " corresponds to pole figures of α -Zr matrix and " b) " corresponds to the pole figures of δ -hydride)

Hoop Stress	Number of	Number of Hydrides following the orientation relationship				
(Mpa)	analyzed locations	(0001)α-Zr// (111)ZrH1.5	{10 1 7}α-Zr// (111)ZrH _{1.5}	{10 1 0}α-Zr// (111)ZrH1.5	{10 1 1}α-Zr// (111)ZrH1.5	
No stress	30	28	2	0	0	0
47	30	12	6	0	0	12
272	34	10	5	4	0	15
497	39	8	4	3	3	20
780	37	4	3	2	2	26

Table 4.3:- Statistics illustrating hydride habit planes at different stresses

4.4. Discussion

The principal stress direction in cladding and pressure tubes is circumferential direction. The tubes manufactured in the pilgering process are cold worked and stress relieved during the final stage of fabrication so that a high compressive strain along the radial direction is developed. The cold work results in a texture with basal planes aligned at an angle of 30-40° to the circumferential direction. The texture of the tubes is such (see Figure 4.5 (a)) that the prismatic plane is parallel to the tube surface and inclined to the radial direction, and the pyramidal plane aligned very close to the radial direction. So if the hydrides have $\{10\overline{1}1\}$ as a habit plane then they will be oriented parallel to the radial direction and if the hydrides grow along (0001) habit plane, circumferential hydrides are observed (see Figures 4.5 (a) and (b)).

Section 4.3 clearly demonstrates the orientation of hydrides under hoop stress and their crystallographic relationship with the zirconium matrix. Circumferentially oriented hydrides were observed in the unstressed sample and if we observe the hydrides in single grain (see Figure 4.4 (I)) the platelets are oriented along one direction only, but when the sample is stressed, hydride platelets are observed within a single grain and oriented along different directions (see Figures 4.4 (IV) and (V)). Based on this observation, it can be said that, the cladding under hoop stress always produces higher number of habit planes for hydride precipitation and growth than the cladding in as-received condition, where only basal habit planes were observed. This might be a reason for shorter length and higher number of hydrides, since the segment of claddings was hydrided under the same condition for the same time.

The proposed origin of hydride platelets is a shear process. The formation of hydride requires the co-operative motion of H atoms and diffusion of Zr atoms by shear [14]. Therefore, when hoop stress is applied, the diffusion of zirconium atoms by shear occurs mainly on pyramidal plane $\{10\overline{1}1\}$, which acts as a habit plane for the radial hydrides. Interestingly apart from prism plane $\{10\overline{1}0\}$, other hydride habit planes observed for hydrides formed under stress are the first order pyramidal planes located between basal (0001) and prism $\{10\overline{1}0\}$ planes.

It was reported that the hydride reorientation usually occurs by dissolution of circumferential hydrides and the formation of radial hydrides [14, 30], which means that the new platelets of hydrides are formed when the sample is under stress. So, the hydrides formed under stress in the present analysis, may also represents the reoriented hydrides formed by applying hoop stress on hydrided sample. Therefore, this study can be therefore helpful in understanding the hydride reorientation experiments conducted by other researchers [30, 31, 32]

The $\{10\overline{1}1\}$ plane, which is the most closely packed pyramidal plane, is the main habit planes for hydrides formed under stress. However, the hoop stress acting on the cladding tubes and the stress state within the grain are deciding factors for the selection of habit plane.



Figure 4.5: a) Schematic view of a) hydride orientation without hoop stress and b) hydride orientation under stress.

4.5. Conclusions

1) Hydrides orientation depends strongly on the hoop stress that is applied. At small hoop stresses hydride platelets have orientation close to the circumferential direction. Subsequently with the increase in hoop stress, apart from the hydrides aligned closely to the radial and circumferential directions, the hydrides which were inclined at an angle to circumferential and radial direction were observed.

2) The hydride formed under hoop stress found to be following {10 $\overline{1}$ 1}Zr //{111} ZrH_{1.5} orientation relation with zirconium matrix. Apart from this pyramidal plane, other habit planes {10 $\overline{1}$ 7}, {10 $\overline{1}$ 3} and {10 $\overline{1}$ 0} are also observed.

3) The size of the hydride platelets formed under hoop stress is less than the size of hydride platelets formed in unstressed condition. The decrease in size of hydride platelet can be due to the availability of higher number of hydride habit planes under hoop stress.

4) The selection of habit planes of hydrides is mainly dependent on the applied hoop stress.

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5.0 EBSD Studies on Microstructure and Crystallographic Orientation of δ- Hydrides in Zircaloy-4, Zr-1Nb and Zr-2.5Nb

Preface

This chapter focuses mainly on providing a better understanding of the structure of, and hydride precipitation in, the E110 alloy. The structure of the E110, and of hydrides in this alloy, was compared with the same structural characteristics of Zircaloy-4 and Zr-2.5Nb alloy. The results and discussions presented in this chapter are of particular importance, as not much data on the E110 alloy is available in the literature Therefore, any new information on better performing E110 is of interest. The paper presented in this chapter is published in *Material Science and Engineering-A*, [Vol. 528 (2011), 6366 – 6374].

Abstract

The Zr-Nb alloys are reported to be showing superior resistance to corrosion and substantially lower hydrogen pickup when compared with Zircaloys. In the present study Zircaloy-4, Zr-2.5Nb and Zr-1Nb (E110) alloys were hydrided using high pressure hydrogen gas furnace at a pressure of 20 MPa. Hydriding was done by thermal cycling on the samples at a temperature of 350°C for 10 cycles with 5h soaking time. The microstructural observations on Zircaloy-4 and Zr-2.5Nb samples show long and interlinked hydride like chains, oriented along the circumferential direction. Whereas, in Zr-1Nb (E110) hydrides were short, thick without any preferential orientation with respect to the sample reference direction. Electron backscatter diffraction (EBSD) map shows the presence of β 1 phase in two phased Zr-1Nb, Zr-2.5Nb samples. Heavy $\{10\overline{1}2\} < 10\overline{1}\overline{1} >$ tensile twins and $\{10\overline{1}1\} < 10\overline{1}2 >$ compression twins were observed in Zr-1Nb. Hydrides in Zircaloy-4 and Zr-2.5Nb have shown $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} orientation with α matrix whereas almost 50 % of hydrides in Zr-1Nb (E110) alloy are showing $(0001)\alpha$ -Zr//{100} δ -ZrH_{1.5} crystallographic relation. The $(0001)\alpha$ -Zr//{100} δ -ZrH_{1.5} orientation of hydrides in Zr-1Nb (E110) is observed for the hydrides formed at the twin boundaries.

Keywords: Zircaloy-4, Zr-1Nb (E110), Zr-2.5Nb, EBSD, Crystallography.

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5.1 Introduction

Zirconium alloys are widely used in nuclear reactors due to their low neutron absorption and high corrosion resistance. The hydrogen is generated inside the core of the reactor due to the process called oxygen starvation, where the steam inside the reactor produces almost pure hydrogen [1]. However, the solubility of hydrogen in zirconium alloys varies as a function of temperature. It decreases rapidly from 50 at.% at 500°C to 0.7 at.% at 300°C and 10⁻⁴ at.% at room temperature [2]. Therefore, excess hydrogen at lower temperatures is precipitated as zirconium hydride.

Hydrogen in the form of hydrides has deleterious influence on the service related properties of the fuel cladding and pressure tubes. Extensive studies are in progress on the precipitation of δ -hydrides in the α -phase of zirconium alloys. Zirconium hydrides were found both within grains and at grain boundaries. Many habit planes have been suggested for hydrides formed in grains [3, 4, 5, 6, 7, 8, 9]. Recently using EBSD technique, K.Une et al. [10] has shown that hydrides mainly following (0001) α -Zr//{111} δ -ZrH_{1.5} orientation relationship with only a few hydrides showing orientation relationship of $\{10\overline{17}\}\alpha$ -Zr//{111} δ -ZrH_{1.5}. Our previous results also showed that irrespective of hydride location, hydrides under no hoop stress always precipitate on the basal plane and

hydride preferential sites are the grains with basal planes parallel to grain boundaries [11].

Many western reactors like CANDU adopted Zircaloy-4 for fuel cladding application. Whereas, Russian reactors like RBMK and VVER uses Zr-1Nb (E110) for fuel cladding. Zr-1Nb (E110) cladding tube was made from a mixture of electrolytic and iodide Zirconium. Although extensive investigations were done on Zr-1Nb (E110) in Russian laboratories, not much is published on this alloy in the literature. However, it has been reported that Zr-1Nb alloy shows superior resistance to corrosion and substantially better mechanical properties when compared with Zircaloy-4 [12, 13]. In-depth microstructural analysis using EBSD is needed to understand the performance of this alloy.

The purpose of the present study was to investigate the microstructures of Zircaloy-4, Zr-2.5Nb and Zr-1Nb (E110) alloy using optical microscopy (OM) and orientation imaging microscopy (OIM). Also hydride structure and the distribution of hydrides in these alloys were investigated. The differences, if identified, can be of fundamental importance for understanding the resistance to hydride related failure.

5.2 Experimental

The cold rolled and stress relieved tubes of Zircaloy-4 and Zr-2.5Nb and α -recrystallized Zr-1Nb (E110) alloy were obtained from GE-Hithachi, Nu-Tech and Russian manufacturers respectively. The chemical composition of the alloys obtained is given in the Table 5.1

Alloy	Sn	Fe	Cr	Ni	Nb	0	Zr
	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)
Zircaloy-4	1.52	0.21	0.11	-	-	0.125	bal
E110	-	0.01	< 0.003	0.0035	0.97	0.06	bal
Zr-2.5%	-	<0.15	-	-	2.5	0.127	bal
Nb							

Table 5.1:-The alloy composition of Zircaloy-4, E110 and Zr-2.5% Nb.

Gaseous hydriding was done on the as received samples using high pressure hydrogen gas furnace. Initially the sample chamber was evacuated using mechanical pump. Then the chamber is flushed with argon gas for 5 minutes. In the final step, the chamber with the experimental samples is filled with hydrogen gas up to experimental pressure of 20 MPa. Hydriding was done by thermal cycling process where, the samples at a temperature of 350°C are soaked for 5h, followed by furnace cooling. This cycling process was repeated on all the samples for ten times (see Appendix-I for more details). Three directions were selected for representing the tube reference frames as shown in Figure 5.1. Where AD denotes axial direction, CD denotes circumferential direction and RD denotes radial direction (RD).



Figure 5.1:- Schematic representation of the tube reference frame

Samples were prepared for EBSD measurement by etching in the solution of 45 % HNO₃, 45 % H₂O and 10 % HF, followed by colloidal silica polishing. The EBSD measurements were carried out with an OIM system, installed on a FEI XL30 scanning electron microscope (FESEM). The EBSD patterns were analyzed by the TSL OIM software.

X-ray diffractometry (Bruker D8) having high star area detector was employed to measure the residual stress of the as received claddings and pressure tube. Co-K α target and high angle reflection peak of {1013} were selected. The Bruker Gadds software which uses conventional 20 $\sin^2\psi$ method was used for calculating the bi-axial residual stress of the samples [14]. The room temperature young's modulus of 94.62 GPa for Zircaloy-4, 93.32 GPa for Zr-2.5 Nb, and 92.61 GPa for Zr-1Nb (E110) [15] and Poisson's ratio of 0.34 were used for the present stress measurements.

5.3 Results

5.3.1 Optical analysis

Optical images of Zircaloy-4, Zr-1Nb (E110) and Zr-2.5Nb are shown in Figure 5.2. As reported earlier [16, 17] long circumferential hydrides, oriented in circumferential direction were observed in Zircaloy-4.



a)



c)

Figure 5.2:- Optical images of hydrided samples a) Zircaloy-4, b) Zr-2.5Nb, c) Zr-1Nb (E110) alloy

Close observation shows that these hydrides consist of several hydride platelets sharing common habit plane (see arrows in Figure 5.2 (a)). In Zr-2.5Nb, relatively short circumferentially oriented hydride platelets were observed. But, the hydride morphology is quite different in Zr-1Nb (E110) sample. The hydrides in this alloy are very short and thick, unlike in Zircaloy-4 and Zr-2.5Nb alloy. However, it was reported that the terminal solid solubility of hydrogen is the same in Zircaloy-4 and Zr-Nb alloys in the temperature range of 100-400°C [18]. Therefore the main factors which can affect the hydride orientation are the residual stresses and the addition of Nb, which acts as β -Zr stabilizer. The solubility of Niobium in Zirconium is 0.4 at.%, so the remaining amount will precipitate as β -Nb [19]. Although we did not find β -niobium precipitates in our EBSD results, it is known that Nb can dissolve up to 50 at.% of hydrogen. Hence, there is less hydrogen to form precipitates. This could be the reason for rather short hydride platelets in Zr-2.5Nb and Zr-1Nb (E110) alloys. OIM is used for further analysis, since details of the structure cannot be obtained from optical micrographs.

5.3.2 EBSD analysis of hydrided samples

5.3.2.1 Hydrides in Zircaloy-4

EBSD patterns and orientation imaging was used to analyze the structure of alloys and the hydrides in Zircaloy-4, Zr-2.5Nb and Zr-1Nb (E110) alloy. The EBSD map shown in Figure 5.3 is the phase map of hydrides in Zircaloy-4. The map represents single phase microstructure with hydride platelets marked in red. The hydrides, found at all locations, are maintaining the known relationship of $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5}. This crystallographic relation was verified using pole-figure method described elsewhere [10]. The coincidence of the hydride and

zirconium matrix planes was measured in the {111} and (0001) pole figures with accuracy of about 3°. The detailed description of crystallographic orientation of hydrides in Zircaloy-4 was presented in our previous paper [11].



Figure 5.3: EBSD map of the microstructure of Zircaloy-4 and the pole figures illustrating $\{111\}\delta$ -ZrH_{1.5}//(0001) α -Zr. relationship. (H-Hydride, Zr-Zirconium matrix)

5.3.2.2 Hydrides in Zr-2.5Nb alloy

The hydride behavior in this alloy is of interest, since the hydride behavior in extruded pressure tubes using EBSD was not reported earlier. Zr-2.5Nb is a two phase alloy with α and retained β -phase. The retained β -phase termed in our experiments as Beta 1 (β 1) is a niobium rich region with bcc crystal structure. Different lattice parameters were proposed for this phase, as it mainly depends on the heat treatment employed on the sample. For the present experiment the lattice parameter of $3.53^{\circ}A$ [20] was used for Beta 1(β 1) phase. This Beta1 (β 1) phase further decomposes in to α -and β -Nb after prolonged heat treatment [21]. But this process is reported to be very sluggish at temperature below 500°C [22, 23]. So the β -Nb phase was not observed in our EBSD phase analysis.

Figure 5.4 (b) shows the typical unique grain color map of Zr-2.5Nb sample. The α -Zr grains are highly elongated in circumferential direction and the average grain size is found to be much smaller (<1µm) than the average grain size of Zricaly-4 and Zr-1Nb (E110) alloy. Figure 5.4 (a) shows the phase map of extruded Zr-2.5 %Nb alloy with hydride phase marked with red color. The dark areas marked in Figure 5.4 (a) are the areas with good band contrast but low confidence index (CI < 0.1). This low confidence index bands can be due to the overlapping Kikuchi bands

of small crystals of beta 1 (β 1) phase or from the beta 1 (β 1) phase, which has different lattice parameter than the used lattice parameter of 3.53°A. Because of low confidence index, the beta 1 (β 1) phase is not completely mapped. However, recent publications using EBSD has showed the dark areas in Zr-2.5Nb as (β 1) phase [24]. In the present experiment we were able to index few parts in the dark regions with (β 1) phase, which is mapped with blue color (see the arrows in Figure 5.4 (a) and (b)).



Color	hehoO	Man	Type:	Phase
00101	Coded	map	TYPE.	1 110/06

	Total	Partition
Phase	Fraction	Fraction
Zirconium (Alpha)	0.958	0.958
Zirconium (Beta)	0.001	0.001
Beta 1	0.022	0.022
Zirconium Hydride (Delta)	0.020	0.020
Zirconium hydride (Gamma)	0.000	0.000

Color Coded Map Type: Phase

	Total	Partition
Phase	Fraction	Fraction
Zirconium (Alpha)	0.912	0.912
Zirconium (Beta)	0.000	0.000
Beta 1	0.029	0.029
Zirconium Hydride (Delta)	0.059	0.059
Zirconium hydride (Gamma)	0.000	0.000





Figure 5.4: EBSD a) phase map of hydrided Zr-2.5Nb, b) unique grain color map, c) pole figures showing orientation relationship.

The hydrides in Zr-2.5 Nb alloys are mainly observed near dark areas (β 1-phase). This observation supports the argument that hydrides nucleate at β -rich regions of zirconium [25]. Also, as observed in Zircaloy-4, the hydrides in Zr-2.5Nb are following (0001) α -Zr//{111} δ -ZrH_{1.5} orientation relationship with the zirconium matrix (see Figure 5.4 (c)). Interestingly, the grain shape and structure and the presence of β 1 phase does not seem to be affecting (0001) α -Zr//{111} δ -ZrH_{1.5} orientation relationship with the zirconium matrix.

5.3.2.3 Hydrides in Zr-1Nb (E110) alloy

Figure 5.5 shows the EBSD of hydrided Zr-1Nb (E110) alloy. Phase map of this alloy is interesting because not much data was available in the literature. Unlike Zircaloy-4, Zr-1Nb (E110) alloy is a two-phase material with both α and β 1-phases. The EBSD imaging system identifies the presence of β 1-phase and δ -hydride precipitates. The β 1-phase is mapped with blue color and δ -hydride phase is mapped with red color.


		Total	Partition
	Phase	Fraction	Fraction
	Zirconium (Alpha)	0.841	0.841
	Zirconium (Beta)	0.000	0.000
	Beta 1	0.011	0.011
	Zirconium Hydride (Delta)	0.148	0.148
1	Zirconium hydride (Gamma)	0.000	0.000
	Niobium (Beta)	0.000	0.000

Figure 5.5: EBSD Map of hydrided Zr-1Nb (E110) alloy.

The β 1-phase is found in the form of small spherical particles distributed within the α - Zirconium matrix. Perhaps the most interesting observation in the present work is a fact that some of hydride habit planes in Zr-1Nb (E110) are different from that observed in Zircaloy-4 and Zr-2.5Nb. Using pole-figure method it was found that some of hydrides in Zr-1Nb (E110) alloy are showing (0001) -Zr//{100}\delta-ZrH_{1.5} with the zirconium matrix, whereas some other hydrides are showing usual $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} orientation relationship, but the $(0001)\alpha$ -Zr//{100} δ -ZrH_{1.5} orientation relationship shown by some of the hydrides in Zr-1Nb (E110) alloy is quite different from reported orientation of $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} for zirconium alloys. Out of 120 analyzed locations about 50 % of hydrides are showing the $(0001)\alpha$ -Zr//{100} δ -ZrH_{1.5} orientation relations. The change in hydride habit plane is of importance, because it was known that hydrides at all locations are following $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} crystallographic relation [11, 26]. So the change in hydride habit plane may influence the mechanical properties, crack initiation and growth mechanism of the cladding.





Figure 5.6: Inverse pole figure map showing twins of Zr-1Nb (E110) alloys, (arrows show full and partial twins having different thicknesses).

Further EBSD analysis at higher magnification was done on Zr-1Nb (E110) alloy to determine the change in hydrides behavior. Apart from the typical grain structure in EBSD map, heavy twins were observed for Zr-1Nb alloy. Although twinning is commonly observed plastic deformation mechanism in hexagonal metals, the heavy twins which were observed in Zr-1Nb (E110) were not seen in Zircaloy-4 and Zr-2.5Nb alloy. Both full and the partial twins with twin thickness varying from few nanometers to microns were extensively found in the investigated samples (see Figure 5.6). Few twins that were extended to surrounding

grains seem to be formed by autocatalytic mechanism, where the stress concentration created by the twin near the grain boundary, initiates twinning in the other grain (see blue arrows in Figure 5.6). The type of twins in the Zr-1Nb (E110) was determined by measuring the misorientations from the twinned and untwined part of the grain [27]. Out of four possible types of twins reported in the literature for the α -Zr lattice, $\{10\overline{1}2\} < 10\overline{1}\overline{1} >$ tensile twins and $\{10\overline{1}1\} < 10\overline{1}2 >$ compression twins with a misorientation $85^{\circ}\pm5^{\circ}$ and $57^{\circ}\pm5^{\circ}$ were often observed in Zr-1Nb (E110) alloy. These twins are known to be thickest of four possible twin types, but the thicknesses were observed in the sample, in which some of the twins with small thickness are not clearly resolved (see red color arrow in Figure 5.6). The effect of the twin structure on the hydride formation and behavior is of great interest.

Hydrides were found both on the twins and untwined grains. Based on EBSD observations at higher magnification, the hydrides in Zr-1Nb (E110) alloy can be classified into three types: (1) Hydrides on grains, (2) hydride in the twins, and (3) hydrides near the twins.



Figure 5.7: EBSD Map of the microstructure of Zr-1Nb (E110) alloy and the pole figures illustrating $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} relationship.





Figure 5.8: EBSD map showing hydride inside twin grains of Zr-1Nb (E110) alloys and the pole figures illustrating orientation relationships, a) hydride inside compressive twins, b) hydrides inside tensile twins, (where UTG – untwined grain, H- hydride, TG- twinned grain).



Figure 5.9: EBSD map showing hydride near twin grains of Zr-Nb(E110) alloys and the pole figures illustrating $(0001)\alpha$ -Zr//{100} δ -ZrH_{1.5} relationship (arrow shows twin grains and hydrides near twins).

The hydrides on the grains are found to be following $(0001)\alpha$ -Zr//{111} δ - $ZrH_{1.5}$ orientation relationship with the zirconium matrix (see Figure 5.7). For the second case, two types of twins need to be considered. The hydrides on the $\{10\overline{1}2\} < 10\overline{1}\overline{1} >$ twins are found to follow $(0001)\alpha$ - $Zr/({111}\delta-ZrH_{1.5})$ orientation relationship with the twinned zirconium matrix and shows random orientation with untwined matrix (see Figure 5.8 (c)). Whereas, the hydrides formed on $\{10\overline{1}1\} < 10\overline{1}2$ twins also found to follow $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} with the twin grain. However, the angle between $\{111\}$, $\{100\}$ planes is $\cong 57^{\circ}$ in hydrides and the misorientation between the untwined and twinned grain is again 57°±5. Therefore, due to the crystal symmetry the hydrides formed on $\{10\overline{1}1\}$ <1012> also twins $(0001)\alpha$ -Zr//{100} δ -ZrH_{1.5} show orientation relationship with the untwined zirconium matrix (see Figures 5.8 (a) and (b)). In the third case, the hydrides close to the twin boundaries (as shown in Figure 5.9) are also found to be following $(0001)\alpha$ -Zr// $(100)\delta$ -ZrH_{1.5} orientation relationship with the zirconium matrix.

5.3.3 Local misorientation

Kernal misorientation was used to characterize the local misorientation caused by plastic deformation. When the sample is subjected to deformation, the dislocation density distribution in each grain will be arranged to produce the Kernel average misorientation (KAM), which is a tool in TSL-OIM analysis software. KAM is high (>1°) in deformed grains and low in recrystallized grains (<1°). The misorientation exceeding some particular value, in general >5°, might be generated at the neighboring grain, it is therefore excluded from the calculation of KAM.

The Kernel average misorientation (KAM) maps of Zr-2.5Nb, Zircaloy-4 and Zr-1Nb (E110) alloys are shown in Figure 5.10. We assume that the KAM value represents the dislocation density, because small misorientations within the grain are generated by local dislocation arrangement. The KAM values in Figure 5.10 are marked with different colors, where the blue color represents the lowest dislocation density and the red color represents the highest. By comparing the maps, one can see that there is a high dislocation density in Zr-2.5Nb, maybe due to high cold work during manufacturing. A low dislocation density is observed for Zr-1Nb (E110) alloy. These results are supported by the residual stress measured on the samples by X-ray diffraction technique.



Figure 5.10 : Kernal misorientation map of, (a) Zr-2.5Nb , (b) Zircaloy-4,

(c) Zr-1Nb.

Residual stress along the axial and circumferential directions of the Zircaloy-4, Zr-1Nb (E110) claddings and Zr-2.5Nb pressure tube is

measured using X-ray diffractometry. The values were shown in Table 5.2. The stress values are the almost same on both axial and circumferential directions. Zr-2.5Nb shows maximum stress and Zr-1Nb (E110) shows minimum stress. Based on the results of KAM and X-ray diffractometry one can clearly observe the difference in the residual stresses between these three alloys.

Samples	Residual stress (MPa)		
	Along axial direction	Along circumferential direction	
Zr-2.5Nb	-443±33	-417±34	
Zircaloy-4	-333±20	-343±20	
Zr-1Nb	-157±18	-211±19	

Table 5.2: Residual stress of the claddings measured using X-ray diffractometry

5.4 Discussion

The microstructures of as-received Zircaloy-4 and Zr-Nb alloys are different. Zircaloy-4 is a single phase whereas both Zr-Nb alloys are two phase. EBSD maps of Zircaloy-4 show slightly elongated grains and Zr-2.5Nb show highly elongated grains in circumferential direction, whereas Zr-1Nb (E110) shows equiaxed grains. The average grain size of Zircaloy-4 is higher than that of the Zr-Nb alloys, where Zr-2.5Nb has the smallest grains. The difference in grain structure and residual stress of

these alloys can be attributed to the different fabrication methods and reduction ratio of the tubes, where the finished Zircaloy-4 and Zr-2.5Nb tubes are in stress relieved condition and Zr-1Nb tube is in recrystallized condition.

The hydride morphology is different in the three alloys and the reasons for the difference of hydride morphology and the orientation of hydrides in Zircaloy-4, Zr-2.5Nb and Zr-1Nb (E110) alloys can be attributed to three factors: (1) the addition of Nb that substantially reduces the hydrogen concentration in zirconium matrix; (2) the existence and distribution of the β -Zr phase in Zr-Nb alloys (3) the differences in the level of the compressive stresses in the specimens investigated.

EBSD map shows that the β -Zr phase in Zr-Nb alloys is distributed in the form of small spherical particles within α -Zr grain and at the grain boundaries. The δ hydrides are found in β -Zr rich regions and in the α/β Zr interfaces. It can be said that, the reduction in hydrogen concentration in Zr matrix and the heterogeneous nucleation in β -Zr rich regions and the α/β Zr interface are the reason why rather short hydride platelets are formed in Zr-Nb alloys. The morphological orientation of hydrides highly depends on the compressive stresses given after the final pass of the tubing [16]. The residual stress measurements using X-ray diffractometry, show differences in residual stresses among Zircaloy-4, Zr-2.5Nb and Zr-1Nb (E110) which can play major role in enforcing the random orientation of hydrides.

The hydrides in Zircaloy-4 and Zr-2.5Nb follow $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} orientation with α -matrix, whereas in Zr-1Nb (E110) alloy, both $(0001)\alpha$ -Zr//{100} δ -ZrH_{1.5} and $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} orientations were observed. The role of β -Zr spherical particles on $(0001)\alpha$ -Zr// $(100)\delta$ -ZrH_{1.5} relationship in Zr-1Nb alloys can be considered to be minimal, because the two phase Zr-2.5Nb alloy with β -Zr particles does not change its orientation relationship of $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} with the zirconium matrix. Kikuchi bands which are sensitive to the cystal defects readily reveal twins in Zr-1Nb (E110) alloy. Heavy $\{10\overline{1}2\} < 10\overline{1}\overline{1} >$ tensile twins and $\{10\overline{1}1\} < 10\overline{1}2$ compression twins with a misorientation 85°±5° and 57°±5 are observed and the hydrides formed near and on the showing new $(0001)\alpha$ -Zr// $(100)\delta$ -ZrH_{1.5} crystallographic twins are relationship with the zirconium matrix and it is interesting to know that the presence of twins will affect the orientation relationship of hydrides with the zirconium matrix. However, the presence of coherent twins strengthens the materials [29, 30, 31] and recently it was reported that the coherent $\{10\overline{1}2\}$ twins can be produced in zirconium by the thermomechanical processing method [31]. The existence of heavy twins in Zr-1Nb (E110) alloys could be the main reason behind the difference in

orientation relationship of some hydrides in Zr-1Nb (E110) alloy. In general the material is more prone to failure, if the interlinked-structure of hydrides aligns in the radial direction of the tube. However, the twins in Zr-1Nb (E110) alloy, which are affecting the orientation of hydrides, can also act as a barrier against the formation of the long interlinked chain of hydrides during the reactor operation. From this point of view, Zr-1Nb (E110) alloy might perform better than Zircaloy-4.

The present paper documents the difference in microstructures of finished Zircaloy-4, Zr-2.5Nb and Zr-1Nb (E110) alloys tubes and its role in influencing the hydride formation and hydride structure.

5.5 Conclusions

The following conclusions can be derived based on the results of the present investigation:

- Microstructural observations on hydrided Zircaloy-4 samples show long and interlinked hydride chains, oriented along the circumferential direction, whereas in Zr-2.5Nb the hydrides are relatively short and oriented along the circumferential direction. Also in Zr-1Nb (E110), hydrides are short, thick and do not show any preferential orientation with respect to the sample reference direction.
- EBSD maps show heavy $\{10\overline{1}2\} < 10\overline{1}\overline{1} >$ tensile twins and $\{10\overline{1}1\} < 10\overline{1}2 >$ compression twins in Zr-1Nb (E110) alloys, which were not

observed in Zircaloy-4 and Zr-2.5Nb alloys. The thickness of the twins varies from few nanometers to micrometers.

EBSD studies show that hydrides in Zircaloy-4 and Zr-2.5Nb follow (0001)α-Zr//{111}δ-ZrH_{1.5} orientation with α-matrix, whereas in Zr-1Nb (E110) alloy, out of 120 analyzed locations, about 50 % of hydrides are found to follow the new (0001)α-Zr//{100}δ-ZrH_{1.5} relation and remaining 50 % hydrides follow (0001)α-Zr//{111}δ-ZrH_{1.5} with the zirconium matrix.

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6.0 Microstructural Studies and Crystallographic Orientation of Different Zones and δ-hydrides in Resistance Welded Zircaloy-4 Sheets

Preface

In this paper, the complicated weld microstructure of the resistance welded Zircaloy-4 sheets has been studied in detail. The influence of change in microstructure at the weld zone on the hydride behavior and mechanical properties has been discussed. The results presented in this paper outline the importance of texture changes in different areas of the weld zone on hydride structure, and help in assessing mechanical strength of the welds. The article presented in this chapter is published in the *Journal of Nuclear Materials [Vol. 414 (2011), 341–351].*

Abstract

The cold worked stress relieved (CWSR) Zircaloy-4 sheet used as endplate in nuclear fuel bundle is resistance welded with an endcap in argon environment. Later the welded sample is hydrided in a gaseous atmosphere at 400°C. Optical microscopy (OM), electron backscatter diffraction (EBSD) and X-ray diffraction (XRD) were used to examine the morphology and crystal orientation of the hydrides. The microstructural changes in different areas of the weld zone, heat affected zone (HAZ) and the as-received zone were analyzed using EBSD technique. Optical examination showed complete random morphological orientation of hydrides and predominantly basket-weave structure in the weld zone, with very few colonies of parallel plate structures. Variant selection for α phase formation inside prior β -grains was identified at the weld center. As we move from the weld center to the as-received zone, the variant selection is found to be less probable. The δ -hydride platelets at the weld zone were always found to be growing perpendicular to the α -colonies having angular difference of 60° and follow $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} orientation relationship with the zirconium matrix. Proposed description of complex distribution of hydrides and alloy microstructure at the weld and heat affected zone will contribute to a better understanding of mechanisms of failure of fuel cladding in various types of nuclear reactors.

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Keywords: Zircaloy-4, Resistance welding, EBSD, Zirconium hydrides

6.1 Introduction

Zircaloy-4 is known for its low neutron absorption, high strength and good corrosion resistance even at elevated temperatures. It is therefore a key structural material in nuclear reactors. In ¹CANDU[®] fuel bundles, Zircaloy-4 cladding tubes, loaded with fuel pellets, are sealed by endcaps at both ends to form fuel elements. To assemble the elements to become a whole bundle, endplates, made of cold work and stress relieved (CWSR) Zircaloy-4 sheets, are welded to the endcaps at each end of the elements (see Figure 6.1). The endcap/endplate assembly joints play a vital role in ensuring integrity of the fuel bundles.

During irradiation, when the hydrogen content exceeds the solubility limit, hydrogen pick-up in Zircaloy-4 leads to hydride precipitation. These hydrides have deleterious influence on mechanical properties of the material [1, 2]. Therefore, studies on hydrogen behavior in Zircaloy-4 and other Zr alloys have been conducted for over 60 years. For CANDU fuel bundles, delayed hydrogen cracking (DHC) in the welds may take place if a bundle experiences an excess mechanical load during irradiation [3], and also, DHC may take place in irradiated bundles after discharge [4]. As initiation of the cracks strongly depends on the

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microstructure of the material and hydride orientation in the material, fundamental study in this area is being undertaken worldwide.

Welding is the critical manufacturing process for successful fabrication of CANDU fuel bundles. As expected, changes in the microstructure of the weld zone and associated heat affected zone (HAZ) affect mechanical and corrosion resistance of the weld joint [5]. For achieving a good combination of strength, ductility and corrosion resistance, the resistance welding technique is utilized to make the assembly welds. The fundamentals of this process are well described elsewhere [6].





Zirconium shows two allotropic forms, α (HCP) stable at room temperature and β (BCC) stable at temperatures above 863°C. Phase transformation of cold worked and stress relieved (CWSR) Zircaloy-4

sheet-material during heating $(\alpha \rightarrow \alpha + \beta \rightarrow \beta)$ and cooling $(\beta \rightarrow \alpha + \beta \rightarrow \alpha)$ gained importance, because it involves both texture and microstructural changes [7, 8 and 9] in the material (similar to titanium), and it takes place during the assembly-welding process. The $\beta \rightarrow \alpha$ phase transformation is reported to follow the Burger relation $\{110\}_{\beta}/(\{0002\}_{\alpha})$ and $<111>_{\beta}//<1\overline{2}10>_{\alpha}$ [10]. If this relation is followed, then because of crystal symmetry, six β -phase orientations may arise during the $\alpha \rightarrow \beta$ transformation and twelve inherent α orientations may arise during the cooling (i.e., the $\beta \rightarrow \alpha$ transformation). If all these orientations are selected during the transformation, it should result in a random texture of the α matrix. However, recent studies on zirconium and titanium have suggested that variant selection takes places, by which some preferred orientations of α phase are developed while others are suppressed during the $\beta \rightarrow \alpha$ transformation [11, 12 and 13]. If the variant selection occurs during phase transformation, the specific crystallographic arrangement of grains in the weld zone may affect the precipitation behavior of the hydrides. To date, this has not been studied in detail; however, such information is important for assessing mechanical strength of the welds.

The aim of the present investigation is to characterize microstructural changes in the assembly weld, and also, to study the effect of microstructural changes on hydride structure and orientation in the weld. This is done mainly by using the electron backscatter diffraction (EBSD) and X-ray diffraction (XRD) techniques.

6.2 Experimental

The chemical composition of the Zircaloy-4 sheet used for the present study is given in Table 6.1. The sheet, with a thickness of 1.6 mm, was cut along the transverse direction (see Figure 6.2). The cut sample, about 50 mm long and 4 mm wide, was welded to a Zircaloy-4 endcap by resistance welding at AECL Chalk River Laboratories. During welding, the weld area was protected with a high purity (99.99%) argon environment to prevent oxygen from raising the upper phase transformation temperature, $T_{\beta/\alpha+\beta}$, which will affect the final microstructure and mechanical properties of the transformed region [14, 15].

Table 6.1: Alloy composition of Zircaloy-4

	Sn(wt.%)	Fe(wt.%)	Cr(wt.%)	Ni(wt.%)	O (wt.%)	Zr(wt.%)
Zircaloy-4						
	1.52	0.21	0.11	<35 ppm	0.125	bal

After the welding (no melt in the weld zone), gaseous hydriding was conducted in a quartz-tube furnace at 400°C. The atmosphere in the furnace was maintained by a continuous flow of ultrahigh purity argon gas containing up to 7500 wt.ppm of hydrogen. The hydriding was done for 1hr; about 40 wt.ppm of hydrogen was charged into the sample. Detailed description of the process can be found elsewhere [16]. The samples for EBSD analysis were prepared by polishing the sample up to 0.05 μ m colloidal silica, followed by etching in a solution of 45% HNO₃, 45% H₂O and 10% HF.

The reference frame for the microstructural analysis has to be defined and three principle Zircaloy-4 sheet directions were used with the light microscopy, EBSD and XRD texture analyses. The directions are RD, TD and ND as shown in Figure 6.2, where RD is the rolling direction of the sheet, TD is the transverse direction and ND is the normal direction.





Bruker Discover D8 X-ray diffraction system equipped with 2dimentional HI-STAR detector is used to measure the texture of the zirconium alloy in the weld zone and as-received zones. Since the weld area is very small $(\approx 2 \text{ mm})$, 0.3 mm collimator, which scans only a small area of the sample, is used to measure the texture of α zirconium in the weld zone.

Orientation Imaging Microscopy (OIM) system installed on a field emission scanning electron microscope (FE- SEM-XL30) is used to measure the crystal orientation of hydride and zirconium matrix of the welded sample. The EBSD patterns were obtained and analyzed by means of the TexSEM Laboratories (TSL) OIM software. The crystallographic orientation relation between the zirconium hydride (ZrH_{1.5}) and the zirconium matrix is deduced by checking the coincidence of orientations in pole figures with an angular difference of < 5°.

The Kearns texture parameter 'f', is used to quantify the level of texture differences at the weld, HAZ and as-received zones [17]. It gives the fraction of basal poles oriented in the three principal directions, i.e., in transverse, rolling and normal directions (f_{TD} , f_{RD} , f_{ND}) of the sheet sample, where the sum of fraction of basal poles is equal to 1 (see equation (6.1)).

$$f_{\rm TD} + f_{\rm RD} + f_{\rm ND} = 1.....(6.1)$$

The value of 'f' for any reference direction can be obtained by summation of the volume fractions (V_i) of crystals having basal poles inclined at angle (Φ_i) with respect to the reference direction, multiplied by $\cos^2 \Phi_i$ which gives the effective fraction of basal poles in the reference direction, as shown in equation (6.2).

$$f = \sum_{\phi=0}^{\phi=\frac{\pi}{2}} (V_i) \cos^2 \Phi_i....(6.2)$$

TexTools ResMat software was used to find the volume fraction of basal planes from $\Phi=0$ to 90° at an interval of 5°. This software uses orientation distribution function (ODF) that is calculated using X-ray diffraction or EBSD technique for calculating the number of planes oriented at an angle Φ .

6.3 **Results and Discussions**

6.3.1 Light examination

6.3.1.1 Hydride distribution in the weld sample

Metallographic examination of the welded specimens revealed that hydride distribution in the weld area is completely different compared with that in the as-received zone. In the weld area, very fine and short hydrides are observed (see Figure 6.3 (a)), and the distribution of the hydrides looks random, i.e., without showing any particular morphological orientation. In contrast, in the as-received region, the hydrides are relatively clustered and they are plates (looking down to the normal of the hydride plates) and aligned along the elongated α -grains. This is typical, because the as-received region is in cold work and stress

relieved condition, and the grains in this region are elongated along the rolling direction [18]. The reason for the random distribution of the hydrides in the weld zone cannot be well understood without examining detailed microstructural features in the weld zone. However, the grains in the weld zone were not discernable using light microscopy due to its limited resolution, so the EBSD and X-ray diffraction techniques were employed for further analysis.





Figure 6.3: Hydride distribution in welded sample at a) Weld Zone b) Weld zone and As-received zone. (Note: - The random morphological orientations of hydrides (arrows) are marked in (a); the weld zone and as-received zone are separated with the black line in (b))

6.3.1.2 Microstructural changes from weld zone to as-received zone

The microstructure of the central weld zone, obtained from EBSD imaging analysis (see description in Section 6.3.2), is shown in Figure 6.4 (a). As shown, colonies of α -phase with no residual β -phase are present. The weld structure is characterized by the presence of fine acicular α -grains inside the colonies in the form of basket-weave structure. These colonies are within the prior- β grains, which were formed during the welding process when the material was heated to the temperature in the β -phase field. This microstructure corresponds to the Widmanstätten structure, due to the $\beta \rightarrow \alpha$ transformation taking place during welding [19, 20].

Figure 6.4 (b) shows the heat affected zone \approx 300 µm wide) of the weld sample, which experienced a temperature that did not reach the $\alpha \rightarrow \beta$ phase transformation temperature of 925°C in Zr-4. This zone is characterized by the presence of recrystallized α -grains with grain size ranging from sub-micron to about 3 µm. Close to the as-received zone, but still in the heat affected zone, partial recrystallization (see Region B) was observed to take place. This is characterized by a mixture of small recrystallized α -grains and large elongated grains, and the size of the recrystallized α grains are much smaller than the grains in Region A. Typical microstructure showing the highly deformed grains with an average grain size of 4 to 6 μ m was observed in as-received region (see Figure 6.4 (c)).



		rotar	Partition
Min	Мах	Fraction	Fraction
0°	30°	0.050	0.050
30*	60*	0.532	0.532
60*	90*	0.324	0.324
	Min 0° 30° 60°	Min 0° 30° 30° 60° 60° 90°	Min Max Fraction 0* 30* 0.050 30* 60* 0.532 60* 90* 0.324

(a)





Figure 6.4: a) Image quality map of the weld zone b) Unique grain color map of heat affected zone, c) Image quality map of as-received zone.

6.3.2 EBSD analysis

To obtain more detailed information in the weld, heat affected and asreceived zones, the microstructures from these areas were analyzed using EBSD technique. The microstructural changes from the weld center to the as-received zone are shown in Figure 6.5; image quality (IQ) and inverse pole figure (IPF) mapping techniques were used to examine the changes. The IQ map is visualized microstructure obtained by mapping electron backscatter Kikuchi patterns at each point of the OIM scan. The quality of the IQ map depends on various factors like strain, topography and the quality of Kikuchi bands. The IPF map is colour coded microstructure where the crystals having similar orientations will be mapped with same color. It is known that the cooling rate at the weld center is lower than the cooling rate at the HAZ as the latter is closer to the cold part of the sample, where the rate of heat transfer is high.

In the weld zone, the basket-weave Widmanstätten structure is the predominant microstructure. The size of the α -phase colonies from the weld center moving towards the heat affected zone is found to vary. The variation in the size of α -colonies is due to non-linear temperature distribution, in both time and space, between the weld center and the heat affected zone during the resistance welding process [21].

The α colonies in the form of basket-weave structure are observed inside the prior β grains as shown in the maps in Figure 6.5. The prior β grains are identified manually based on the change in orientations (colors) in the inverse pole figure map. The increase in cooling rate and decrease in local maximum temperature from the weld center to the as-received zone seems to be affecting the size of the prior β grains, as the prior β grain size is found to be decreasing from the weld center to the heat affected zone.

At the weld center



At 125 μm from weld center



At 950 μm from weld center



(c)

At 1567 μm from weld center


At 1700 μm from weld center



(e)

At 1850 μm from weld center





At 2000 μm from weld center



(g)

At 2200 μm from weld center







At 2300 µm from weld center



(i)

At 2650 μm from weld center





(j)

<image>

At 2900 μm from weld center



(**k**)

Figure 6.5 : EBSD Image Quality and Inverse Polefigure maps from weld center to as-received zone. (Distance from the weld center at which each image was obtained is listed on the top of each figure)

If inherited α -colonies from the same β grain follow the Burgers relation, then they can only take 0° , 60° and 90° selections of angles (in the literature, they sometimes are called as misorientation) [11]. So when the misorientations of α -colonies is different from the above mentioned misorientations, the neighbouring α -colony must be inherited from a prior β grain with a different orientation. Based on this concept, the prior β grains, which are not clearly identified in Figure 6.6 (a), can be reconstructed, as shown in Figure 6.6 (b). In Figure 6.6 (b), the prior β grains reconstructed by this method are mapped with yellow colour and other misorientations are mapped with black colour. Various algorithms have been reconstructing the pre-transformation reported for microstructure using the Burgers relationship [22, 23]; essentially, the concept of distinguishing orientation difference between two neighboring α colonies plays a vital role in identifying the prior β grain boundaries.



(a)



(b)

Figure 6.6 : Shows a) α - colonies at the weld zone b) Reconstructed prior β grains from α - misorientations.

Figure 6.7 shows the orientation difference between α colonies calculated from different regions of the weld sample. It appears that in the weld zone the angular differences of 0°, 60°, 90° are observed which mean that the Burgers relation is strictly followed in the weld zone, but as we move farther from the weld center to HAZ zone (Figure 6.7c) the preferential misorientation due to Burgers relation is observed to be weakening. In the as-received zone (see Figure 6.7d), the Burgers relation does not exist, as expected.





6.3.3 Texture analysis

The basal plane texture in the sample varies in areas from the weld center to the as-received zone, where normal rolling texture of zirconium appears [18]. In the weld zone, at the weld center, two additional texture maxima appeared along the rolling direction and in the rolling plane along with two strong rolling texture maxima of the basal poles (see Figure 5.8 (a)). The strong initial texture of the α -phase and existence of the variant selection during the phase transformation is also reported to be responsible for the new texture at the weld zone [13]. However, the reason for the observed variant selection is still not clear. Humbert and Gey [24] based on their model of the variant selection have proposed that among all the variants only those for which strain energy increase is lower than a threshold value are formed. Although the variant selection during the $\alpha \rightarrow \beta$ transformation in the $\alpha \rightarrow \beta \rightarrow \alpha$ transformation cycle of Zircaloy-4 is not clearly understood, it was reported that strong prior beta texture and variant selection during $\beta \rightarrow \alpha$ transformation is responsible for a strong texture of the final alpha lamella [13]. This characteristic basal plane texture, as shown in Figure 5.8a, is weakening as we move towards the heat affected zone. The probability of the variant selection is reported to be reduced when axial stress is applied during the $\beta \rightarrow \alpha$ phase transformation [25], and thus, the crystallographic relation between α and β phases is more often not followed. For the

present sample, the increase in cooling rate near the heat affected zone and the presence of untransformed α -grains may lead to increase in local stress and seem to be affecting the probability of variant selection.





Figure 6.8: EBSD measured basal plane pole figure of the welded sample at different distances from the weld center in (μm). a) 0 , b) 125, c) 950 , d) 1274 , e) 1700 , f) 2000, g) 2200, h) 2800 (Pole figures (a, to e) represent weld zone, (f, g) represents HAZ and (h) represents as-received zone)

X-ray diffraction was used to measure the macro-texture in the weld and as-received zones. The basal pole figure of the inherited α phase in the weld zone (see Figure 6.9a) shows the same main components as those observed with EBSD (micro-texture analysis, see Figure 6.8a), indicating the results of the X-ray measurements and EBSD analysis are in good agreement. Also, for the as-received region, the results of the X-ray measurements (see Figure 6.9b) and EBSD analyses (see Figure 6.8h) are in good agreement as well.



Figure 6.9: Basal pole figure measured using X-ray diffraction at a) weld zone, b) as-received zone. (Note: - The new maxima at the weld zone is shown with arrows)

6.3.4 Crystallography of δ - ZrH_{1.5} hydride in the weld and heat affected zones EBSD Kikuchi pattern analysis indicated that the hydrides in the sample are δ - ZrH_{1.5} phase. The crystallographic relation between the hydrides and zirconium matrix in the weld and heat affected zones was examined by EBSD pole figure method. Figure 6.10 shows a typical region in the weld zone, where crystallographic orientation of two hydride platelets, labeled as A and B in the inverse pole-figure image-map, was analyzed. The hydride platelets were mainly observed inside prior β - grains, where the lamella of the α -grains have the misorientations of 0°, 60° and 90°. These hydride platelets are present both inside the grains and at grain boundaries of the prior β -grains. Most of the hydride platelets grow perpendicular to alternating α -lamellas having a misorientation of 60° as shown in Figure 6.10.



Figure 6.10: Crystallographic orientation of hydrides analyzed using $\{0001\}$ $\{10\overline{1}1\}$ and $\{111\}$ pole figures of the matrix and the hydride grains. The

coincidence of Pole figures is obtained from regions A and B

If we label the two alternating α -lamellas on which hydride is growing, as variants V_a and V_b , the crystallographic relationship between these two variants is:

$$\{10\overline{1}1\}V_{a} / / \{0001\}V_{b}, and$$

 $\{0001\}V_a / / \{10\overline{1}1\}V_{b}$

Where, $\{10\overline{1}1\}$ is the pyramidal plane of the hcp α -grains. This relationship also exists for variants V_a and V_b in Region B of the figure.

Results of the EBSD analysis show that the hydrides in the weld zone follow the $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} crystallographic relationship with the zirconium matrix. As clearly seen in Figure 6.10 (a) and (b), the orientation of the basal planes of the matrix, {0001}, coincides with the orientation of the {111} planes of the hydrides, as denoted by the circles in the figure. Also, because of the crystallographic relation between the variants V_a and V_b, the orientation of {1011} plane of α -zirconium matrix will also coincide with the orientation of {111} planes of the hydride (see Figure 6.10 (a) and (b)). Similar analysis was conducted in the HAZ, and it was observed that the (0001) α -Zr//{111} δ -ZrH_{1.5} crystallographic relationship is also maintained in the region.

Zry-4	f _{ND}	f rd	fтD
Weld Zone	0.364	0.272	0.351
HAZ	0.354	0.305	0.340
As-received Zone	0.646	0.119	0.234

Table 6.2: Kearns 'f' parameters of welded Zircaloy-4

The quantitative basal pole textures represented by the Kearns parameter for different zones are presented in Table 6.2. The calculated fractions of the basal planes oriented in ND, RD and TD directions are significantly different at the weld zone, HAZ and as-received zone. It has been shown that the change in basal pole components will influence the crack growth rate during delayed hydride cracking process [26, 27, 28 and 29], and also create stress accumulation resulting from the anisotropic thermal expansion behavior of zirconium [30]. The texture inhomogeneity at the weld zone and heat affected zone may therefore increase the probability of failure due to increase in residual and intergranular stresses.

This investigation documents the microstructural changes that exists in areas from the weld zone to the as-received zone resulting from $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformation process and explains differences in the crystallographic orientation of hydrides. Understanding structural transformations at the weld zone is of fundamental importance for improvement of life expectancy of fuel cladding in nuclear reactors.

6.4. Conclusions

A cold work and stress relieved Zircaloy-4 sheet was resistance welded to an endcap, and the welded sample was charged with hydrogen using a gaseous method. The microstructures and hydride behavior at different distances from the weld centre were characterized and analyzed mainly using light microscopy, EBSD and X-ray techniques. Based on the results obtained, the following conclusions are made.

- Optical examinations show a completely random morphological orientation of hydrides in the weld and heat affected zones. In contrast, in the as-received zone (in cold worked and stress relieved condition) the hydrides are aligned along the rolling direction of the Zircaloy-4 sheet.
- 2) EBSD imaging analysis revealed that a basket-weave Widmanstätten structure with very fine basket-weave αlamellas was present, predominantly in the weld zone. The αlamellas are arranged as variants inside the prior β grains, and the crystallographic relationship between two neighboring variants is:

$$\{10\overline{1}1\}V_a / / \{0001\}V_b$$
, and

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 $\{\!0001\}V_a\,/\,/\,\,\{10\,\overline{l}\,1\}V_{b,}$

Where, $\{10\overline{1}1\}$ is the pyramidal plane of the hcp α -grains, and V_a and V_b denote neighboring variants A and B, respectively. When moving from the weld centre to the as-received zone, the variant selection was less apparent.

3) The EBSD Kikuchi pattern analysis concluded that the hydrides in the sample are δ - ZrH_{1.5}. In the weld zone, the hydrides in the form of platelets were mainly present inside the prior β - grains, where the lamella of the α -grains have the misorientations of 0°, 60° and 90°. The hydride platelets are also present at boundaries of the prior β -grains. Most of the hydride platelets grow perpendicular to the alternating α -lamellas having a misorientation of 60°. The δ - ZrH_{1.5} hydride platelets in the weld, heat affected and as-received zones all follow the (0001) α -Zr//(111) δ -ZrH_{1.5} orientation relationship with the zirconium matrix.

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7.0 Summary and Conclusions

In this dissertation, the in-depth analysis on the formation and behaviour of zirconium hydrides in the stress relieved tubes and sheets with varied hydrogen composition has helped in identifying the strong preferential behaviour of zirconium hydrides. This information has subsequently helped, in explaining the complex behaviour of hydride platelets at the weld zone, and also in understanding the superior resistance to corrosion of the Zr-1Nb alloys. In addition, the high temperature experiments under the presence of hoop stress and hydrogen atmosphere has helped in developing a new understanding on radial hydrides. The proposed description of complex behaviour of hydrides in various conditions such as 1) stress relieved tubes and sheets, 2) influence of hoop stress, temperature and hydrogen pressure 3) the twins, and 4) the weld zone, will contribute to a better understanding of the mechanisms of fuel cladding failure in various types of nuclear reactors.

The main findings and conclusions from the investigations in this thesis are:

7.1 Preferential precipitation of hydrides in textured Zircaloy-4 sheets

In this study, cold-worked and stress relieved (CWSR) Zircaloy-4 sheet samples were charged with 45–247 wt. ppm of hydrogen using an electrolytic technique in 0.125 M H₂SO₄ solution at the AECL Chalk River Laboratories. Morphology and orientation of hydrides were examined using optical microscopy (OM) and EBSD techniques. The following conclusions are obtained based on the results of this investigation:

- 1. Kikuchi patterns indexed with the EBSD system showed that the hydride formed in Zircaloy-4 are δ -phase. Out of 150 analyzed locations, 97 were observed to be grain-boundary hydrides in the hydrided sample (247 wt. ppm), where 53 were the intra-granular hydrides. The ratio of the intra-granular hydrides to the inter-granular hydrides was about 1.8. Inter-granular hydride precipitation was predominate;
- 2. Both inter-granular and intra-granular hydrides were found to follow the $(0001)\alpha$ -Zr// $(111)\delta$ -ZrH_{1.5} orientation relationship with the zirconium matrix;
- 3. The micro and macro texture data were obtained respectively using XRD and EBSD techniques. The peaks of the basal plane of

zirconium and the {111} plane of hydride were at the same location when comparing orientations marked on the pole figures. This means {111} planes of hydrides prefer to orient parallel to the (0002) basal plane of the matrix, regardless of whether the hydrides precipitate at the grain boundaries or within the Zr grains;

- 4. Three types of grain boundary hydrides were observed. EBSD at higher magnification showed that hydrides very close to the grain boundaries followed a $(0001)\alpha$ -Zr// $(111)\delta$ -ZrH_{1.5} orientation relationship;
- 5. Hydride preferential sites were found to be on the grains that have a basal plane close to a grain boundary, and decreasing hydrogen concentration had no effect on the $(0001)\alpha$ -Zr// $(111)\delta$ -ZrH_{1.5} orientation relationship;
- 6. Experiments performed on a sample with low concentration of hydrogen (117 wt. ppm) showed that the decrease in hydrogen concentration has no effect on the frequency of the (0001)α-Zr//{111}δ-ZrH_{1.5} crystallographic relationship.

7.2 Hydride formation under hoop stress in Zircaloy-4 cladding tubes

Zircaloy-4 claddings were hydrided in a high-pressure hydrogen gas furnace at a temperature of 350°C and a pressure of 20 MPa. During hydriding, hoop stresses from 0-780 MPa were applied on the cladding tube using a special copper rod. The stresses were generated by the dimensional changes of the copper rod inside the cladding tube, as a result of the latter's thermal expansion. The effect of different hoop stresses on the orientation of hydride platelets were studied using optical microscopy and EBSD techniques. The following conclusions are obtained:

- Hydrides orientation depends strongly on the hoop stress that is applied. At lower hoop stresses, hydride platelets have orientations close to the circumferential direction. Subsequently, with the increase in hoop stress, apart from hydrides aligned closely to the radial and circumferential directions, hydrides which were inclined at an angle to the circumferential and radial directions were also observed;
- 2. The hydrides in an unstressed condition follow the $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} relationship with the zirconium matrix. With increasing hoop stress, this relationship is no longer observed for hydrides that deviate from the circumferential direction. The

hydrides formed under hoop stress were found to form mainly on the {1011} plane, following a { $1011a-Zr/{111}\delta-ZrH_{1.5}$ relationship. Other relationships, e.g., { $1017a-Zr/{111}\delta-ZrH_{1.5}$, { $1013a-Zr/{111}\delta-ZrH_{1.5}$ and { $1010a-Zr/{111}\delta-ZrH_{1.5}$, were also observed. In addition, it was found that, the hydrides under hoop stress prefer to form in the grain boundaries along the radial direction;

- The size of hydride platelets formed under hoop stress is smaller than the size of hydride platelets formed in unstressed conditions. The decrease in size of hydride platelets might be due to the higher number of hydride habit planes created under hoop stress;
- 4. The selection of habit planes of hydrides depends mainly on the applied hoop stress.
- 7.3 EBSD studies on microstructure and crystallographic orientation of δhydrides in Zircaloy-4, Zr-1% Nb and Zr-2.5 % Nb

Three alloys were hydrided using a high-pressure hydrogen gas furnace at a pressure of 20 MPa. Thermal cycling was done on the samples at a temperature of 350°C for 10 cycles with a 5 h soaking time. The following conclusions are obtained:

- Microstructural observations on hydrided Zircaloy-4 samples showed long and interlinked chains of hydrides oriented along the circumferential direction, whereas in Zr-2.5Nb, the hydrides were relatively short and oriented along the circumferential direction. But in Zr-1Nb, the hydrides were short, thick, and did not show any preferential orientation with respect to the sample reference direction;
- 2. The difference of hydride morphology and orientation in Zircaloy-4, Zr-2.5Nb and E110 alloys are attributed to three aspects: (1) the addition of Nb, (2) differences in the distribution of the β-Zr phase in the form of small spherical particles within α-Zr grains or at the grain boundaries, (3) the difference in the strength of residual stresses in Zircaloy-4, Zr-2.5Nb and Zr-1Nb;
- EBSD maps showed heavy {1012} twins in the Zr-1Nb alloy, which were not observed in Zircaloy-4 and Zr-2.5Nb alloys. The thickness of the twinned grains varied from a few nanometres to micrometers;
- 4. EBSD studies show that hydrides in Zircaloy-4 and Zr-2.5Nb follow a $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} orientation with the α -matrix, whereas in E110 alloy, out of 120 analysed locations, about 50 % of hydrides follow a new $(0001)\alpha$ -Zr//(100) δ -ZrH_{1.5} relation, and

the remaining 50 % hydrides follow a $(0001)\alpha$ -Zr//{111} δ -ZrH_{1.5} relationship with the zirconium matrix.

7.4 Microstructural studies and crystallographic orientation of different zones and δ-hydrides in resistance welded Zircaloy-4 sheets

End plate welding is an important step in the fabrication of nuclear fuel bundles, because the cladding Zr tubes sealed with end-caps need to be held in fuel bundles at the both ends using end plates. A cold-work and stress relieved Zircaloy-4 sheet was resistance-welded to such an end cap, and the welded sample was charged with hydrogen gas. The microstructures and hydride structure at different distances from the weld center were characterized and analyzed, mainly using optical microscopy, EBSD and X-ray techniques. Based on the results obtained, the following conclusions are made:

1. In the centre of the welded zone, a α -Zr matrix has mainly a fine basket-weave structure (short plates intersecting each other within the parent β -Zr grains, i.e., so-called Widmanstätten microstructure). The reason for the formation of such a microstructure is a $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformation. Heating during welding causes a $\alpha \rightarrow \beta$ transition, and cooling after welding transforms the β -phase back to the α -phase. Since the transition process follows a Burger relation of $\{110\}_{\beta}//\{0002\}_{\alpha}$ and $<111>_{\beta}//<1210>_{\alpha}$, a high number of nucleation sites in β -Zr grains can lead to the formation of the fine basket-weave structure in α phase;

- 2. Optical examinations show a completely random morphological orientation of hydrides in the weld and heat affected zones. In contrast, in the as-received zone (in cold-worked and stress relieved condition) the hydrides are aligned along the rolling direction of the Zircaloy-4 sheet;
- 3. EBSD imaging analysis revealed the presence the of basket-weave Widmänstatten structure, predominantly in the weld zone. The α lamellas were arranged as variants inside the prior β -grains, and the crystallographic relationship between two neighbouring variants was:

 $\{10\overline{1}1\}V_a / / \{0001\}V_b$, and

 $\{0001\}V_a / / \{10\overline{1}1\}V_b,$

where, $\{10\overline{1}1\}$ is the pyramidal plane of the hcp α -grains, and V_a and V_b denote neighbouring variants A and B, respectively.

When moving from the weld center to the as-received zone, the variant selection was less apparent;

4. The EBSD Kikuchi pattern analysis concluded that the hydrides in the sample were δ -ZrH_{1.5}. In the weld zone, hydrides in the form of platelets were mainly present inside the prior β -grains, where the lamella of the α -grains had misorientations of 10°, 60° and 90°. Hydride platelets were also present at the boundaries of prior β grains. Most of the hydride platelets grew perpendicular to the alternating α -lamellas, which had a misorientation of 60°. For δ -ZrH_{1.5} hydride platelets in the weld, heat affected and as-received zones followed the (0001) α -Zr//(111) δ -ZrH_{1.5} orientation relationship with the zirconium matrix.

8.0 Contributions to the Original Knowledge

8.1 Preferential precipitation of hydrides

• The preferential precipitation of hydrides on grain boundaries and within grains has been analyzed for the first time. The present experiments show, for the first time, that in addition to grainboundary structure, the grain orientation of zirconium along the grain boundaries plays an important role in the formation of intergranular hydrides.

8.2 Hydrides under hoop stress

• The procedure of applying hoop stress, temperature, pressure, and a corrosive environment, simultaneously on the cladding has been established. For the first time, it was shown, that hoop stress not only induces the reorientation of hydrides, but can also change the morphology, and the crystallographic orientation of hydrides, in the zirconium matrix.

8.3 δ- hydrides in Zr-1% Nb (E110) alloy

• It has been reported elsewhere that Zr- 1Nb alloys show superior resistance to corrosion, and substantially better mechanical properties, compared to Zircaloy-4. The hydrides in E110 alloy and Zircaloy-4 have been compared and it was found that in the E110 alloy, the hydrides have a different structure and orientation. It was discovered that in the E110 alloy, the existence of a high density of twin boundaries can prevent the formation of long interlinked chains of hydrides that are responsible for crack propagation. The structure of hydrides at twin boundaries, as far as this author's knowledge, has been discussed for the first time.

8.4 Microstructural changes and δ-hydrides at the welded region

• For the first time, a complex distribution of hydrides at the weld and heat-affected zones were analyzed. This analysis will contribute to a better understanding of the mechanisms of failure of welds in fuel channels of nuclear reactors.

Future work

The future work presented in the following paragraphs is based on the conclusion made from the chapters, which would help in presenting some ideas for potential path forward. The areas that are of at-most importance are to further understand the behavior of hydrides and ways to limit the formation of hydrides in chain-like structures.

The in-depth analyses of the hydrides in the chapters have showed the influence of grain orientation and texture of zirconium matrix on the preferential behavior of hydrides. As the hydride rims (chain-like structure) formation in circumferential direction was mainly due to the strong texture of the zirconium matrix, it would be interesting to make some experimental studies on producing a Zircaloy-4 cladding with a random texture and analyze the hydride behavior in such cases.

An atomistic scale understanding of the relation between hydrides and the zirconium matrix can be obtained using molecular dynamics approach. Such simulations can help in obtaining the interfacial energy and elastic strain energy components of hydrides, which could explain the overall influence of grain-boundary energy and hydride habit plane on the behavior of the hydrides. The potential future work also includes the in-situ studies of hydride growth using synchrotron radiation. These in-situ studies of hydride in the absence and presence of hoop stress at elevated temperatures would help in better understanding the growth kinetics and the hydride reorientation mechanism.
Appendix I

Hydrogen Charging System

As mentioned in chapters 4 and 5, gaseous charging was done on zirconium alloys in-order to obtain uniform distributed hydrides. This appendix shows the parts of the system employed for hydrogen charging. Figure I.1 shows the schematic diagram of high pressure hydrogen gas system and its components.





Gas Constituent	Content
Argon	99.999%
Oxygen	<3 ppm
Carbon Monoxide	<1 ppm
Carbon Dioxide	<1 ppm
Hydrocarbons	<0.5 ppm
Water	<2 ppm

Table I.1: Composition of ultra-high-purity Argon gas

Table I.2: Composition of ultra-high-purity hydrogen gas

Gas Constituent	Content
Hydrogen	99.999%
Oxygen	<2 ppm
Nitrogen	<7 ppm
Carbon Dioxide	<0.5 ppm
Hydrocarbons	<0.5 ppm
Water	<3 ppm

The argon gas (see Table I.1 was used to purge the chamber, before filling the chamber with ultra-high purity hydrogen gas (see Table I.2). A pressure of 20 MPa was maintained. Thermal cycling was done on the samples at temperatures from 350°C to room temperature. This process is repeated 10 times with 5h soaking time at 350°C per each cycle, followed by furnace cooling.

Appendix II

Fundamentals of Texture

In a polycrystalline material, we rarely observe random orientation of grains, with respect to the specimen reference frame. Grains in almost all naturally occurring or fabricated materials have some preferential orientation. This preferred orientation is called texture. The grain orientation is described by defining the orientation of the crystal reference frame in the specimen reference frame. Based on such definitions, various statistical representations of orientation of grains, in the polycrystalline materials were developed. The study on texture of materials has gained importance, because many of the materials properties are texture dependant [1].

To simplify the description of texture, the orientation of grains are often described using Miller indices *(hkl)[uvw]*. Where (hkl) represents the crystallographic plane parallel to the surface of the specimen, or to the reference plane, and [uvw] represents the crystallographic direction parallel to reference direction. For example, If the crystallographic plane (110) is parallel to the sample surface, and if crystallographic direction [001] is parallel to one of the sample reference direction (let's say X axis). Then, the orientation of the yellow grain is represented as (110) [001] (see Figure II.1)



Figure II.1: Schematic representation of grain orientation [2]

Techniques like X-ray diffraction, neutron diffraction, and electron diffraction are employed to study the crystal structure, and the preferred orientation of grains, in the polycrystalline materials. The results of texture measurements are represented using 1) Pole figure, 2) Inverse Pole Figure (IPF), or 3) Orientation Distribution Function (ODF).

1) Pole figure: Pole figure is a stereographic projection of the vectors normal to the selected crystallographic plane, defined in the specimen reference frame. For example, Figure II.2 shows how the crystallographic directions are projected on the specimen surface.





Figure II.2: a) Stereographic projection of three <100> poles, b) Pole figure showing the orientation of single crystal, c) Pole figure showing the orientations of textured polycrystalline material, d) Representation of pole figure with pole density [3]

 Inverse pole figure (IPF): Here, the orientation of the selected direction of the sample is observed in the crystal reference frame.
For example, Figure II.3 shows the inverse pole figure of the normal direction ND, and this direction is aligned with the highest frequency with the poles of $\{\overline{1}11\}$ planes.



Figure II.3: Inverse pole figure [3]

3) Orientation distribution function: ODF is a mathematical function, used to describe the orientation density in a polycrystalline material. It shows the probability of occurrence of particular orientation in 3-D Euler angle space. The ODF is constructed using pole figures. For example, Figure II.4 shows the typical representation of ODF, where the Euler space is cut into slices at $\varphi_2 = 5^\circ$ interval.



Figure II.4: a) 3D view of ODF b) Orientation distribution function (ODF) ploted

at $\varphi_2 = 5^\circ$ interval [5]

In a material with volume V, the volume of grains (dV) of orientation g within the orientation space dg is give as (see Equation II.1) [1].

$$\frac{d\mathbf{V}}{\mathbf{V}} = f(\mathbf{g})d\mathbf{g}....(II.1)$$

Where, f(g) is the orientation distribution function

The complete description of texture and related terminologies can be obtained from references [4, 5].

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Appendix-III

Fundamentals of EBSD and Orientation Imaging

Electron backscatter diffraction technique (EBSD) is a powerful technique, which provides the crystallographic information on metals, minerals, semiconductors, ceramics and inorganic crystalline materials [1]. This technique has also been referred as backscatter Kikuchi diffraction (BKD) or backscatter electron Kikuchi diffraction (BEKD). Moreover, EBSD when combined with scanning electron microscopy (SEM) can be used to measure orientation of individual grains, micro texture, and also in phase identification [2]. The typical combination of SEM and EBSD is also known as OIM (Orientation Imaging Microscopy). The angular resolution of EBSD is about $0.5-1^{\circ}$, and a spatial resolution of 10 - 20 nm can be achieved [2, 3].

III.1: How the EBSD patterns are obtained:

In EBSD, a stationary electron beam strikes the sample tilted at an angle of 20° to the incident electron beam. The electrons are scattered when they enter the sample in various directions. If the scattered electrons

beam satisfies the Bragg condition, it results in formation of a high angle diffracted bands in the form of large cones. These bands, known as Kikuchi bands, contain wealth of information about the structure of material investigated (see Figure III.1).

The first observation of back scattered diffraction was recorded by Nishikawa and Kikuchi in 1928 [4]. The patterns were first described as the pairs of black and white lines [4]. Later, these patterns were described in detail by Alam et al. [5]. For example, Figure III.2 shows the Kikuchi pattern of Ge single crystal, where the Kikuchi lines characterize the orientation of the plane of crystal lattice and the width 'W' of Kikuchi lines depends on electron wavelength and lattice spacing.



Figure III.1: Schematic diagram showing the origin of Kikuchi line from the tilted sample. [6]



(a)



(b)

Figure III.2: a) Kikuchi pattern of Ge single crystal, b) Indexed Kikuchi pattern [7]

The Kikuchi bands obtained from the sample are projected on a phosphor screen, which in turn converts the diffracted electron into light

that is recorded by charge-coupled CCD devices. Then, the Kikuchi patterns are digitalized and analyzed using Hough transform. This transform uses co-ordinates ρ and θ to convert Kikuchi lines to points by Equation III.1.

$$\rho(\theta) = x_i \cos\theta + y_i \sin\theta$$
.....III.1

Where (x_{i}, y_{i}) describes a set of pixel coordinates forming a line and the coordinate ρ represents distance of line from the origin and coordinate θ describes the angular direction.

After all the Kikuchi bands have been digitalized and detected, the *d* spacing is derived based on the angles between the Kikuchi lines. Wright et al. [8], in 1992, have invented a voting scheme, for indexing of Kikuchi bands with the database containing crystallographic diffracting planes and its corresponding crystal structures. At least three Kikuchi bands are required for automatic indexing [9]. First, all possible sets of triplets are formed from the detected bands. For example, in FCC, only the planes {111}, {200}, {220} and {311} are included. A look-up table of all possible inter-planar angles is generated from the above mentioned four planes. Then, the coincidence triplets are checked with the look-up table. When a solution is found for the triplet, the solution receives a vote and in this way, the most probable solution receives maximum votes (see

Figure III.3). In addition, the angular fit between the detected and indexed patterns is described by Fit parameter. The lower the fit value, higher the probability that the solution is right.





(c)

Figure III.3: a) detected bands b) voting table c) indexed pattern [10]

The uniqueness of the geometry of each crystal structure helps the software in determining the orientation and crystal phase at each and every point. The microstructure of the sample is mapped by using the collected information.

Several terminologies are used while analyzing the data obtained from the EBSD scan. Some of the most common terms are given below

 Image Quality (IQ) Map: Image Quality map, is a grey scale map of the microstructure obtained by mapping electron backscatter Kikuchi patterns at each point of the EBSD scan. The IQ parameter is defined as the average height of the detectable peaks
[5]. The quality of the IQ map depends on various factors like strain, topography and the quality of Kikuchi bands. Thus, the parameter, IQ, will help in qualitative description of strain in the microstructure and it indicates the sharpness and quality of the Kikuchi pattern (see Figure III.4).



Figure III.4: Image Quality map [11]

2) Phase map: The geometry of a Kikuchi pattern is unique for a particular crystal structure, and the dissimilar phases can be identified. For example, in Figure III.5, austenite is face centered cubic (fcc) and ferrite is body centered cubic (bcc).



Figure III.5: Phase map of duplex steel (yellow color: ferrite, pink color: austenite) [12]

3) Texture: The crystallographic texture can be calculated from the information on orientation of individual grains. This texture is generally termed as microtexture (see Figure III.6)





Figure III.6: The region of map contributing to $\{879\} < \overline{1}119$ texture and (001)

pole figure showing this texture. [12]

Terminologies defined above are nothing more than the introduction of few common terms. The complete list of the terminologies used in OIM analysis can be found in the following references [9, 11, 13, 14, 15].

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