MICROSTRUCTURES CHARACTERIZATION
OF
PRECIPITATES IN ZIRCONIUM ALLOYS

GAIHUAN YUAN

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ABSTRACT

Zirconium alloys are used as the fuel cladding materials in nuclear power reactors. Corrosion resistance is one of the most important factors for the application of zirconium alloys, which involves the lifetime of fuel assemblies, and the safety and reliability of the operation for nuclear power reactors. According to the current research, the characterizations of precipitates in zirconium alloys affect the corrosion resistance significantly. However, the investigation results about the precipitates in zirconium alloys are variable. Zr-4 (Zr-1.2Sn-0.2Fe-0.1Cr), E110 (Zr-1Nb) and Zirlo (Zr-1Sn-1Nb-0.1Fe) are commercial alloys to be widely applied for pressurized water reactors (PWRs).

Zr-4, E110 and Zirlo, as the representatives of Zr-Sn, Zr-Nb and Zr-Sn-Nb alloys, are widely applied for PWRs. Three alloys were developed in the early time, and there are many data and experience for the performance in reactors. As the references, three alloys are studied and the precipitates and microstructures are systematically analyzed.

The transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS) and High-resolution transmission electron microscopy (HRTEM) have been used to study the composition, structure, defects and orientation relationship of the precipitates in commercially available Zr-based alloys.

The main experimental results and conclusions are as follows:

1. The formation of Laves phase in Zr-4 alloy was studied concerning the dependence of structure on the stoichiometry ratio. The Fe/Cr ratio of C15 structure was slightly lower than that of C14 structure for Zr-Fe-Cr phase. The formation of \{0001\} stacking faults in C14 was observed and analyzed at the first time. The orientation relationships of C14 and C15 phases with \(\alpha\)-Zr were identified as \((11\overline{2}0)_{\text{sp}}//\langle0002\rangle_{\alpha-Zr}, [2\overline{2}01]_{\text{sp}}//\langle01\overline{1}0\rangle_{\alpha-Zr}\) and \((20\overline{2})_{\text{sp}}//\langle10\overline{1}\overline{1}\rangle_{\alpha-Zr}, [101]_{\text{sp}}//[\overline{1}2\overline{1}0]_{\alpha-Zr}\), respectively. The formation of hydrides in Zr-4 alloy was also researched. The structure of stable \(\delta\)-ZrHx hydride is face-centered cubic and the hydrides are crystallographically related to the \(\alpha\)-Zr solid solution with 24 equivalent variants, typically summarized as: \(<\overline{1}2\overline{1}0>_\alpha // <101>_\delta\) and \{0001\}_\alpha // \{111\}_\delta. Most of the \(\delta\)-hydrides are plate morphology, aligned on the \{0001\}_\alpha habit.
plane of the α-Zr solid solution phase. It was interesting to observe the twinning in δ-hydrides. The twinning plane is (h11)d. The hydrides became more blocky in shape, with twin boundaries formed through complete consumption of the matrix phase between separately nucleated precipitates.

2. β precipitates were found as the dominant precipitates in E110 (Zr-1Nb) alloy. After annealing at 600 °C for 3 hours, the precipitate is spherical β phase with 30-60 nm diameter, ~2.5 % volume fraction and ~68 wt.% Nb content. After annealing at 700 °C for 3 hours the precipitate is stick-shaped β phase with ~100 nm in diameter, ~300 nm in length, ~9.8 % volume fraction and ~10 wt.% Nb content. The orientation relationship between α and β phases met Burgers’ orientation relationship, i.e., (1010)α//(112)β for the broad face, (0001)α//(110)β for the side facet and (1120)α//(111)β for the edge. When Nb content of β phase increased, the lattice misfits on broad face, side facet increased and their interfacial structures changed from coherent (obtained at 700°C) into incoherent (obtained at 600°C). When the misfits of edge decreased, the interfacial structures were always incoherent for the two heat treatments. Therefore, the curved interfaces had a higher growth rate than the straight interfaces at 700 °C and stick-shape β phase was formed. While every plane has a comparable growth rate for three planes at 600 °C and spherical β phase was formed.

3. Intermetallic nano-particles, with the C14 Laves-phase structure, are the dominant precipitates and typically larger than 60 nm in sizes in Zirlo. The precipitates are assigned to the Zr(Fe,Nb)2 formula with Fe and Nb mixed on the second sublattice sites in the bracket. The orientation relationship between the Laves phase and the matrix was close to (100)α//zr (110)C14 and [0001]α//zr [010]C14. Stacking faults were also observed in the ternary Laves phase, together with dislocations presenting on prism planes of the matrix solid solution. Besides, some fine spherical β-Nb particles, about 30 nm in size, were also found to precipitate within the α-Zr grains, with the α/β interface being crystallographically coherent.

Based on the R&D, the types of the precipitates were identified and more information was obtained on the morphology, chemical composition and crystal orientation. The results support the research between the precipitates and physical chemical properties in the future, and optimization of the commercial or new zirconium alloys.
Keywords: Zirconium alloy; Precipitate; Microstructural characteristics; Orientation relationship; Formation of nanocrystalline.
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<td>BF</td>
<td>Bright field</td>
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<td>BSE</td>
<td>Back-scattered electrons</td>
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<td>Second phase particle</td>
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<td>TEM</td>
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Chapter 1 Introduction

1.1 Background

Nuclear energy has been considered as an effective method to power the modern world without the emission of carbon dioxide. Currently, almost 15% of the world’s electricity consumption is generated from nuclear power. However, nuclear reactors present a harsh environment for materials, especially for the cladding tubes, which are used as the structural materials of the radioactive fuel. Fuel assemblies within a reactor core must tolerate exposure to the coolant (high temperature water, liquid metals, gas, or liquid salts), stress, vibration, an intense field of high energy neutrons, or gradients in temperature. Degradation of materials in this environment could lead to reduce fuel reliability, and in some cases, sudden failure.

Zirconium alloys have been used for fuel cladding tubes in nuclear reactors due to the low absorption cross-section for thermal neutrons, good mechanical properties and high corrosion resistance. There has been continuing effort in prolonging the service life of the fuel-cladding materials, in order to meet the challenging request for ever-increasing burn-up (the amount of fuel used up in a nuclear reactor). The performance of zirconium alloys can be improved through the introduction of alloying elements with low absorption cross-section of thermal neutrons, to induce solution and/or precipitate strengthening while maintaining good corrosion resistance. Therefore, only a certain limited numbers of alloying elements are suitable for cladding Zirconium alloys, also with low acceptable concentrations. So far the recognized alloying elements for such materials include Nb, Sn, Fe, Cr, O etc. Zr-4 (Zr-1.2Sn-0.2Fe-0.1Cr), E110 (Zr-1Nb) and Zirlo (Zr-1Sn-1Nb-0.1Fe) are the typical Zirconium alloys for commercial application.

Zirconium alloys are characteristically made of solid solution phases (usually alpha Zirconium in cladding tubes) and particles of intermetallic compounds, which are precipitated during the fabrication of zirconium products due to the limited solubility of alloying elements. The size, distribution and type of precipitates have effects on the corrosion resistance, mechanical properties, anti-radiation properties etc. The previous researches related to the precipitates were variable, but the details were not enough for material investigation. Thus, it is significant to further analyze the characteristics of precipitates such as chemical composition, morphology, crystal structure, defect structure and orientation relationship with matrix, which can provide a theoretical
basis to improve the in-pile performance of Zirconium alloys and develop new higher-burnup zirconium alloys. As a well developed material, Zr-4 alloys were applied for cladding materials in the 1950s. Many scientists studied the precipitates. In 1974, Vander Sande introduced the precipitates in the zirconium alloys. The precipitates are ZrCr₂ (HCP structure: a=0.5079 nm c=0.8279 nm). Meng found Zr(Fe, Cr)₂ precipitates. One is MgCu₂-type (FCC structure: a=0.7015~0.7207 nm). The other is MgZn₂ type (HCP structure: a=0.5034~0.5075 nm, c=0.8209~0.8275 nm). Meng found single diffraction pattern of the laves phases were identified hexagonal or cubic structure at the same time, but could be identified by the higher order laue spot. Kuwae studied the precipitates after α and α+β annealing. Zr-Fe-Cr precipitates are HCP-ZrCr₂ type after α annealing; Zr-Fe-Cr precipitates are FCC-ZrCr₂ after α+β annealing. Bangaru researched the precipitates after three heat treatment. Zr₃(Fe, Cr)₂, Zr(Fe,Cr)₂, Zr(Fe, Cr)₃, Zr₂(Fe, Cr) precipitates are possible formed in different heat conditions. But he did not provide the data of the diffraction pattern and EDS, so the further verification is needed. The research is focus on the micro-structure and stacking defects based the previous work on the types of the precipitates.

The structural zirconium alloy components in nuclear reactors absorb hydrogen through various sources, such as moisture present in fuel pellets, reaction between zirconium and coolant water (Zr + 2H₂O→ZrO₂+ 2H₂) etc. Although zirconium alloys can dissolve up to 450 ppm hydrogen in solid solution at around 500 °C, the solubility of hydrogen decreases markedly as the temperature is lowered, with 65 ppm hydrogen at 300 °C and 0.05 ppm hydrogen at room temperature. During the cooling, the excess hydrogen will precipitate as zirconium hydrides. Generally, there exist three kinds of hydride phases including the stable face-centered cubic δ phase, the metastable face-centered tetragonal γ phase, and the face-centered tetragonal ε phase. The most commonly observed hydride in Zr alloys is δ-hydrides with a plate-like shape. The δ-hydrides preferentially precipitate on certain habit planes of the zirconium solid solution matrix (α-Zr), such as the frequently reported {0001} and {1017} planes, with the latter being slightly deviated from the former. In the past four decades, the influence of hydride precipitates on the performance of Zr based cladding materials was investigated by electron back-scattered diffraction, acoustic emission, and
transmission and scanning electron microscopy\textsuperscript{[15-18]}. Due to the significant structural difference between hydrides and α-Zr, the structural transformation between them involves a large volume expansion, and the interfacial energy is anisotropic because of the mixed coherency of the interfaces (the habit plane is coherent and the edge plane is semicoherent or incoherent)\textsuperscript{[16]}. It was observed that the nucleation of cracks depended strongly on the orientation and morphology of hydrides\textsuperscript{[20,21]}. Radically orientated hydrides can drastically reduce the ductility of Zr alloy tubes.

Thus, the morphology and spatial distribution of hydrides are very important for improving the long-term stability of Zr alloys. The simulation of morphology and spatial distribution of γ-hydride in zirconium alloys has been reported\textsuperscript{[22]}. It shows that the hydrides arrangement strongly depends on the external stress. The stress effect and variant alignment are most evident during the initial nucleation stage. However, in their simulation only single hydride is allowed to grow, and the interactions between hydrides are not considered.

Zirconium hydrides are always treated as compounds with low ductility and crack easily on the initial stage of plastic deformation\textsuperscript{[23-25]}. However, the discover of substructure due to the formation of a high density of dislocations, the glide through and observation of dislocations in hydrides in deformed alloys somewhat indicates the possibility of plastic deformation of hydrides\textsuperscript{[21,26]}. In spite of great importance of structural evolution in hydrogen containing Zr alloys, further efforts are still desired particularly about the crystallographic relationship and associated kinetic process for nucleation, growth and deformation behavior of hydride containing alloys.

Zr-1Nb alloy has been used as fuel cladding and structure materials in Russian VVER and in France nuclear reactors for many years\textsuperscript{[25,26]}. In this alloy, precipitates have an intense influence on the physical, mechanical and corrosion properties. Therefore, lots of efforts have been made over several decades to reveal the influence of hot working, heat treatment and service conditions on the characterizations of the precipitates, such as crystal structure, composition, shape, size, volume fraction and distribution.

There are many possible solid phase transformations in Zr-1Nb alloy, such as 1) $\beta \rightarrow \alpha$ ($\alpha'$) during cooling from the β phase field, 2) $\beta \rightarrow \omega$ during quenching from the β phase field or aging at low temperature, 3) $\beta \rightarrow \alpha + \beta_1$ (Nb-impoverished), 4) $\beta \rightarrow \alpha + \beta_2$ (Nb-enriched) monotectoid reaction and 5) $\alpha \rightarrow \alpha + \beta_1$ (Nb-enriched or Nb-impoverished)\textsuperscript{[27,28]}. It has been reported that the precipitates
in Zr-1Nb alloy are mainly Nb-impoverished or Nb-enriched β phases \cite{27,29-33}, and a small amount of intermetallic compounds \cite{33-36}. Generally, annealing below the monotectoid temperature for a long time Nb-enriched β\textsubscript{2} phase could be formed, while annealing above the monotectoid temperature or for a short time Nb-impoverished β\textsubscript{1} phase could be formed \cite{37-39}. As almost all the studies on the relationship between precipitates and corrosion properties show that an increase in the amount of Nb-impoverished β\textsubscript{1} phase precipitates increases the corrosion rate, the microstructure containing stable Nb-enriched β\textsubscript{2} phase precipitates is preferred for materials stability under corrosive conditions \cite{30,39}. Although the phase transformations in Zr-Nb alloy have been extensively investigated, little effort has been made to study the β\textsubscript{2}→β\textsubscript{1} phase transformation and associated crystallographic characteristics.

In the present study, the β phase particles in a Zr-1Nb alloy annealed below and above the monotectoid temperature were investigated by transmission electron microscopy. Currently, almost 15% of the world’s electricity consumption is generated from nuclear power. Zr-based alloys, or ZIRLO, have been used for fuel cladding tubes in nuclear reactors due to their low absorption cross-section for thermal neutrons, good mechanical properties and high corrosion resistance. There has been continuing effort in prolonging the service life of the fuel-cladding materials, in order to meet the challenging request for ever increasing burn-up of nuclear reactors \cite{40}. This can be achieved through the introduction of alloying elements with low absorption cross-section of thermal neutrons to induce solution and/or precipitate strengthening while maintaining good corrosion resistance. Therefore, only a limited number of alloying elements are suitable for cladding Zr alloys, with their acceptable contents being fairly low. So far the recognized alloying elements for such materials include Nb, Sn, Fe, Cr, O etc. The ZIRLO alloy is one of the few successfully developed and commercially applied alloys, which was introduced to pressurized water reactors in 1987 \cite{41}. The nominal ZIRLO composition (wt\%) contains 1% Nb, 1% Sn, and 0.1% Fe. In addition to the improvement of corrosion resistance achieved by ZIRLO cladding with respect to that of the Zircaloy-4 material, the in-service growth and creep were also significantly slower, resulting in an improved dimensional stability \cite{42}. The compositions and crystalline structures of precipitates in ZIRLO are reckoned to be influenced by the solubility of Nb and Fe in a-Zr, as well as by the empirical ratio \( R = \frac{Fe}{(Fe+0.3\%Nb)} \) \cite{43}. As for the solubility limit of Sn, Toffolon-Masclet et al. updated the Zr-Sn binary phase diagram through experimental
investigation together with first principle calculation, and thus reevaluated the Sn solubility limit in α-Zr\[^{[44]}\]. Based on their work there would be no Sn containing precipitates in ZIRLO. According to the parameter R proposed by Shishov, the precipitates should be the body-centered-cubic β-Nb and the hexagonal Zr-Fe-Nb phase. For the Zr-Fe-Nb phase, Granovsky\[^{[45]}\], Ramos\[^{[46]}\], Barberis\[^{[47]}\], and Toffolon-Masclet\[^{[48]}\] independently prepared some Zr-Sn-Nb-Fe alloys, and carried out structural study of precipitated phases. They concluded that the Zr-Nb-Fe particles can be divided into FCC and HCP structures, the former space group were Fd\(\bar{3}\)m (Ti\(\text{2Ni}\) type), while the latter had P6\(\text{3}^{\text{m}}\)mc space group (MgZn\(\text{2}\) type, C14).

When serving in nuclear reactors, the inner surface of cladding tubes is in contact with fission products at high temperature while the outer surface endures high temperature and high pressure water (280-350 °C, 10-16 MPa). In such a harsh working environment, the corrosion resistance of Zr alloys is very important. Numerous experiments have shown that the size distribution and type of second phase/s affect the penetration of oxygen ions and associated nodular corrosion. The optimized corrosion performance of Zr alloys was achieved when the fine second phase particles were uniformly precipitated in α-Zr matrix. Rudling et al. showed that the SPPs distribution and chemical composition heavily affected the corrosion behavior, since the barrier layer (dense zirconia) which influence the diffusion of oxygen ions was closely related to the SPPs\[^{[49]}\]. On the other hand, the defects of precipitates make them prone to amorphization and elemental migration, which would change the stability of precipitates and chemical compositions of the matrix, thereby lowering the working performance of Zr alloys\[^{[50,51]}\].

While moderate incorporation of alloying elements such as Fe, Cr and Ni etc within the α-Zr may help strengthen the materials without evident negative impact on corrosion resistance, the precipitation of intermetallic compounds will occur when their contents are above the rather low solid solubility. The formation of such second phases rich in alloying elements will affect their mechanical properties, corrosion resistance and as well as possible hydrogen pickup process in service. It is therefore important to understand the precipitation process and associated crystallographic phenomena and compositional redistribution\[^{[52-55]}\]. In spite of years of investigation, such data, particularly defect evolution and crystallographic details, are yet lacking for Zr alloys containing Nb and Fe as the main alloying element.
The ZIRLO alloy is one of the few successfully developed and commercially applied alloys, which was introduced to pressurized water reactors in 1987. The nominal ZIRLO composition (wt. %) contains 1 % Nb, 1 % Sn, and 0.1 % Fe. In addition to the improvement of corrosion resistance achieved by ZIRLO cladding with respect to that of the Zircaloy-4 material, the growth and creep in the nuclear power reactor were also significantly slower, resulting in an improved dimensional stability. The compositions and crystalline structures of precipitates in ZIRLO are reckoned to be influenced by the solubility of Nb and Fe in α-Zr, as well as by the empirical ratio $R = \frac{Fe}{Fe+Nb-0.3 \%}$. As for the solubility limit of Sn, Toffolon-Masclet et al. updated the Zr-Sn binary phase diagram through experimental investigation together with first-principle calculation, and thus reevaluated the Sn solubility limit in α-Zr. Based on their work there would be no Sn containing precipitates in ZIRLO. According to the parameter $R$ proposed by Shishov, the precipitates should be the body-centered-cubic β-Nb and the hexagonal Zr-Fe-Nb phase. For the Zr-Fe-Nb phase, Granovsky, Ramos, Barberis, and Toffolon-Masclet independently prepared some Zr-Sn-Nb-Fe alloys, and carried out structural study of precipitated phases. Granovsky concluded that the Zr-Nb-Fe particles were mainly of two kinds: Ti$_2$Ni type face-centered cubic structure or the MgZn$_2$ (C14) type hexagonal structure. Barberis and Toffolon-Masclet also proposed that the Zr-Nb-Fe particles can be divided into FCC and HCP structures, the former space group was $Fd\bar{3}m$ (Ti$_2$Ni type), while the latter had $P6_3/mmc$ space group (MgZn$_2$ type, C14).

When serving in nuclear reactors, the inner surface of cladding tubes is in contact with fission products at high temperature while the outer surface endures high temperature and high pressure water (280~350 °C, 10~16 MPa). In such a harsh working environment, the corrosion resistance of Zr alloys is very important. Numerous experiments have shown that the size distribution and type of second phase/s affect the penetration of oxygen ions and associated nodular corrosion. Nodular corrosion is the corrosion test at the temperature of 500 °C and the pressure of 10.3 MPa for 8 hours. In addition, the weaker anti-radiation ability of second phases makes them prone to amorphization and elemental migration under neutron irradiation, which would change chemical compositions of the matrix as well as the type of precipitates, thereby lowering the corrosion resistance of Zr alloys.
While adding a certain concentration of alloying elements such as Fe, Cr and Ni etc into α-Zr may help strengthen the materials without evident negative impact on corrosion resistance, the precipitation of intermetallic compounds will occur when their contents are above the rather low solid solubility. The formation of such second phases rich in alloying elements will affect their mechanical properties, corrosion resistance and as well as possible hydrogen pickup process in service. It is therefore important to understand the precipitation process and associated crystallographic phenomena and compositional redistribution\textsuperscript{9,10,65,66}. In spite of years of investigation, such data, particularly defect evolution and crystallographic details, are yet lacking for Zr alloys containing Nb and Fe as the main alloying element. This work is focused on the refined structural/crystallographic characterization of nano-precipitates in a thermomechanically processed ZIRLO alloy, with particular interest in orientation relationship, compositional redistribution across phases, defects formation and phase interfaces.

1.2 Instruments

1.2.1 TEM Introduction

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through it. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a charge-coupled device. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons. This enables the instrument's user to examine fine detail—even as small as a single column of atoms, which is thousands of times smaller than the smallest resolvable object in a light microscope. TEM forms a major analysis method in a range of scientific fields, in physical, chemical and biological sciences.

The most common mode of operation for a TEM is the bright field imaging mode. In this mode the contrast formation, when considered classically, is formed directly by occlusion and absorption of electrons in the sample. Thicker regions of the sample, or regions with a higher atomic number will appear dark, whilst regions with no sample in the beam path will appear bright – hence the term “bright field”.

Samples can exhibit diffraction contrast, whereby the electron beam undergoes Bragg scattering,
which in the case of a crystalline sample, disperses electrons into discrete locations in the back focal plane. By the placement of apertures in the back focal plane, i.e. the objective aperture, the desired Bragg reflections can be selected (or excluded), thus only parts of the sample that are causing the electrons to scatter to the selected reflections will end up projected onto the imaging apparatus.

If the reflections that are selected do not include the unscattered beam (which will appear up at the focal point of the lens), then the image will appear dark wherever no sample scattering to the selected peak is present, as such a region without a specimen will appear dark. This is known as a dark-field image.

By adjusting the magnetic lenses such that the back focal plane of the lens rather than the imaging plane is placed on the imaging apparatus a diffraction pattern can be generated. For thin crystalline samples, this produces an image that consists of a pattern of dots in the case of a single crystal, or a series of rings in the case of a polycrystalline or amorphous solid material. For the single crystal case the diffraction pattern is dependent upon the orientation of the specimen and the structure of the sample illuminated by the electron beam. This image provides the investigator with information about the space group symmetries in the crystal and the crystal's orientation to the beam path. This is typically done without utilizing any information but the position at which the diffraction spots appear and the observed image symmetries.[67]

1.2.2 Scanning electron microscope

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures.

The most common SEM mode is detection of secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons that can be detected depends, among other things, on specimen topography. By scanning the sample and collecting the secondary
electrons that are emitted using a special detector, an image displaying the topography of the 
surface is created.

The types of signals produced by an SEM include secondary electrons (SE), reflected or 
back-scattered electrons (BSE), photons of characteristic X-rays and light (cathodoluminescence) 
(CL), absorbed current (specimen current) and transmitted electrons. Secondary electron 
detectors are standard equipment in all SEMs, but it is rare that a single machine would have 
detectors for all other possible signals.

The signals result from interactions of the electron beam with atoms at various depths within the 
sample. In the most common or standard detection mode, secondary electron imaging or SEI, the 
secondary electrons are emitted from very close to the specimen surface. Consequently, SEM 
can produce very high-resolution images of a sample surface, revealing details less than 1 nm in 
size. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by 
estatic scattering. They emerge from deeper locations within the specimen and consequently the 
resolution of BSE images is generally poorer than SE images. However, BSE are often used in 
analytical SEM along with the spectra made from the characteristic X-rays, because the intensity 
of the BSE signal is strongly related to the atomic number of the specimen. BSE images can 
provide information about the distribution of different elements in the sample. For the same reason, 
BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter, which would 
otherwise be difficult or impossible to detect in secondary electron images in biological specimens. 

Characteristic X-rays are emitted when the electron beam removes an inner shell electron from 
the sample, causing a higher-energy electron to fill the shell and release energy. These 
characteristic X-rays are used to identify the composition and measure the abundance of 
elements in the sample.

Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a 
characteristic three-dimensional appearance useful for understanding the surface structure of a 
sample. This is exemplified by the micrograph of pollen shown above. A wide range of 
magnifications is possible, from about 10 times (about equivalent to that of a powerful hand-lens) 
to more than 500,000 times, about 250 times the magnification limit of the best light 
microscopes.\[68]\
1.2.3 Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum.

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a beam of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured.[69]

1.2.4 Electron backscatter diffraction

Electron backscatter diffraction (EBSD) is a microstructural-crystallographic characterisation technique to study any crystalline or polycrystalline material. The technique involves understanding the structure, crystal orientation and phase of materials in the SEM. Typically it is used to explore microstructures, revealing texture, defects, grain morphology and deformation. It can be combined with complementary techniques within the SEM for phase discrimination. Traditionally these types of studies have been carried out using X-ray diffraction (XRD), neutron diffraction and/or electron diffraction in a TEM.

Inside the SEM, the electron beam is focused onto the surface of a crystalline sample. The electrons enter the sample and some may backscatter. Escaping electrons may exit near to the Bragg angle and diffract to form Kikuchi bands which correspond to each of the lattice diffracting crystal planes. If the system geometry is well described, it is possible to relate the bands present
in the diffraction pattern to the underlying crystal phase and orientation of the material within the
electron interaction volume. Each band can be indexed individually by the Miller indices of the
diffracting plane which formed it. In most materials, only three bands/planes which intercept are
required to describe a unique solution to the crystal orientation (based upon their interplanar
angles) and most commercial systems use look up tables with international crystal data bases to
perform indexing. This crystal orientation relates the orientation of each sampled point to a
reference crystal orientation.

While this ‘geometric’ description related to the kinematic solution (using the Bragg condition) is
very powerful and useful for orientation and texture analysis, it only describes the geometry of the
crystalline lattice and ignores many physical processes involved within the diffracting material. To
adequately describe finer features within the electron beam scattering pattern (EBSP), one must
use a many beam dynamical model (e.g. the variation in band intensities in an experimental
pattern does not fit the kinematic solution related to the structure factor.\cite{70}

1.3 Objective and Procedure
This work is focused on microstructures and characterization of precipitates in zirconium alloys,
including the formation of nanocrystalline $\delta$-ZrHx and stacking faults of Laves phase in
Zr-4; microstructure characteristics of $\beta$ precipitates in E110; and formation and fine-structures of
nano-precipitates in Zirlo. Transmission electron microscopy (TEM), energy dispersive X-ray
spectroscopy (EDS) and High-resolution transmission electron microscopy (HRTEM) have been
used to study the chemical composition, structure, defects and orientation relationship of the
precipitates.
Chapter 2 Manufacture of Experimental Materials, Instrument and Sample Preparation

The samples of Zr-4, E110 and Zirlo alloys used in this work were manufactured by State Nuclear BaoTi Zirconium Industry Company (SNZ). The nominal compositions of these alloys were shown in Table 2-1.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Types</th>
<th>Sn</th>
<th>Nb</th>
<th>Fe</th>
<th>Cr</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-4</td>
<td>plate</td>
<td>1.2</td>
<td>/</td>
<td>0.2</td>
<td>0.1</td>
<td>balance</td>
</tr>
<tr>
<td>E110</td>
<td>bar</td>
<td>/</td>
<td>1.0</td>
<td>/</td>
<td>/</td>
<td>balance</td>
</tr>
<tr>
<td>Zirlo</td>
<td>plate</td>
<td>1.0</td>
<td>1.0</td>
<td>0.1</td>
<td>/</td>
<td>balance</td>
</tr>
</tbody>
</table>

2.1 Manufacture of Experimental Materials

Raw materials are zirconium sponges. Zirconium Sponges are prepared from zirconium tetra-chloride and magnesium. The byproduct is MgCl₂, which is easily dissolved in the water. So the pure zirconium materials look like the sponge. That’s the reason that pure zirconium is called zirconium sponge. Ingots of zirconium alloy were prepared by vacuum arc melting, using a self-consuming electrode of the same composition to avoid impurity pickup. The sponges were pressed into the electrodes with adding some alloys, and the electrodes were melted into the ingot(Φ700mm). At room temperature, zirconium exhibits a hexagonally close-packed crystal structure, α-Zr, which changes to β-Zr a body-centered cubic crystal structure at 863 °C. Zirconium exists in the β phase until the melting point. The billet is heated to 1030 °C for 10 minutes to ensure the zirconium material is transferred to β phase. Each ingot was forged in the β phase field into feeding billets(Φ220mm) for subsequent thermal mechanical processing. The forged billets were water-quenched from β phase field down to room temperature, and manufactured into different products. Zirconium β-quenching treatment was conducted to homogenize the composition. Flow chart is as following (Fig. 2-1).

For the bar samples: The billets was extrudes to the intermediate bar(Φ86mm). The intermediate bar was swagged to the final bar(Φ10mm). The samples was taken from the final bar with polishing process and annealing process. The heat treatment was carried out at 500- 550°C.

For the plate samples: The billet was rolled to the thick plate in the hot temperature. Then the final plates were obtained from the thick plate in terms of the cold-rolling process. as shown in Fig.
2-1. The final plates in this work were finally annealed at 600°C-700°C to achieve complete recrystallization. The samples were taken from the final plate after the polishing process.

5000T Press machine is used to compress the electrodes. VAR FURNACE is used to melt the ingot. Induction heating furnace is used to heat the billet to β phase. 1250T extrusion press is used to extrude the bar. Hot rolling machine is used to obtain the intermediate plate. Cold-rolling machine is used to obtain the final product. Anneal furnace is used to achieve the re-crystallization. Polish machine is used to remove the oxide of the product.

Fig. 2-1 Manufacture flow chart of experimental materials
2.2 Instrument and Sample Preparation

2.2.1 Zr-4 sample preparation

Thin foils for transmission electron microscopy (TEM) were mechanically polished to 60-80 µm in thickness, and then the central region of each disc was dimple-polished down to about 20 µm in thickness. Twin-jet electro-polishing was then followed, using an electrolyte consisting of a solution of 10 % perchloric acid and 90 % ethanol. The working temperature for the electrolyte was maintained at -40 °C and the working voltage was 45 V. Finally, the foils were polished by ion milling at 5 eV, with a liquid nitrogen cooling stage. The power of ion gun was 4.5K eV and the vacuum was kept at 5×10⁻⁴ Pa. TEM and Energy Dispersive X-ray Spectroscopy (EDS) were carried out at 200 kV, using a JEM 2010FEF microscope equipped with an energy dispersive X-ray spectroscopy (EDS) detector (Oxford UTW Isis). HRTEM analysis was performed in a FEI Tecnai G2 F20 microscope, operated at 200 KV.

2.2.2 E110 sample preparation

A rod 9.6 mm in diameter below the monotectoid temperature, finally the rod was annealed at 600 °C and 700 °C (below and above monotectoid temperature, respectively) for 3 hours to achieve a fully recrystallized structure. Transmission electron microscopy (TEM) and composition analysis were performed using a FEI Tecnai G2F20 transmission electron microscope equipped with energy dispersive X-ray spectroscopy (EDS) analyzer. TEM foils were mechanically thinned to 50 µm in thickness and further reduction was carried out using a Tenupol-5 twin-jet electrolytic polisher in a solution of 10% perchloric acid and 90% ethanol (volume fraction).

2.2.3 Zirlo sample preparation

Thin foils (0.5~1mm) for transmission electron microscopy (TEM) were mechanically polished to about 60 µm in thickness, and then the central region of each disc was dimple-polished down to about 20 µm in thickness. Twin-jet electro-polishing was then followed, using an electrolyte consisting of a solution of 10 % perchloric acid and 90 % ethanol. The working temperature for the electrolyte was maintained at -40°C and the working voltage was 45 V. Finally, the foils were polished by ion milling at 5 eV, with a liquid nitrogen cooling stage. TEM and energy dispersive X-ray spectroscopy (EDS) were carried out at 200 kV, using a JEM 2010FEF microscope equipped with an EDS detector (Oxford UTW Isis).
Chapter 3 The formation of stacking faults of Laves phase and nanocrystalline δ-ZrHx in Zircaloy-4

3.1 The Formation and Stacking Faults of Fe and Cr Containing in Zr-4 Alloys

3.1.1 Typical microstructure of Zr-4 alloy

Electron diffraction analysis has been done in the selected zone and the incident direction for α-Zr was [0001] zone axis. The equiaxed morphology of α-Zr grains indicated the complete re-crystallization of Zr-4 alloy and the dislocation slip lines intersecting with each other also can be observed. The precipitates were shown to distribute largely evenly across the gains of the matrix phase. It can be seen from the microstructure that the precipitates were with variable shapes, such as spherical, ellipsoid or irregular shapes. The precipitates of Zr-4 alloy are mainly Zr-Fe-Cr phase, of which the structure is thought to be similar to ZrCr$_2$ Laves phase, and the stoichiometric formula is Zr(Fe$_x$Cr$_{1-x}$)$_2$, with crystalline structure of either C14 (HCP) or C15 type (FCC)\[^{11-13}\]. In this work both C14 and C15 type Laves phases were observed. Fig. 3-1 shows the bright field (BF) image and SEAD pattern area of the typical microstructure of Zr-4 alloy.

![Fig. 3-1 (a) The bright field image of microstructure of Zr-4 alloy; (b) The SAED pattern of selected area](image)

Fig. 3-2 shows the selected area electron diffraction (SAED) pattern and corresponding EDS mapping of a typical spherical particle. As it can be observed, Fe and Cr distribute in this particle uniformly. EDS analysis shows that the atomic ratio of Fe and Cr is approximately 2. The diffraction pattern can be indexed as C15 type ZrCr$_2$ Laves phase and the zone axis for second phase particle (SPP) is [101]. The orientation relationship (OR) of C15 phase with matrix was characterized as $(20\bar{2})_{\text{SPP}}// (10\bar{1}1)_{\alpha-\text{Zr}}, [101]_{\text{SPP}}// [\bar{1}2\bar{1}0]_{\alpha-\text{Zr}}$ in Fig. 3-2(b). On this basis, the atomic configuration of the mentioned OR was schematically reconstructed and shown in Fig. 3-3. It can be obviously found that the atomic mismatch is 0.065 along the [101] direction of C15-Zr(Fe,Cr)$_2$. 
Fig. 3-2  (a) The bright field image of Zr(Fe,Cr)$_2$; (b) The corresponding SAED pattern; (c,d) EDS mapping of Zr(Fe,Cr)$_2$

Fig. 3-3 The schematic diagram of orientation relationship between C15-Zr(Fe,Cr)$_2$ and α-Zr

Fig. 3-4(a) is a BF image typical of a short rod-like particle. Three SAED patterns of the corresponding phase from different zone axis were obtained through systematic tilting (Fig. 3-4(b-d)). This phase could only be indexed as C14 type ZrCr$_2$. The typical OR that derived from Fig. 3-4(b) is (1120)$_{spp}$//(0002)$_{α-Zr}$, [0110]$_{spp}$//[0110]$_{α-Zr}$. EDS result of this precipitate showed that the atomic ratio of Fe and Cr was 3. The atomic configuration of the above OR was illustrated in
Fig. 3-5. It can be obviously found that along C14-Zr(Fe,Cr)\(_2\) [2\overline{2}01] \text{ direction the lattice mismatch is as small as 0.029.}

Fig.3-4 (a) Bright field image of C14 type Zr(Fe,Cr)\(_2\) and corresponding EDS analysis; 
(b) A set of diffraction patterns of the C14 type Zr(Fe,Cr)\(_2\)

Fig. 3-5 The schematic diagram of orientation relationship between C14 type Zr(Fe,Cr)\(_2\) and α-Zr

Fig. 3-6 is a set of bright field image and the corresponding SAED of short rod-like phase. The SAED patterns consist of two kinds of phases (Fig. 3-6(b)). One is from matrix and the other is
from precipitate. The SAED from matrix gave a diffraction pattern with the \([17\bar{8}3]\) zone axis and diffraction pattern in terms of the precipitate can be indexed as the C14-[\(\bar{1}2\bar{1}0\)] zone axis. The corresponding OR was nearly \([\bar{1}2\bar{1}0]_{\text{sp}}/ [17\bar{8}3]_{\alpha-Zr}\) and \((0001)_{\text{sp}}// (\bar{1}\bar{1}02)_{\alpha-Zr}\). The matrix crystal plane for the C14 phase to nucleate from and grow on is \((\bar{1}\bar{1}02)_{\alpha-Zr}\). There are optimum lattice matching of atom patterns and spacings at this relationship. Such a relationship may lower the strain energy of nucleation and promote the precipitation in Zr matrix. Thus preferred extension of the plane leads to the formation of short rod-like phase. The \((0001)\) plane is also with the lowest surface energy, which is favored thermodynamically during the crystal growth.

3.1.2 stacking faults in Zr-4 alloys

The diffraction pattern of the precipitate shows the streaking along the \([0001]\) vector, owing to the presence of stacking faults in the \((0001)\) plane. The high magnification image in Fig. 3-6(c) exhibited contrast stripe, which provided evidence for the presence of long period stacking variants in the C14 structure. The stacking faults occurred on \((0001)\) crystal plane. From SAED (Fig. 3-6(b)) we can see the 2H long-period structures existed as Meng reported\[^{14}\]. Long period structure in Laves phase is mainly affected by the ordering of component and stacking faults. The orderly occupation of solutes on C14 lattice probably originated from the sufficient migration since the stacking faults in precipitates provide sufficient space for the solute atoms to move. The formation of long period structure in precipitates will strengthen alloy in some way.

![Image](image.jpg)

Fig. 3-6 (a) Bright field image of C14-Zr(Fe,Cr)\(_2\) phase; (b) The corresponding SEAD pattern; (c) high magnification image of C14-Zr(Fe,Cr)\(_2\) phase
According to the literatures reports\textsuperscript{[6,8]}, at room temperature the Zr(Fe,Cr)\textsubscript{2} phase is stable with a hexagonal structure (C14), meanwhile this phase is identified as face-centered cubic structure (C15) at high temperature. This phenomenon is just on the opposite of ZrCr\textsubscript{2} phase. According to Zr-Cr phase diagram, the ZrCr\textsubscript{2} phase is stable with C15 type structure at low temperature. Shen reported that C14 type Zr(Fe,Cr)\textsubscript{2} is retained at room temperature because the transformation to C15 structure is very sluggish\textsuperscript{[15,16]}. In addition to the presence of Zr(Fe,Cr)\textsubscript{2} phase, researchers also reported the existence of Zr\textsubscript{4}(Fe,Cr)\textsuperscript{[17]}, Zr\textsubscript{3}(Fe,Cr)\textsubscript{2}\textsuperscript{[18]}, Zr(Fe,Cr)\textsubscript{3}\textsuperscript{[18]} in Zr-4 alloy based on the EDS results. However, because SPPs are very small and embedded into matrix, the characteristic X-rays generated by Zr that belongs to matrix may also be detected. In that case, the contribution of the matrix is very serious. Therefore, to get a reliable determination, structural and composition analysis should be applied at the same time. Pluralistic Zr-Fe-Cr particles with size ranged from 100 nm to 500 nm were analyzed by TEM and EDS in this work. Electron diffraction patterns proved the formation of two kinds of structure, namely face-centered cubic structure and hexagonal structure. The composition of Zr-Fe-Cr phases was summarized and shown in Fig. 3-7. Taking into consideration the influence of matrix we only count Fe/Cr atomic ratio. Although the morphology and size varied much, Fe/Cr ratio varied from 2~3. It is interesting to note the atomic ratio of Fe/Cr in C14 type phase was larger than that in C15 type phase. Some researchers have reported that the decisive factor for the formation of C14 phase was the content of Cr, since Cr can stabilize C14 hexagonal structure and because of its much higher valence electrons/atomic ratio\textsuperscript{[19,20]}. However, in this work we found that C15 type phase contains more Cr than C14 type phase. This may be related to the reason that the diffusion coefficient of Fe in \(\alpha\)-Zr matrix is faster than Cr\textsuperscript{[21]}. Thus Cr has no enough time to diffuse into the SPPs due to the short annealing time. It can be concluded that the formation of C15 and C14 type phase is not determined by atoms distribution solely.
3.2 Orientation Relationship and Morphology-Change Mechanism of Nanocrystalline δ-ZrHx in Zr-4 Alloy

3.2.1 Orientation relationship between α-zirconium matrix and δ-ZrHx

In the Zircaloy-4 thin foils, the microstructure is mainly consist of equiaxed α-Zr grains. However, it was rather shocking that in some thin foils sampled near the surface of the alloy sheets, there existed δ-ZrHₓ (x = 1.55 or 1.66) hydrides, considering that careful chemical analysis showed that the overall hydrogen content of the alloy was less than 20 ppm. The morphology of hydrides was found to depend upon their population. Fig. 3-8(a) is a centered-dark field TEM image corresponding to the [0121] zone axis of α-Zr matrix, showing the cross section of the hydride plates with thickness about 50-80 nm and a diameter about several hundreds of nanometers. The spot used to acquire the dark field image was circled in Fig. 3-8(b). The thin hydride plates are parallel with each other. The corresponding selected-area electron diffraction (SAED) patterns taken from the areas marked with A and the circled region in the matrix next to it (B) in Fig. 3-8(a) are shown in Fig. 3-8(b) and (c), respectively. The former contained two sets of single crystal patterns from the hydride and the matrix respectively. The latter (Fig. 3-8(c)) shows the pattern from the matrix only, and comparing to Fig. 3-8(b), one can easily tell the pattern of the hydride phase (weaker spots due to much smaller contribution in the selected area) from that of the matrix (linked with dotted lines in Fig. 3-8(b)). The magnetic rotation between the image and the diffraction patterns is about 90°, and the trace plane (edge-on) for the matrix is
Electron diffraction analysis through systematic tilting showed that the hydride is of the crystal structure of face-centered cubic δ-ZrH$_x$ phase (B1 structure, a=0.471 nm), which is the stable phase at room temperature (though deficiency in hydrogen was reported in the literature, e.g. ZrH$_{1.66}$). Tilting around the normal vector of the trace planes [0001]$_{α}$//[111]$_{δ}$ showed that the δ hydrides are of the disk shape, so that no significant change in aspect size was observed through a large range of tilting over 60°. Fig. 3-9 shows a set of SAED patterns obtained from the same region of Fig. 3-9(a). The orientation relationship between the hydride and the matrix is [1210]$_{ω}$(110)$_{δ}$ and (0001)$_{ω}$/(111)$_{δ}$, among overall 24 crystallographically equivalent orientation variants.

Fig. 3-9(a) shows the typical morphology of edge-on hydride plates taken at [101]$_{δ}$ zone axis. The typical orientation relationship (OR) can be derived from Fig. 3-9(d) as (0001)$_{ω}$//(111)$_{δ}$, and [1210]$_{ω}$/[101]$_{δ}$. One notes from Fig. 3-9(c) an equivalent orientation variant with its zone axis 60°off at [2110]$_{δ}$. Owing to the symmetry of the cubic hydride phase, there were altogether 24 equivalent ORs between the hydride and the hexagonal matrix phase, which can be summarized...
as: $<\overline{1}2\overline{1}0>_{d}/<101>_{\delta}$ and $(0001)_{d}/(111)_{\delta}$ (Noticing that “]” or “)” here implies that the indices corresponding to the c and a-axes of the hexagonal phase cannot be exchanged).

Fig. 3-9 (a) TEM image showing the presence of parallel hydride plates. (b) - (d) A set of diffraction patterns from the circled region containing a hydride plate, obtained through tilting the sample around the normal vector of the habit planes $[0001]_{\alpha}/[111]_{\delta}$.

A representative high-resolution electron microscopy (HREM) image corresponding to the $[\overline{1}2\overline{1}0]_{d}/[101]_{\delta}$ is shown in Fig. 3-10(a). The corresponding fast-Fourier-Transformed (FFT) images from the same region are shown in Fig. 3-10(b) together with FFT images from the matrix and hydrides to aid indexing. The matching plane and direction pairs between the hydride and the matrix phase are indicated in Fig. 3-10. The habit plane for the hydride to nucleate from and grow on is $(0001)_{\delta}$, and interestingly little lattice mismatch exists between $[\overline{1}1\overline{1}5]_{d}/[\overline{2}\overline{4}2]_{\delta}$. The parallel direction pair $[\overline{1}2\overline{1}0]_{d}/[\overline{1}2\overline{1}]_{\delta}$ is consistent with the above representative OR between the phases. The sketch on the right of Fig. 3-10(a) illustrates the OR between the hydride and the matrix, on the atomic planes of the $(0001)_{d}/(111)_{\delta}$ of the corresponding phases. For a more extensive envisage of the OR between a face centered cubic phase and a close packed hexagonal phase, one may refer to Fig. 12 in Shao et al.[22].
3.2.2 Morphology-Change Mechanism of nanocrystalline δ-ZrHx in Zr-4 alloy

In the initial stage for the precipitation of δ hydrides, nucleation occurred on the plane with the lowest surface energy, the (0001) plane for the hexagonal matrix phase, which acted as the habit plane for the hydride nucleation. On the other hand, there are optimum lattice matching of atom patterns and spacings at the relationship of (0001)\(_a\)/(111)\(_b\). Such a relationship may lower the surface energy of hydride nucleation and promote the hydride precipitation in Zr matrix. Thus preferred extension of the (111) plane leads to the formation of the hydride plates. Owing to the low symmetry of the hexagonal phase, each matrix crystal was only able to provide one (0001) habit plane, thus leading to the formation of hydride plates parallel to one another. The edges of the hydrides tended to follow the matching lattice plane pairs of [242]\(_b\)/[1015]\(_a\). This is highlighted in Fig. 3-10(c), which shows such a pair ledged interface at the edge of a hydride plate.

It is worth pointing out that some researchers reported that \{101n\}\(_a\) could be the habit plane for the cubic zirconium hydride\(^{18}\). The observation from this work suggests that the (0001) plane is the preferred habit plane owing to energetic advantage (minimum energy). The observation of plane pairs such as [242]\(_b\)/[1015]\(_a\) is crystallographically consistent to the same set of OR. Any \(n\) larger than 5 for \{101n\} could also be viewed as slight deviation from the (0001)\(_a\) plane, which could occur when evident strain/stress is involved.
Fig. 3-10 Illustration of orientation relationship between the hydride and a-Zr matrix. (a) HRTEM image containing a hydride. (b) Overall FFT from the same area with smaller FFT images from the hydride and the matrix respectively on the right. (c) The matching lattice plane pair at the edge of hydride.

In regions of higher density of hydrides in the annealed material, the morphology of hydrides became more chunky, as shown in Fig. 3-11(a). One notes from Fig. 3-11(a) that an overall alignment is evident in the orientation of the hydrides. The overall morphologies of these hydride crystals are rather blocky. The same OR and habit plane as those associated with the hydride plates applied to such blocky hydrides. Fig. 3-11(c) show a SAD pattern taken at \([\overline{1}\overline{2}0]\) zone axis, which exhibits two sets of twin-related hydride spots in addition to those from the matrix phase. The two sets of twin spots are of similar intensities (linked with green (in web version) and red (in web version) lines), owing to the existence of plenty twin boundaries (e.g. the arrow indicated in Fig. 3-11(a)). The corresponding HRTEM image from twin related hydride crystals is shown in Fig. 3-11(b). The twinning plane is \((\overline{1}\overline{1}1)\), which is parallel to the \((0001)\) habit plane in the matrix phase. The formation of such twin-related crystals can be readily attributed to separately nucleated hydride crystals from crystallographically equivalent OR, such that there are 6 sets of \(<110>\) zone axes to offer for each \([\overline{1}\overline{2}0]\) zone axes from the matrix solid solution phase. Each \(<110>\) then offers two sets of parallel \((111)\) planes, and with 180° ambiguity considered, there are altogether 24 different choices for the hydride phase to orient in the matrix.
phase. With a chosen \{111\}_δ plane to align with the habit plane of (0001)_α, there are in reality only two options excluding the 180 ambiguity, leading to separately nucleated hydride crystals that are of mirror symmetry with respect to the habit plane. Twin boundaries would form when separately nucleated hydride crystals consumed the matrix phase in between through growth. Generally, the δ-hydrides crystal will grow preferential along the direction of the habit plane because of the minimum surface/interface energy. Thus the δ-hydrides always show a plate-like shape. However, in this research we found that the joining of twin related hydride crystals would result in more bulky morphology, due to the multiple stacking of individual crystals. Fig. 3-12 shows a simplified sketch for the “grow-in” of two twin related crystals. The zone axes for the two crystals are \{110\}_δ and \{101\}_δ respectively, with both containing the (111)_δ plane to align on the (0001)_α habit plane in the matrix phase. When the two crystals impinge on each other through growth, a twin boundary will form, thus leading to doubled thickness in the [111]_δ direction. One sees that it is highly probable that multiple of twin boundaries may arise from such a ‘grow-in’ mechanism, when a high nucleation rate of hydride is involved. This can be facilitated through a high level of hydrogen incorporation in the Zr solid solution, through enhanced thermodynamic driving force for nucleation and growth.

Fig. 3-11.(a) TEM image of hydride with blocky morphology. (b) HRTEM of twin crystal structure in δ-hydride, (c) SAD patterns of twin crystal
A thermodynamic database for the Zr-H alloy system has been established through the calculation of phase diagram (CALPHAD) method. Fig. 3-13 shows the calculated Gibbs energy curves for the hydride and the solid solution phase at 400 °C. The blue (in web version) and red (in web version) curves represent the Gibbs free energy for α-Zr and δ phase, respectively. The common tangent defines the equilibrium chemical potential, with the tangent points on the two curves defining the equilibrium H contents. The thermodynamic driving force for phase separation in the α-Zr matrix via nucleation and growth of the δ phase is indicated by the energetic difference (△G) from the blue curve to the common tangent line, as is shown in the enlarged inset. It is apparent from Fig. 3-13 that the higher the hydrogen content, the larger the driving force for phase separation via precipitation of hydrides. This will lead to higher density of nuclei and larger growth rates. Understandably, when there is higher density of nuclei, it is more likely that “grow in” twin boundaries will form, leading to blocky morphologies, with each blocky hydride made of a collection of nano-platelets.

According to the calculated Zr-H phase diagram, the solubility of hydrogen in the α-Zr solid solution decreases with lowering temperature, so that extraneous hydrogen pickup at higher temperature could be forced out of it at lower temperatures. Due to the high content of hydrogen in the δ phase, their precipitation would involve significant long-range diffusion. As most of the steps for the processing of the materials examined in this work were fairly clean, except for water quenching the forged feeding blocks from 1050 °C. Beta quench is the process that the billet was heated to a certain high temperature then put into the water for high-speed cooling rate, It is highly possible this was when intentional hydrogen pickup occurred because zirconium is reacted with
the water to produce the hydrogen. Also, we don’t rule out the possibility that hydrogen was introduced during the ion milling process for TEM sample \[^{24}\]. In the milling process, the ions hit the sample to generate a lot of heat, and water is used as the coolant to reduce the temperature, so it is possible that zirconium is reacted with the water to form the hydride. The readiness in hydrogen picking up means that it is very important to understand the precipitation behavior of hydrides, as cladding materials do work in contact of water. It is therefore desirable for one to develop protection coating in the form of chemically inert diffusion barriers, in order to prolong service life and enhance structural stability of such materials.

![Fig. 3-13 Free Gibbs energy curve of α-Zr phase and δ-phase](image)

3.3 Conclusion

1) Zr\((\text{Cr,Fe})_x\) Laves phases as the dominant precipitates were found either in the grain or the grain boundary with a variable types of shape such as spherical, ellipsoid or irregular shape, which belong to C14 or C15 type structures. The Fe/Cr ratio in C14 type Zr-Fe-Cr phase is larger than that in C15 type, which proved that the formation of Zr-Fe-Cr phase was not determined by atoms redistribution solely. As for the C14 structure, the orientation relationship was \((11\overline{2}0)_{\text{spp}}//(0002)_{\alpha-\text{Zr}}\), \([2\overline{2}01]_{\text{spp}}//[(01\overline{1}0)_{\alpha-\text{Zr}}. The orientation relationship of C15 structure was \((202)_{\text{spp}}//(10\overline{1}1)_{\alpha-\text{Zr}}, [101]_{\text{spp}}// [1\overline{2}1\overline{0}]_{\alpha-\text{Zr}}.

2) High-resolution electron microscopy was used to study hydrides formation in a typical Zircaloy-4 material, due to hydrogen picking up near the surface region during water quenching the forged feeding billets. The stable δ-ZrH\(x\) hydride is of the face-centered cubic structure and crystallographically related to the α-Zr solid solution with 24 equivalent variants, typically
summarized as: \( \langle 1210 \rangle_\alpha \parallel \langle 101 \rangle_\delta \) and \( (0001)_\alpha \parallel (111)_\delta \). It is also interesting to note that a plane pairs of \( [242]_\delta \parallel [1015]_\alpha \) exist at the edge of a hydride plate when strain/stress is involved. Most of the \( \delta \)-hydrides assume plate morphology and align on the \( (0001)_\alpha \) habit plane of the \( \alpha \)-Zr solid solution phase. It was interesting to observe the twinning in \( \delta \)-hydrides. The twinning plane was \( (111)_\delta \). The hydrides became more blocky in shape, with twin boundaries formed through complete consumption of the matrix phase between separately nucleated precipitates.
Chapter 4 Microstructural Characteristics of β Precipitates in Zr-1Nb Alloy

4.1 The Relationship between the micro-hardness and annealing time in the E110 samples

The monotectoid temperature is 620°C for E110 alloys. To determine the annealing time, the relationship between the micro-hardness and the time was studied. Two different time, 600 and 700 °C, was selected. JSK 11-3 Maffle furnace is used for the heating treatment. Generally the samples annealed at 600 °C had higher micro-hardness than that at 700 °C. In the first hour the micro-hardness of both samples increase. After 2 hours’ annealing at 600 °C or 3 hours annealing at 700 °C, the micro-hardness for the annealed samples became constant. Thus the samples annealed at 600 °C for 3 h (600 °C/3h-AC) and at 700 °C for 3 h (700 °C/3h-AC) were chosen for detailed TEM study. Fig. 4-1 shows the changes in the micro-hardness with annealing time at 600 °C and 700 °C respectively.

![Micro-hardness with annealing times at 600 °C and 700 °C, respectively](image_url)

Fig. 4-1 Micro-hardness with annealing times at 600 °C and 700 °C, respectively

4.2 Characterization of the precipitates at 600 °C/3h-AC and 700 °C/3h-AC in E110 samples

Fig. 4-2 shows the typical bright-field TEM microstructure of the 600 °C/3h-AC sample. The spherical precipitates were uniformly distributed within the equiaxed α grains. The diameter was 30-60 nm and the volume fraction was ~2.5 %, as shown in Fig. 4-2( a ) and 4-2( b ). The selected area electron diffraction (SAED) pattern revealed that the precipitates were β phase with body-centered cubic crystal structure, as shown in Fig. 4-2( c ). EDS analysis under TEM indicated that the precipitates contain ~68 wt.% Nb.
Fig. 4-2 (a and b) Bright-field TEM images of precipitates in Zr-1Nb alloy after annealing at 600 °C for 3h followed by air cooling, showing spherical precipitates; (c) the selected area electron diffraction (SAED) pattern of the precipitate along the [001]β zone axis.

Fig. 4-3 (a and b) Bright-field TEM images of precipitates in Zr-1Nb alloy after annealing at 700 °C for 3h followed by air cooling, showing stick-like precipitates; (c) the selected area electron diffraction (SAED) pattern of the precipitate along the [111]β zone axis and the corresponding SAED pattern of α-Zr matrix.

Fig.4-3 shows the typical bright-field TEM microstructure of the 700 °C/3h-AC sample. The morphologies of the precipitates were obviously different from that in the 600 °C/3h-AC sample. The precipitates had a stick-shaped morphology ~100 nm in diameter and ~300 nm in length. The volume fraction was ~9.8 %, as shown in Fig. 4-3 ( a ) and 4-3 ( b ). Selected area electron diffraction (SAED) revealed that the precipitates were also β phase with body-centered cubic crystal structure, as shown in Fig. 4-3 ( c ). The TEM-EDS analysis indicated that the precipitates contained ~10 wt.% Nb. In this case, through the combination of bright- and dark-field imaging with the consideration of magnetic rotation, it was noticed that the straight boundary of the needles corresponded to the (101) plane of the β-Zr. When a dark-field image was taken using
the (101)_β diffraction spot from a β-Zr precipitate, almost all precipitates containing the same axial direction were highlighted in the dark field (DF) image, which suggested that these precipitates maintained an orientation relationship with the α-Zr matrix.

4.3 Discussion
Comparing the characteristics of precipitates in the 600 °C/3 h-AC and 700 °C/3 h-AC samples, one noted that when the annealing temperature changes from 600 °C (below monotectoid temperature) to 700 °C (above monotectoid temperature), the volume fraction increased from ~2.5% to ~9.8%, while the Nb content decreased from ~68 wt.% to ~10 wt.%. At the same time, the size increased and the morphology changed from spherical to stick-shaped. The changing trends in volume fraction and composition are consistent with the lever rule of the Zr-Nb binary phase diagram. The Zr-Nb phase diagram shows that at 600 °C α and β_2 (Nb-enriched) phases exist. The Nb content of β_2 (Nb-enriched) phase is ~93 wt.% and the volume fraction is ~0.2%. At 700 °C α and β_1 (Nb-impoverished) phases exist. The Nb content of β_1 (Nb-impoverished) phase is ~11 wt.% and the volume fraction is ~3.7%. The distinctions between the experimental and theoretical data may result from several factors. On the one hand, the impurities, such as Fe, O, N, H, etc., will change the phase boundaries in Zr-Nb binary phase diagram. On the other hand, the annealing times were not long enough to reach full equilibrium. Because the compositions of α, β_1 (Nb-impoverished) and β_2 (Nb-enriched) phases are substantially different, the growth rate of β precipitates will be mainly controlled by the diffusion coefficients of Nb and Zr atoms.

Fig. 4-4 HRTEM image of the boundary between α-Zr matrix and β precipitate in Zr-1Nb alloy with annealing of 700°C for 3 h/AC. a) and b) display the crystal orientation of α-Zr matrix and β
precipitate, respectively.

Fig. 4-5 A diagram illustrating the boundaries of a precipitate in Zr-1Nb alloy with annealing of 700°C for 3 h/AC

Fig. 4-4 shows the HRTEM image of the boundary between α-Zr matrix and β precipitate in Zr-1Nb alloy with annealing of 700°C for 3h/AC. The outline of the stick-like β-precipitates is composed of straight and curved interfaces from the longitudinal section point of view. As showed in Fig.4-4, the orientation relationship between α and stick shaped β phase precipitate for a straight interface is (0001)α//(110)β, and the [111] zone axis of the β phase precipitate is parallel to the [1120] zone axis of α-Zr matrix, so the orientation relationship between α-matrix and β phase precipitate satisfies Burgers orientation relationship, i.e., (1010)α//(112)β for the broad face, (0001)α//(110)β for the side facet and (1120)α//(111)β for the edge, just like the orientation relationship of phase transformation from β-matrix to α lath. Therefore the broad faces and side facets together form the straight interface perpendicular to the S-axis, and the edges form the curved one perpendicular to the L-axis, as shown in Fig.4-5.
The distinction in the morphologies of β phase precipitates indicates that at 600 °C the growth rate of β₂ (Nb-enriched) is isotropic while at 700 °C the growth rate of β₁ (Nb-impoverished) is anisotropic. A lot of studies have revealed that the migrating rate of the phase interface is intensely influenced by the interfacial structure. The more disordered the arrangement of atoms in the interface is, the faster migrating rate of the phase interface is. The extent of disorder can be reflected by the lattice misfit.

As the increase of Nb content of β phase, the lattice parameter of β phase gets larger. We calculate the lattice misfits of different interfaces at 600 °C and 700 °C. For β₂ (Nb-enriched) with Nb content of 68 wt.% and Zr content of the remaining; and α phases the lattice misfits of broad face, side facet and edge are ~7.7%, ~6.4% and ~32.1%, respectively at 600 °C.

Process on the lattice misfits can be listed as follows (taking the interface of α-Zr / β-Nb(Zr-60Nb) for example):

Step 1: Lattice parameters of α-Zr / β-Nb(T=700°C)
α-Zr:a=3.249 (Angstrom, Å), c=5.205Å; β-Nb:a = 3.4348 Å

Step 2: Equation of misfit[71]

\[ \delta_{(hkl)} = \frac{1}{3} \sum_{i=1}^{3} \left| \frac{(d_{uvw})^i \cos \theta - d_{uvw}^i}{d_{uvw}^i} \right| \times 100 \]

Tips: 1. Reason of choosing this model: α/β interface is composed of the stage of fine facet with low Miller indices, which is close to this model.

Step 3: the process (121)β/(1-10)α and [-101]β/[001]α.
Table 4-1: Data for [1-11]₀/[110]₀ and [0-12]₀/[112]₀

<table>
<thead>
<tr>
<th>Face</th>
<th>α-Zr</th>
<th>β-Nb</th>
<th>Misfit</th>
<th>Planar misfit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Broad face</td>
<td>[001]</td>
<td>[-101]</td>
<td>6.91</td>
<td>7.7%</td>
</tr>
<tr>
<td></td>
<td>[110]</td>
<td>[1-11]</td>
<td>8.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[112]</td>
<td>[0-12]</td>
<td>7.441761</td>
<td></td>
</tr>
<tr>
<td>Side facet</td>
<td>[010]</td>
<td>[1-11]</td>
<td>6.91</td>
<td>6.4%</td>
</tr>
<tr>
<td></td>
<td>[-1-10]</td>
<td>[-1-1-1]</td>
<td>8.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[-2-10]</td>
<td>[-1-3-1]</td>
<td>7.441761</td>
<td></td>
</tr>
<tr>
<td>Edge facet</td>
<td>[10-10]</td>
<td>[1-12]</td>
<td>39.69</td>
<td>32.1%</td>
</tr>
<tr>
<td></td>
<td>[001]</td>
<td>[-101]</td>
<td>6.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[323]</td>
<td>[101]</td>
<td>49.5612</td>
<td></td>
</tr>
</tbody>
</table>

While for β₁ (Nb-impoverished) with Nb content of 10 wt.% and Zr content of the remaining; and α phases the lattice misfits of broad face, side facet and edge are ~3.6%, ~4.8% and ~33.3%, respectively at 700 °C. The results indicate that the arrangements of atoms in the edges for both β₁ (Nb-impoverished) and β₂ (Nb-enriched) are always intensely disordered, while the arrangements of atoms in the broad face and side facet for β₂ (Nb-enriched) are more disordered than that for β₁ (Nb-impoverished). The misfit dislocation observation of straight and curved interfaces also supports the calculated results as shown in Fig. 4-6, which is from the inverse FFT in the curved and straight interface areas of the stick-shaped particle in the 700 °C/3 h-AC conditions in the Fig.4-4. c and d, respectively. It is well known that when the lattice misfit is larger than 5% the coherent interfacial structure will be destroyed. This means that as the Nb content of β phase increasing, the lattice misfits on broad face and side facet increase and their interfacial structures change from coherent (obtained at 700 °C) into incoherent (obtained at 600 °C), and the edge is always
incoherent. Therefore, the edge interface has a higher movement rate than the broad face and side facet at 700 ℃ and stick-shaped β particle forms. While the three interfaces have a comparable movement rate at 600 ℃ and spherical β particle forms.

4.4 Conclusion

1) After annealing at 600 °C for 3 hours the precipitate in Zr-1Nb alloy is spherical β phase with the diameter of 30-60 nm, volume fraction of ~2.5 % and Nb content of ~68 wt.%.

2) After annealing at 700 °C for 3 hours the precipitate in Zr-1Nb alloy is stick-shaped β phase with ~100 nm in diameter and ~300 nm in length, volume fraction of ~9.8 % and Nb content ~10 wt.%.

3) The changing trends in volume fraction and composition are accordant to the lever rule in Zr-Nb binary phase diagram.

4) The distinction in the morphologies of β phases results from the change in the interfacial structure.
Chapter 5 Formation and fine-structures of nano-precipitates in ZIRLO

The equiaxed morphology of α-Zr grains indicates complete re-crystallization, and nano-precipitates are shown to distribute largely evenly across the gains of the matrix phase. The precipitates can be classified into two size groups, the larger second phase particle1 (SPP1) above 60 nm (mostly 60-80 nm) in size and ultrafine nano-crystals below 30 nm in size for second phase particle 2 (SPP2). Fig. 5-1 shows bright field (BF) image typical of the microstructure of the ZIRLO alloy. EDS analysis showed that SPP1 contained similar atomic levels of Zr, Fe and Nb without evidence of Sn, and is thus a ternary Zr-Fe-Nb phase. While the size of the SPP2 are below the limit of the spatial resolution for EDS, EDS quantification with 1 nm electron probe centered on such ultrafine precipitates did indicate that even under the influence of the matrix composition, they were significantly richer in Nb than the former. This offers strong indication that the two kinds of precipitates are of different type of phases. This is consistent with the work of Toffolon-Masclet[59], as the Zr-rich ZIRLO alloy is located within the three phase region (α-Zr + C14 + β-Nb) on the isothermal section at 550 °C of the Zr rich corner of the Zr-Nb-Fe phase diagram, as show in Fig. 5-2. This leads to Zr being the major phase of matrix and the other two phases being minor precipitates formed through precipitation from the Zr solid solution.

![Fig. 5-1 bright field (BF) image typical of the microstructure of the ZIRLO alloy](image)
5.1 β-Nb precipitate

Ultrafine spherical precipitates were observed within the grains of the matrix α-Zr phase (Fig. 5-3(a)). EDS result shows that it contained more than 44 at.% Nb, considering the influence of the matrix phase composition. The solubility limit of Nb in β-Zr is about 36 at.%, which is lower than the tested Nb content in the spherical phase, indicating that the spherical phase should be β-Nb.[60].

Due to the low diffusion coefficient and low content of Nb in α-Zr, most Nb would be kept in the matrix phase to form supersaturated α-Zr, during quenching the alloy from the forging temperature in the β-Zr phase field. The precipitates including the ultrafine β-Nb particles were formed via a solid state precipitation process during thermomechanical processing and annealing at 600 °C when the alloy was in the three-phase field (α-Zr + C14 + β-Nb).
HRTEM study was carried out to study the refined crystallographic characteristics between the precipitates and the matrix phase. Fig. 5-3(b) shows a HREM image corresponding to the [0001] zone axis of the matrix phase, revealing excellent coherency at the interface, owing to small lattice mismatches between the hcp and bcc structures involved. The corresponding orientation relationship was \([0001]_\alpha/[110]_\beta\) and \((1\bar{1}00)_\alpha/(1\bar{1}1)_\beta\), which satisfies the so-called Burgers orientation relationship between hcp and bcc solid solution phases. Such typical Burgers orientation relationship is generic for alloys based on the group IV transition metals, such that it also holds in Ti alloys\(^{[22]}\).

5.2 The Ternary Zr-Fe-Nb Precipitate

In selected area electron diffraction (SAED) showed that the larger ternary SPP1 particles were of the hexagonal C14 Laves phase structure, consistent with the alloy phase diagrams near the 600 °C thermomechanical processing temperature (Fig. 5-2). Fig. 5-4 shows the orientation relationship between the SPP1 C14 compound and the matrix, with a SAED pattern from the region of Fig. 5-4(a) containing two sets of low-index diffraction patterns from the matrix and a spherical SPP1 precipitate, respectively. The diffraction pattern from the matrix is at the \(\alpha\)-Zr [0001] zone axis, and that from the precipitate corresponds to the \([0001]\) zone axis of the C14 phase. The orientation relationship is therefore near: \((\overline{2}1\overline{1}0)_{\text{app}}//(10\overline{1}0)_{\alpha\text{-Zr}}, \ [0001]_{\alpha\text{-Zr}}/[\overline{0}1\overline{1}0]_{\text{app}}\). Fig. 5-4(c) shows the corresponding atomic illustration for such an orientation relationship. Using the \(\alpha\)-Zr
SAED pattern as an in situ reference, the lattice parameters of the precipitate were calculated to be $a = 0.559$ nm, $c = 0.842$ nm. The orientation relationship is only approximate, based on the evidence that the precipitate was somewhat off the corresponding zone axis. This could be attributed to geometrical relaxation in reducing interface stress.

![Fig. 5-4](image)

Fig. 5-4 the orientation relationship between the SPP1 C14 compound and the matrix

There was evidence for the existence of stacking faults in the C14 compounds, shown in Fig. 5-5(a), which reveals parallel lines corresponding to the traces of the habit planes for the faults. Corresponding diffraction pattern, Fig. 5-5(b), shows streaking in some spots along the $\{10\bar{1}0\}$ vector, owing to the presence of stacking faults in the $\{10\bar{1}0\}$ plane. The stacking fault was found before[72,73], but the researchers did not specify the stacking fault plane. Usually, the formation of stacking fault is related with the moving of dislocation. The dislocations in alloys generally start at the most close-packed crystal plane. In a hexagonal phase with the $c/a$ ratio being the ideal 1.633 value, the close-packed plane is $\{0001\}$. If the phase is not close packed, the $\{0001\}$ plane may not be the most close-packed plane any more. Dislocations can then move preferentially on the prism $\{10\bar{1}0\}$ plane when it is the most closely packed. Even for the $\alpha$-Zr phase, its $c/a$ ratio is 1.593. Interestingly, even for pure $\alpha$-Zr, the spacing of the prism plane $\{\bar{1}0\bar{1}0\}$ is 2.798 Å, while the spacing of its basal plane $\{0002\}$ is only 2.573 Å. So the prism plane for $\alpha$-Zr is most closely packed in the $\alpha$-Zr[74,75]. On the other hand, the $c/a$ ratio of C14 Zr-Fe-Nb phase is only about 1.5, making the prism planes the most closely packed. The orientation relationship between the C14 Zr-Fe-Nb phase and $\alpha$-Zr is, as noted above, $(\bar{2}1\bar{1}0)_{\text{spp}}//((10\bar{1}0)_{\alpha-zr}. Presumably, dislocations could
move from a matrix (10\overline{1}0) plane to a SPPs (\overline{2}1\overline{1}0) plane. However, because the (\overline{2}1\overline{1}0) plane is not the close-packed plane, dislocations tend to transfer to the {10\overline{1}0} planes of the Zr-Fe-Nb phase. The dislocations can then cross slip between intersecting {10\overline{1}0} planes, in a way similar to that between the closely packed {11\overline{1}} planes in a face centered cubic phase, thus leading to dissociation of dislocations into partials with stacking fault in between. The trace of the habit planes will then exhibit as parallel lines such as observed in Fig. 5-5(a).

![Fig. 5-5 (a) BF image showing a Zr-Fe-Nb precipitate exhibiting contrast of parallel lines; (b) Corresponding diffraction pattern showing streaking is strong spots from the phase](image)

EDS was used to quantify the concentration of Nb and Fe in the Zr-Fe-Nb SPPs with different sizes (Fig. 5-6). Because SPPs are very small and embedded into the matrix, the characteristic X-rays generated from the matrix will also contribute to the results, with the high concentration of Zr in the matrix leading to most serious error in the analysis. We therefore only quantified the ratio of Fe/Nb for the C14 phase, with the consideration that the rather low contents of Nb and Fe in the matrix would not lead to evident errors. A second phase with different sizes could represent different growth stages. The Fe/Nb ratio of Zr-Fe-Nb phase varied with the increase of particle size (Fig. 5-7). The bigger the particle size, the smaller the ratio of Fe/Nb became. When the particle size increased beyond 100nm, the ratio of Fe/Nb is close to what Barberis et al. reported[76], meaning that the SPPs were then largely in the stable state. This phenomenon confirmed that during the growth of Zr-Fe-Nb phase, elemental evolution was controlled by solid state diffusion. Due to the fact that the order of Fe diffusion coefficient is faster than that of Nb in α-Zr (D_{Nb}=10\times10^{-21}~10\times10^{-25} \text{ m}^2/\text{s}, D_{Fe}=10\times10^{-10} \text{ m}^2/\text{s})[117], the surrounding Fe atoms would diffuse
into the Zr-Fe-Nb nucleus prior to Nb. This led to higher Fe content than Nb in the initial growth state. Fig. 5-7 shows the relationship between Fe/Nb ratio and particle size from data of this work and published data from the literatures 77-79. Although different manufacturing processes were adopted, all data showed the same trend in that the Fe/Nb ratio decreases with increasing particle size in all samples.

Fig. 5-6: The contents of Nb and Fe in the Zr-Fe-Nb SPPs with different sizes.

Fig. 5-7: Fe/Nb ratio against particle size of C14 precipitates.
As a class of phase structures due to geometrical packing of atoms of rather different sizes, the atomic configurations of Laves phases are dependent upon the relative atomic radii of the constituents. The atomic radii for Zr, Fe and Nb are $R_{Zr} = 0.216$ nm, $R_{Nb} = 0.208$ nm, and $R_{Fe} = 0.172$ nm, correspondingly. In the AB$_2$ stoichiometry of the C14 Laves phase, Zr occupies the 4f site (0.33,0.67,0.062) due to its large atomic radius, and Fe as the smaller atom occupies the 2a (0.0.0) and 6h sites (0.83,0.66,0.25). In the Zr-Fe-Nb system, it has been debatable however about the position of Nb atoms in the C14 Laves phase. In the late 1960s, Kanematsu$^{[80]}$, Tanaka$^{[81]}$, Alfieri$^{[82]}$, Petkov$^{[83]}$ proposed that laves phase (C14, C15, C36) were of the atomic formula of $(Zr_{1-x}Nb_x)Fe_2$, with the Zr site being partially occupied by Nb. On the basis of the valence electron concentration, they reported a cubic C15-type structure for $x < 0.35$ and a hexagonal C14-type structure for $x > 0.5$. However, recent experimental work by Ramos et al. showed that Nb mainly substitute Fe in the 2a, 6h site in the C14 laves phase instead$^{[61]}$. Ramos et al. obtained different compositions of the C14 compound by adjusting the contents of alloying constituents Fe and Nb. The Zr content of the compound phase was found to be largely constant and the content of Fe and Nb varies inversely. This suggests that Nb preferred to occupy the positions of Fe atoms instead, which is consistent with the calculated phase diagram by Toffolon-Masclet et al$^{[59]}$.

Fig 5-8 C14 Laves Structure

An effort was made in this work to test the latest phase equilibrium data$^{[60,62]}$, with the preparation
of an alloy close to the C14 composition in the (α-Zr + C14 + β-Nb) region at 550 °C. Toffolon-Masclet[83] observed that at 550 °C in the three-phase region (α-Zr + C14 + β-Nb) for the ternary Zr-Fe-Nb system, the atomic composition was nearly constant at 33.5Zr-38.5Nb-28Fe (at.%). As this three-phase region is of particular interest to the ZIRLO alloy, here we prepared the alloy with the nominal composition of the melted alloy being 34Zr-38Nb-28Fe (at.%), on the tip of the C14 ternary phase (marked as a black dot on the isothermal section of Zr-Nb-Fe ternary system at 900 °C[60], Fig. 5-9).

Fig. 5-9 Zr-Nb-Fe ternary isothermal section calculated at 900 °C[59]

Fig. 5-10 shows three diffraction patterns from different areas. It was found that the alloy only consisted of the C14 type Zr-Fe-Nb phase with composition being close to the nominal composition, indicating the great accuracy in the latest phase diagram. Fig. 5-11 shows an interface between two Zr-Fe-Nb grains. From the HRTEM of Fig. 5-11(b,d) it can be seen that both grains (A and B) had the hexagonal C14 structure and the zone axis are C14-[0110], C14-[0001], respectively. Fig. 5-11(c) clearly shows the two grains are coherently related, and the orientation relationship between two particles is A (0002)/B (1010); A [0110]/B[0001]. It can be determined that d_A(0002)= d_B(1010). However, in the C14 structure, the spacing of (0002) planes is slightly smaller than that of {1010} planes. Thus, we concluded that the spacing of (0002) plane in grain-A (0.429 nm) is larger than that in grain-B (0.403 nm), and the corresponding lattice constant
of grain-A is larger than grain-B. From the perspective of components, grain-A has more Nb but less Fe compared with grain-B, while the content of Zr is largely unchanged in both grains. Taking into account the atomic radius of Fe, Nb, Zr (R_{Zr} = 0.216 \text{ nm}, R_{Nb} = 0.208 \text{ nm}, R_{Fe} = 0.172 \text{ nm}), we can conclude that the chemical composition of C14 type Zr-Fe-Nb phase should be Zr(Fe,Nb)\textsubscript{2}, which means that the lattice constant will increase when Nb atoms replacing Fe. Thus it is reasonable to conclude that the formation of Zr-Fe-Nb precipitates can be attributed to the substitution of Fe at 2a, 6h site by Nb in C14 laves phase.

![Fig. 5-10 Composition and structure of C14 type Zr-Fe-Nb alloy](image1.png)

![Fig.5-11 Interface between two C14 type Zr-Fe-Nb phases and corresponding HRTEM image](image2.png)
The fact that Nb and Fe contents could be swopped between two neighboring grains, while maintaining largely a constant Zr content, offers strong evidence that Nb and Fe can be readily mixed on the B sublattice sites of the AB$_2$ stoichiometry of the C14 phase. As this phase structure does not exist as a stable phase in either the Zr-Fe or the Zr-Nb system, their coexistence is essential to stabilize such a structure in the Zr-Fe-Nb system. It is reasonable that the two later transition metals (Nb and Fe), atoms replace the same B sublattice sites of the C14 phase, as both play a similar role in stabilizing the same crystal structure of the β phase and thus are of rather different electronic nature from that of the group IV element Zr.

5.3 Conclusion

The Zr alloy with the typical ZIRLO composition lies in a three-phase equilibrium region containing the ground state phases of α-Zr, β-Nb and a ternary C14 Laves phase, which does not exist as an equilibrium phase in the constituent binary systems.

In the current thermomechanically processed material, the β-Nb and a ternary C14 Laves phases presented in the α-Zr matrix as nano-precipitates. Ultrafine spherical β-Nb particles about 30 nm in size were found to precipitate within the α-Zr grains, with the α/β interface being crystallographically coherent, with a Brugers orientation relationship between the two phases. Intermetallic nano-particles with the C14 Laves-phase structure were found to be the coarser precipitates typically larger than 60 nm in sizes, with the Zr(Fe,Nb)$_2$ stoichiometric formula wherein Fe and Nb are mixed on the second sublattice sites. Stacking faults were also observed in the ternary Laves phase. The orientation relationship between the Laves phase and the matrix was close to (1010)$_{α}$∥(2110)$_{C14}$ and [0001]$_{α}$∥[0110]$_{C14}$. The significant difference in the diffusion coefficients of Fe and Nb in the α-Zr solid solution led to delayed enrichment of Nb in the C14 phase, with the Nb/Fe ratio increasing during the coarsening of the Laves phase.
Chapter 6 Summary

The composition, structure, defects and orientation relationship of the precipitates in Zr-4, E110 and Zirlo alloys were researched in this work. The results about the precipitates are significant to improve the in-reactor performance of Zirconium alloys and develop new higher-burnup zirconium alloys. The main innovation points are as follows:

1) The formation of \{0001\} stacking faults in C14 structure of Zr-Fe-Cr phase in Zr-4 alloy was observed and analyzed at the first time. The orientation relationships of C14 and C15 phases with \(\alpha\)-Zr were identified respectively.

2) \(\delta\)-ZrHx hydride in Zr-4 alloy are crystallographically related to the \(\alpha\)-Zr solid solution with 24 equivalent variants. The twinning with (1\(1\overline{1}\))\(\delta\) plane in \(\delta\)-hydrides was observed.

3) The characterizations of two types of \(\beta\) precipitates in E110 alloy were analyzed. The orientation relationship between \(\alpha\) and \(\beta\) phases was analyzed, and the mechanization about the formation \(\beta\) phases was explained.

4) The orientation relationship between the Zr(Fe,Nb)\(_2\) Laves phase in Zirlo alloy and the matrix was observed and analyzed. Stacking faults were also observed in the ternary Laves phase, together with dislocations presenting on prism planes of the matrix solid solution.
Chapter 7 Future work

Based on the research, the types and characteristics of precipitates in typically commercial zirconium alloys were obtained. It is only the first step for the R&D of new zirconium alloys and process improvement. In the future, the relationship between the different precipitates and the properties (including the corrosion resistant, mechanics and hydrogen pick-up) will be investigated. The processes will be optimized to control the types and morphologies of the precipitates or the alloy elements will be selected for R&D of new zirconium alloys based on the results. The precipitates, especially for containing Fe or Cr elements, are brittle in initially experiments, so it is difficult to prepare the pure alloy with the same concentration. The following work is to select the materials with same brand and same concentration, and to obtain the different precipitates in terms of optimizing zirconium alloy manufacturing process. The properties will be analyzed and compared to deduce the effect of the precipitates. Verification will be done to confirm the relationship between the properties and the precipitates, which will be applied for process optimization and R&D of new alloys.
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[70] https://en.wikipedia.org/wiki/EBSD(access December 2016)


Appendix  Published Works

1. THE FORMATION AND STACKING FAULTS OF Fe AND Cr CONTAINING LAVES PHASE IN Zr-4 ALLOY
2. FORMATION OF NANOCRYSTALLINE δ-ZrHx IN ZIRCOLOGY-4 ORIENTATION RELATIONSHIP AND TWINNING
3. MICROSTRUCTURAL CHARACTERISTICS OF β PRECIPITATES IN Zr-1NB ALLOY
4. FORMATION AND FINE-STRUCTURES OF FINE-STRUCTURE OF NANO-PRECIPITATES IN ZIRLO
The formation and stacking faults of Fe and Cr containing Laves phase in Zr-4 alloy
The formation and stacking faults of Fe and Cr containing Laves phase in Zircaloy-4 alloy

Guoqin Cao\textsuperscript{a,b}, Yifan Yun\textsuperscript{a,b}, Lei Yang\textsuperscript{a,b}, Gaithuan Yuan\textsuperscript{1}, Qiang Yue\textsuperscript{c}, Guosheng Shao\textsuperscript{a}\textsuperscript{b}\textsuperscript{c}, Junhua Hu\textsuperscript{a,b}\textsuperscript{c}\textsuperscript{d}

\textsuperscript{a}School of Material Science and Engineering, Zhejiang University, Hangzhou 310027, China
\textsuperscript{b}State Center for International Cooperation on Designing Low-carbon & Environmental Materials, Zhejiang University, 100 Xuefu Avenue, Hangzhou 310027, China
\textsuperscript{c}State Nuclear Indus Zirconium Industry Co, Ltd (SNZ), No. 721, Hangzhou 310023, China

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\textbf{Abstract}

The crystallographic characterization and defect structure of precipitates plays a key role in the properties of Zr alloys. The precipitates in Zircaloy-4 alloy are studied in this work. The Fe–Fe–Cr particles are identified as the dominant precipitates at room temperature with C14 or C15 type Laves structure. The Fe/Cr ratio of C15 type Fe–Fe–Cr phase is slightly lower than that of C14 type phase. The (0001) stacking fault in C14 phase is observed and analyzed for the first time. Some new orientation relationships of C14 and C15 phases with α-Zr are identified.

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\textbf{1. Introduction}

Zr alloys are currently heavily used in nuclear reactor as cladding materials. The primary advantages associated with Zr for fuel cladding are very low absorption of neutrons, good fabricability and strength. The cladding materials within a reactor core must tolerate the exposure to coolant (high temperature water, liquid metals, gas, or liquid salts), intense field of high energy neutrons and gradients in temperature. Degradation of materials in this environment can lead to reduced performance or even sudden failure [1,2].

Thus efforts should be taken to improve the properties of Zr-based alloys at high burn-up environment. This can be achieved through the introduction of alloying elements with low absorption cross-section of thermal neutrons to induce solution and/or precipitate strengthening while maintaining good corrosion resistance [3]. Only a limited number of alloying elements are suitable for cladding Zr alloys, with their acceptable contents being fairly low. Due to the limited solubility of alloying elements in α-Zr, most of them tend to precipitate as second phase particles (SPPs), which strongly influence the properties of Zr alloys [4,5].

The optimized corrosion performance of Zr alloys was achieved when the fine SPPs were uniformly precipitated in α-Zr matrix [6,7]. Meanwhile, the weak anti-radiation ability of precipitates with planar defect makes them prone to amorphization and elemental migration under neutron irradiation, which would change chemical compositions of the matrix as well as the type of precipitates, thereby lowering the corrosion resistance of Zr alloys [8,9]. Thus, it is significant to further analyze the properties and characteristics of second phases, which can provide a material basis for improving the performance of Zr alloys during reactor operation. This work is focused on the precipitates in a thermomechanically processed Zircaloy-4 Alloy, with particular interest in orientation relationship, composition distribution and SPPs structure.

\textbf{2. Experimental methods}

The ingots of alloy with the typical Zircaloy-4 composition (Zr – 1.2 wt% Sn – 0.2 wt% Fe – 0.1 wt% Cr [10]) were prepared by vacuum arc melting, using self-consuming electrode. Each ingot was forged at 1070°C into feeding blocks, then water-quenched down to room temperature and annealed in vacuum at 630°C for 1.5 h before being hot-rolled at 700°C into sheets of 2 mm in thickness. The hot-rolled sheets were finally annealed at 650°C for 1.5 h to achieve complete re-crystallization.

This fails for transmission electron microscopy (TEM) analysis were mechanically polished to about 60 μm in thickness, and then
the central region of each disc was dimple-polished down to about 20 μm in thickness. Finally, the foils were polished by ion milling at 4 keV. To make reliable results, dozens of Zr-Fe-Cr particles from more than 10 grains in Zircaloy-4 alloy have been analyzed using TEM (JEM 2010FPE microscope) equipped with an energy dispersive X-ray detector.

3. Results and discussion

The precipitates of Zircaloy-4 alloy are mainly Zr-Fe-Cr phase, the structure of which is similar to ZrCr2 Laves phase, and the stoichiometric formula is Zr(Fe, Cr)2 with crystalline structure of either C14 (HCP) or C15 type (FCC) [11,12]. Both C14 and C15 type Laves phases were found in this research. Fig. 1 shows the bright field (BF) image of two typical particles in Zircaloy-4 alloy. The energy dispersive X-ray spectroscopy (EDS) results confirmed that they were Zr-Fe-Cr particles, though the morphology were quite different. The selected area electron diffraction (SAED) patterns of each particles have presented accordingly. In Fig. 1a the diffraction pattern can be indexed as C14 type phase. The C14 and C36 type phase both belong to Laves phase as hexagonal structure. Only C14 type phase matches the SAED patterns in this work. The orientation relationship (OR) with matrix in Fig. 1a was characterized as (1120)_{spp}/(0002)_{zr}, (2201)_{spp}/(01T0)_{zr}. On this basis, the atomic configuration of the mentioned OR was reconstructed and shown in Fig. 1c. The lattice mismatch is as small as 0.020 along the [2201] vector. The particle in Fig. 1b was indexed as C15 type phase. The typical OR that derived from the SAED pattern B is

\[ (11\overline{2}0)_{spp}/(0002)_{zr}, (22\overline{0}1)_{spp}/(01\overline{1}0)_{zr}. \]

The atomic configuration was illustrated with the lattice mismatch as small as 0.0055 along [1011] direction.

According to the literature report, at room temperature, the Zr-[FeCr]2 particle is hexagonal structure (C14), while this particle is identified as FCC structure (C15) at high temperature [11,12]. Elliot reported that the decisive factor for the formation of C14 phase was the content of Cr, since Cr can stabilize C14 hexagonal structure because of its much higher valence electrons/atomic ratio [13].

In this work, dozens of Zr-Fe-Cr particles with size from 100 nm to 500 nm were analyzed. SAED patterns proved the formation of two kinds of structure, namely FCC structure and hexagonal structure. The composition and structure of Zr-Fe-Cr phases was summarized and shown in Fig. 2. Because SPBs are very small and embedded into matrix, the characteristic X-rays generated by Zr that belong to matrix may also be detected. Taking into consideration the influence of matrix we only count Fe/Cr atomic ratio. Although the morphology and size varied very much, Fe/Cr ratio varied from 2 to 3. It is interesting to note that C15 type phase contains more Cr than C14 type phase. This may be related to the kinetic factor that the diffusion coefficient of Fe in Zr-2Cr matrix is faster than Cr [14]. Thus the formation of C15 and C14 type phase is not determined by atoms distribution solely. According to Zr-Cr phase diagram, the ZrCr2 phase is stable with C15 type structure at low temperature. Yuan also reported that C14 type Zr(Fe,Cr)2 retained at room temperature because the transformation to C15 structure is very sluggish [13]. Fig. 3 is a set of bright field image and the corresponding SAED pattern of a cuboidal-like phase. The SAED pattern of the precipitate can be indexed as C14-\( \gamma_1\)~T20 zone axis. The corresponding OR with \( \gamma_2\)-Zr is nearly (1210)_{spp}/(11\overline{7}8)_{zr} and (0001)_{spp}/(1\overline{1}02)_{zr}. There are optimal lattice matching on this relationship, which may lower the strain energy of nucleation and promote the formation of cuboidal-like precipitation in Zr matrix [15].

The diffraction pattern of the precipitate shows streaking along the [0001] vector, owing to the presence of stacking faults in the (0001) plane. The high magnification image in Fig. 3c exhibited contrast stripe, which provided evidence for the presence of long period stacking variants in the C14 structure. From SAED (Fig. 3b) we can see the 21T long-period structures existed as Meng reported [16]. Long period structure in Laves phase is mainly affected by the ordering of component and stacking faults [18]. The orderly occupation of solutes on C14 lattice probably originated from the sufficient migration since the stacking faults in precipitates provide sufficient space for the solute atoms to migrate.

![Fig. 1. (a) The bright field image of C14 Laves type phase (b) the bright field image of C15 Laves type phase A and B show the corresponding SAED pattern, respectively. The insets in (b) show the mappings of Cr and Fe. (c) The schematic diagrams of orientation relationship between C14 phase and zr-2.](image)

![Fig. 2. The Fe/Cr atomic ratio of Zr-Fe-Cr SPBs.](image)
Fig. 3. (a) Bright field image of C14-(Ce,C) phase; (b) the corresponding SEM pattern; (c) high magnification image of C14-(Ce,C) phase.

4. Conclusion

Zr(Cr,Fe)$_2$ Laves phases as the dominant precipitates in Zircaloy-4 alloy were found with C14 or C15 type structure. The Fe/Cr ratio in C14 type Zr-Fe-Cr phase is larger than that in C15 type, which proved that the formation of Zr-Fe-Cr phase was not determined by atoms redistribution solely. As for the C14 structure, the orientation relationship was $\{1\overline{1}20\}_{\text{YZ}}//\{0002\}_{\text{Zr}}\$, $\{2\overline{1}0\}_{\text{Y}}//\{01\overline{1}0\}_{\text{Zr}}$. The orientation relationship of C15 structure was $\{202\}_{\text{Y}}//\{1\overline{1}1\}_{\text{Zr}}$, $\{10\overline{1}\}_{\text{Y}}//\{1\overline{2}0\}_{\text{Zr}}$. The stacking faults in $\{0001\}$ plane were also observed in the ternary C14 Laves phase with sub-segment-like morphology. Further work need to be done to study the changes of ORs and defects under in situ ion irradiation.

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References

Formation of nanocrystalline $\delta$-ZrH$_x$ in Zircloy-4 Orientation relationship and twinning
Formation of nanocrystalline δ-ZrHₓ in Zircloy-4: Orientation relationship and twinning

Gaizhuan Yuan a, b, c, 1, Guoqin Cao a, b, c, 1, Qiang Yue c, Lei Yang b, Junhua Hu b, c, 1, Guosheng Shao a, b, c, 1, *

a Institute for Renewable Energy and Environmental Technologies, University of Bolton, Bolton BL3 5AR, UK
b International Joint Research Laboratory for Low-carbon & Environmental Materials of Henan province, Zhengzhou University, Zhengzhou 450002, China
c State Nuclear Fuel Zirconium Industry Co., Ltd (SNF), Baoshan, 216013, China

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Abstract
An important aspect of materials phenomena during the service of structural Zr alloys for nuclear cladding components is associated with hydrogen pickup, which leads to the formation of δ-hydrides ZrHₓ (x = 1.55 or 1.66), the structural evolution of which is essential to the mechanical stability of the cladding components. In this work, we report the formation of δ-hydrides due to accidental hydrogen pickup, using high-resolution transmission electron microscopy (HRTEM). The results showed that the habit plane for relatively large δ-hydrides was (0001)ₓ, with the plate morphology. The morphology for regions with porous nano-sized hydrides is irregularly blocky, albeit being of the same orientation relationship between hydrides and matrix. Such remarkable morphological change is associated with multi-orientation and twining in the hydrides crystals in the nano-scale.

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1. Introduction
Zirconium alloys, particularly those based mainly on Zr solid solution, are widely used as structural cladding materials in nuclear reactors due to their low absorption cross-section of thermal neutrons, good mechanical properties and high corrosion resistance. During the reactor operation, such zirconium alloy components experience a combination of thermal and reactive working conditions, including irradiation, oxidation and hydrogen pickup.

The structural zirconium alloy components in nuclear reactors absorb hydrogen through various sources, such as moisture present in fuel pellets, reaction between zirconium and coolant water (Zr + H2O → ZrO2 + 2H2) etc. [1,2]. Although zirconium alloys can dissolve up to 480 ppm hydrogen in solid solution at around 500 °C, the solubility of hydrogen decreases markedly as the temperature is lowered, with 65 ppm hydrogen at 300 °C and 0.05 ppm hydrogen at room temperature [3]. During the cooling, the excess hydrogen will precipitate as zirconium hydrides. Generally, there exist three kinds of hydride phases including the stable face-centered cubic δ phase, the metastable face-centered tetragonal γ phase, and the face-centered tetragonal ε phase [4,5]. The most commonly observed hydride in Zr alloys is δ-hydrides with a plate-like shape. The δ-hydrides preferentially precipitate on certain habit planes of the zirconium solid solution matrix (z-Zr), such as the frequently reported (0001) and (1010) planes, with the latter being slightly deviated from the former [6–9].

In the past few decades, the influence of hydride precipitates on the performance of Zr-based cladding materials was investigated by electron back-scattered diffraction, acoustic emission, and transmission and scanning electron microscopy [10–13]. Due to the significant structural difference between hydrides and z-Zr, the structural transformation between them involves a large volume expansion, and the interfacial energy is anisotropic because of the mixed coherency of the interfaces (the habit plane is coherent and the edge plane is semicoherent or incoherent) [14]. It was observed that the nucleation of cracks depended strongly on the orientation and morphology of hydrides [15,16]. Radically oriented hydrides can drastically reduce the ductility of Zr alloy tubes.

Thus, the morphology and spatial distribution of hydrides are very important for improving the long-term stability of Zr alloys.
The simulation of morphology and spatial distribution of $\gamma$-hydride in zirconium alloys has been reported [17]. It shows that the $\gamma$-hydrides arrangement strongly depends on the external stress. The stress effect and variant alignment are most evident during the initial nucleation stage. However, in their simulation only single hydride is allowed to grow, and the interactions between hydrides are not considered.

Zirconium hydrides are always treated as compounds with low ductility and crack easily on the initial stage of plastic deformation [18-20]. However, the discovery of substructure due to the formation of a high density of dislocations, the glide through and observation of dislocations in hydrides in deformed alloys somewhat indicate the possibility of plastic deformation of hydrides [16,21]. In spite of great importance of structural evolution in hydrogen containing Zr alloys, further efforts are still desired particularly about the crystallographic relationship and associated kinetic process for nucleation, growth and deformation behavior of hydride containing alloys. In this work we report for the first time the twinning phenomenon in the stable $\gamma$ hydrides, using high-resolution transmission electron microscopy (HRTEM), with their formation mechanism and implication on morphological evolution being elaborated.

2. Experiment

Alloy ingots of Zircaloy-4 (Zr-12 wt.%Sn-0.2 wt.%Fe-0.1 wt.%C) were prepared by vacuum arc melting, using a self-consuming electrode of the same composition to avoid impurity pickup. Each ingot was then forged at 1050°C (in the $\beta$ phase field) into feeding blocks for subsequent thermal mechanical processing. The forged blocks were water-quenched down to room temperature, and annealed in vacuum at 630°C for 15 h before being hot-rolled at 700°C into sheets of 0.2 mm in thickness. The hot-rolled sheets were finally annealed at 650°C for 1.5 h to achieve complete recrystallization. Chemical analysis showed that the overall hydrogen content of the bulk material thus prepared was below 20 ppm. The content of hydrogen in Zr-4 alloys was measured by LECO RH-600.

Thin foils for transmission electron microscopy (TEM) were mechanically polished to about 80 nm in thickness, followed by twin-jet electropolishing using an electrolyte consisting of a solution of 10% perchloric acid and 90% ethanol. The working temperature for the electrolyte was maintained at -40°C and the working voltage was 45 V. Finally, the foils were polished by ion milling with a liquid nitrogen cooling stage. The power of ion gun was 4.5 kW and the vacuum was kept at 5 x 10^{-4} Pa. HRTEM analysis was performed in a FEI Tecnai C² F20 microscope, operated at 200 kV.

3. Result and Discussion

Most of the thin foils of the alloy sheets were typical of the Zircaloy-4, consisting mainly of equiaxed $\alpha$-Zr grains. However, it was rather shocking that in some thin foils sampled near the surface of the alloy sheets, there existed $\beta$-ZrHx ($x \approx 0.55$ or 1.65) hydrides, considering that careful chemical analysis showed that the overall hydrogen content of the alloy was less than 20 ppm.

The morphology of hydrides was found to depend upon their population. Fig. (a) is a centered-dark field TEM image corresponding to the $[\overline{1}1\overline{0}]$ zone axis of $\alpha$-Zr matrix, showing the cross section of the hydride plates with thickness about 50-80 nm and a diameter about several hundreds of nanometers. The spot used to acquire the dark field image was circled in Fig. (b). The thin hydride plate is parallel with each other. The corresponding selected-area electron diffraction (SAED) patterns taken from the areas marked with A and the circled region in the matrix next to it (b) in Fig. (a) are shown in Fig. (b) and (c), respectively. The former contained two sets of single crystal patterns from the hydride and the matrix respectively. The latter (Fig. (c)) shows the pattern from the matrix only, and comparing to Fig. (b), one can easily tell the pattern of the hydride phase (weaker spots due to much smaller contribution in the selected area) from that of the matrix (linked with dotted lines in Fig. (b)). The magnetic rotation between the image and the diffraction patterns is about 90°, and the trace plane (edge-on) for the matrix is (001)_{z}.

Electron diffraction analysis through systematic tilting showed that the hydride is of the crystal structure of face-centered cubic $\beta$-ZrHx phase (8f) structure, $a \approx 0.471$ nm, which is the stable phase at room temperature (though deficiency in hydrogen was reported in the literature, e.g. $\text{ZrH}_{16.8}$ [22]). Tiling around the normal vector of the trace planes (001)_{y}/[\overline{1}1\overline{0}] showed that the $\delta$ hydrides are of the dark shape, so that no significant change in aspect size was observed through a large range of tilting over 60°. Fig. 2 shows a set of SAED patterns obtained from the same region of Fig. 2a. The orientation relationship between the hydride and the matrix is $(\overline{1}2\overline{1}0)_{y}/(11\overline{2})_{z}$ and $(0001)_{y}/(11\overline{2}0)_{z}$, among overall 24 crystallographically equivalent orientation variants.

Fig. (a) shows the typical morphology of edge-on hydride plates taken at [101]_{z} zone axis. The typical orientation relationship (OR) can be derived from Fig. 2d as (0001)_{y}/(\overline{1}1\overline{0})_{z}, and $(\overline{2}1\overline{2}0)_{y}/[1\overline{1}1]_{z}$. One notes from Fig. 2c an equivalent orientation variant with its zone axis 60° off at $(21\overline{1})_{z}$. Owing to the symmetry of the cubic hydride phase, there were altogether 24 equivalent ORs between the hydride and the hexagonal matrix phase, which can be summarized as $(\overline{1}2\overline{1}0)_{y}/(11\overline{2}0)_{z}$ and $(0001)_{y}/(11\overline{2}0)_{z}$ (Noticing that "1" or "$\overline{1}$" here implies that the indices corresponding to the c- and a-axes of the hexagonal phase cannot be exchanged).

A representative high-resolution electron microscopy (HREM) image corresponding to the $(\overline{2}1\overline{2}0)_{y}/(11\overline{2}0)_{z}$ is shown in Fig. 3a. The corresponding fast-Fourier-Transformed (FFT) images from the same region are shown in Fig. 3b, together with FFT images from the matrix and hydrides to aid indexing. The matching plane and direction pairs between the hydride and the matrix phase are indicated in Fig. 3. The habit plane for the hydride to nucleate from and grow on is (001)_{y} and interestingly little lattice mismatch exists between (10\overline{1}5\overline{5})_{z}/(24\overline{2}4\overline{2})_{y}. The parallel direction pair $(10\overline{1}5\overline{5})_{z}/(21\overline{1}0)_{y}$ is consistent with the above representative OR between the phases. The sketch on the right of Fig. 3a illustrates the OR between the hydride and the matrix, on the atomic planes of the $(0001)_{y}/(11\overline{2}0)_{z}$ of the corresponding phases. For a more extensive envisage of the OR between a face-centered cubic phase and a close packed hexagonal phase, one may refer Fig. 12 in Shao et al. (1985) [23].

In the initial stage for the precipitation of hydrides, nucleation occurred on the plane with the lowest surface energy, the $(001)_{y}$ plane for the hexagonal matrix phase, which acted as the habit plane for the hydride nucleation. On the other hand, there are optimum lattice matching of atom patterns and spacings at the relationship of $(001)_{y}/(11\overline{2}0)_{z}$. Such a relationship may lower the strain energy of hydride nucleation and promote the hydride precipitation in Zr matrix. Thus preferred excess of the $(11\overline{2}0)_{z}$ plane lead to the formation of the hydride plates. Owing to the low symmetry of the hexagonal phase, each matrix crystal was only able to provide one $(001)_{y}$ habit plane, thus leading to the formation of hydride plates parallel to each other. The edges of the hydrides tended to follow the matching lattice plane pairs of $(21\overline{1}0)_{y}/(10\overline{1}5\overline{5})_{z}$. This is highlighted in Fig. 3c, which shows such a pair hedged interface at the edge of a hydride plate. It is worth pointing out that some researchers reported that $(10\overline{1}5\overline{5})_{z}$ could be the habit plane for the cubic zirconium hydride [24]. The observation from this work suggests that the $(001)_{y}$ plane is the
preferred habit plane owing to energetic advantage. The observation of plane pairs such as (242)_{\alpha}/(1015)_{\alpha} is crystallographically consistent to the same set of OR. Any n larger than 5 for (101\bar{4}) can also be viewed as slight deviation from the (0001)_{\alpha} plane, which could occur when evident strain/stress is involved.

In regions of higher density of hydrides in the annealed material, the morphology of hydrides became more chunky, as shown in Fig. 4(a). One notes from Fig. 4(a) that an overall alignment is evident in the orientation of the hydrides. The overall morphologies of these hydride crystals are rather blocky. The same OR and habit plane as those associated with the hydride plates applied to such blocky hydrides. Fig. 4(c) show a SAD pattern taken at (T2T0)_{\alpha}. 

Fig. 1. (a) TEM dark field image showing cross sections of hydrides plates. (b) SAD patterns from area A in (a). (c) SAD pattern from the matrix only (area B).

Fig. 2. (a) TEM image showing the presence of parallel hydride plates. (b–d) A set of direction patterns from the circled region containing a hydride plane, obtained through tilting the sample around the normal vector of the habit plane (0001)_{\alpha}/(111)_{\alpha}. 

**Fig. 3.** Illustration of orientation relationship between the hydride and α-Zr matrix. (a) HREM image containing a hydride; (b) Differ FID from the same area with another FID images from the hydride and the matrix respectively on the right. (c) The matching lattice plane pair at the edge of hydride.

**Fig. 4.** (a) TEM image of hydride with blocky morphology (b) HREM of twin crystal structure in δ-hydride, (c) SAD patterns of twin crystal.
zone axis, which exhibits two sets of twin-related hydride spots in addition to those from the matrix phase. The two sets of twin spots are of similar intensities (linked with green (in web version) and red (in web version) lines), owing to the existence of plenty twin boundaries (e.g. the arrow indicated in Fig. 4(a)). The corresponding HREM image from twin related hydride crystals is shown in Fig. 4(b). The twinning plane is (T11)$_{0}$, which is parallel to the (0001)$_{z}$ habit plane in the matrix phase. The formation of such twin-related crystals can be readily attributed to separately nucleated hydride crystals from crystallographically equivalent 0K, such that there are 6 sets of <110>$_{z}$ zone axes to offer for each (1210)$_{z}$ zone axes from the matrix solid solution phase. Each <110>$_{z}$ then offers two sets of parallel [111]$_{z}$ planes, and with 180° ambiguity considered, there are altogether 24 different choices for the hydride phase to orient in the matrix phase. With a chosen (111)$_{z}$ plane to align with the habit plane of (0001)$_{z}$, there are in reality only two options excluding the 180° ambiguity, leading to separately nucleated hydride crystals that are of mirror symmetry with respect to the habit plane. Twin boundaries would form when separately nucleated hydride crystals consumed the matrix phase in between through growth. Generally, the δ-hydrides crystal will grow preferential along the direction of the habit plane because of the minimum surface/interface energy. Thus the δ-hydrides always show a plate-like shape. However, in this research we found that the joining of twin related hydride crystals would result in more bulky morphology, due to the multiple stacking of individual crystals. Fig. 5 shows a simplified sketch for the “grow-in” of two twin related crystals. The zone axes for the two crystals are [110]$_{z}$ and [101]$_{z}$, respectively, with both containing the (T11)$_{0}$ plane to align on the (0001)$_{z}$ habit plane in the matrix phase. When the two crystals impinge on each other through growth, a twin boundary will form, thus leading to doubled thickness in the [111]$_{z}$ direction. One sees that it is highly probable that multiple of twin boundaries may arise from such a “grow-in” mechanism, when a high nucleation rate of hydride is involved. This can be facilitated through a high level of hydrogen incorporation in the Zr solid solution, through enhanced thermodynamic driving force for nucleation and growth.

A thermodynamic database for the Zr-H alloy system has been established through the Calculation of Phase Diagram (CALPHAD) method. Fig. 6 shows the calculated Gibbs energy curves for the hydride and the solid solution phase at 400°C. The blue (in web version) and red (in web version) curves represent the Gibbs free energy for α-Zr and δ phase, respectively. The common tangent defines the equilibrium chemical potential, with the tangent points on the two curves defining the equilibrium H contents. The thermodynamic driving force for phase separation in the α-Zr matrix via nucleation and growth of the δ phase is indicated by the energetic difference (△G) from the blue curve to the common tangent line, as is shown in the enlarged inset. It is apparent from Fig. 6 that the higher the hydrogen content, the larger the driving force for phase separation via precipitation of hydrides. This will lead to higher density of nuclei and larger growth rates. Understandably, when there is higher density of nuclei, it is more likely that “grow-in” twin boundaries will form, leading to blocky morphologies, with each blocky hydride made of a collection of nano-plates.

According to the calculated Zr-H phase diagram, the solubility of hydrogen in the α-Zr solid solution decreases with lowering temperature, so that extraneous hydrogen pickup at higher temperature could be forced out of α at lower temperatures. Due to the high content of hydrogen in the δ phase, their precipitation would involve significant long-range diffusion. As most of the steps for the processing of the materials examined in this work were fairly clean, except for water quenching the forged feeding blocks from 1050°C. It is highly possible this was when intentional hydrogen pickup occurred. Also, we don’t rule out the possibility that hydrogen was introduced during the ion milling process for TEM sample [25].

The readiness in hydrogen pickup means that it is very important to understand the precipitation behavior of hydrides, as cladding materials do work in contact of water. It is therefore desirable for one to develop protection coating in the form of chemically inert diffusion barriers, in order to prolong service life and enhance structural stability of such materials.

4. Conclusion

High-resolution electron microscopy was used to study hydrides formation in a typical Zircaloy-4 material, due to hydrogen pickup near the surface region during water quenching the forged feeding blocks.

The stable δ-ZrH$_{3}$ hydride is of the face-centered cubic structure and they are crystallographically related to the α-Zr solid solution with 24 equivalent variants, typically summarized as: <1210>$_{z}$/ <101>$_{z}$ and (0001)$_{z}$/[111]$_{z}$. It is also interesting to note that a plane pairs of <224>$_{z}$/[1015]$_{z}$ exist at the edge of a hydride plate when strain/stress is involved.

Most of the δ hydrides assume plate morphology and align on the (0001)$_{z}$ habit plane of the α-Zr solid solution phase. It was interesting to observe the twinning in δ-hydrides. The twinning plane was (111)$_{z}$. The hydrides became more blocky in shape, with twin boundaries formed through complete consumption of the
matrix phase between separately nucleated precipitates.

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References

Microstructural characteristics of β precipitates in Zr-1Nb alloy
Microstructural characteristics of $\beta$ precipitates in Zr–1Nb alloy

Gaihuan Yuan a,*, Lifeng Zhang a, Qiang Yue b, Hengfei Gu c, Ceping Li c, Jianyun Shen d

a University of Bolton, Bolton BL3 5AB, UK
b State Nuclear Power Division Industry Company, Shenyang 110216, China
c Institute of Metal Research Chinese Academy of Sciences, Shenyang, 110016, China
d General Research Institute for Nonferrous Metals, Beijing 100088, China

ABSTRACT

The $\beta$ phase precipitates in a Zr–1Nb alloy annealed at 600 °C and 700 °C (below and above the monoclinic temperature, respectively) for 3 h were investigated by transmission electron microscopy. It was found that the uniformly distributed $\beta$ phase obtained at 600 °C was spherical with a diameter of 30–60 nm, volume fraction of ~2.5% and Nb content ~0.88 wt%. However, the $\beta$ phase obtained at 700 °C was stick-shaped, with ~100 nm in diameter and ~100 nm in length, volume fraction of ~5.89% and Nb content ~10 wt%. The distinction in volume fraction and compositions were consistent with the lever rule of the Zr–Nb phase diagram. The distinction in shapes resulted from the change in the interfacial structure, which depended on the lattice mismatch. The orientation relationship between a matrix and stick-shape $\beta$ precipitates satisfied Burgers' orientation relationship, i.e., [101]B//[110]M for the broad face, [0001]B//[110]M for the side facet and [112]M//[111]B for the edge of the outlined stick-shape $\beta$ precipitate. It was composed of elongated and curved interfacial interfaces, and the broad faces and side facets together formed the straight interface, and the edges formed the curved one. As the Nb content of $\beta$ phase increased, the lattice mismatch on both broad face and side facet increased, and the interfacial structures changed from coherent (obtained at 700 °C) into incoherent (obtained at 600 °C), and the midline of edge decreased, and their interfacial structures were always incoherent for the two heat treatments. Therefore, the curved interfaces had a higher growth rate than the straight interfaces at 700 °C and stick-like $\beta$ phase precipitate was formed. While the three planes have a comparable growth rate at 600 °C, and spherical $\beta$ phase precipitate was formed.

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1. Introduction

Zr–1Nb alloy has been used as fuel cladding and structure materials in Russian VVER and in France nuclear reactors for many years [1,2]. In this alloy, precipitates have an intense influence on the physical, mechanical and corrosion properties. Therefore, lots of efforts have been made over several decades to reveal the influence of hot working, heat treatment and service conditions on the characteristics of the precipitates, such as crystal structure, composition, shape, size, volume fraction and distribution.

There are many possible solid phase transformations in Zr–1Nb alloy, such as 1) $\beta \rightarrow \alpha$ (α') during cooling from the $\beta$ phase field, 2) $\beta \rightarrow \alpha$ during quenching from the $\beta$ phase field or aging at low temperature, 3) $\beta \rightarrow \alpha + \beta$ (NB-impoverished), 4) $\beta \rightarrow \alpha + \beta$ (NB-enriched), 5) $\alpha' \rightarrow \alpha + \beta$ (α', or $\beta$) [6,15]. It has been reported that the precipitates in Zr–1Nb alloy are mainly Nb-impoverished or Nb-enriched $\beta$ phase precipitates [3–8], and a small amount of intermetallic compounds [8–11]. Generally, annealing below the monoclinic temperature for a long time Nb-enriched $\beta$ phase precipitate could be formed, while annealing above the monoclinic temperature or for a short time Nb-impoverished $\beta$ phase precipitates could be formed [12–14]. As almost all the studies on the relationship between precipitates and corrosion properties show that an increase in the amount of Nb-impoverished $\beta$ phase precipitate increases the corrosion rate, the microstructure containing stable Nb-enriched $\beta$ phase precipitate is preferred for materials stability under corrosive conditions [4,14]. Now the investigation on the $\beta \rightarrow \alpha + \beta$ phase transformations and the crystal structure of $\beta$ phase precipitate in Zr–1Nb alloy have been extensively undertaken, however little effort has been made to study the composite-phase transformation.

* Corresponding author.
E-mail address: gpy@hrbmu.edu.cn (G. li).
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(βf → β + γ + βf) and associated crystallographic characteristics.
In the present study, the β phase particles in a Zr–1Nb alloy
annealed below and above the monotectoid temperature were
investigated by transmission electron microscopy.

2. Experimental procedures

The as-received material was Zr–1Nb (wt.%) alloy manufactured
by the State Nuclear Plant Zirconium Industry Company (SNP).
The alloy was forged in the β phase field and quenched to room
temperature, and then hot and cold rolled to a rod 9.6 mm in
diameter below the monotectoid temperature, finally the rod was
annealed at 600 °C and 700 °C (below and above monotectoid
temperature respectively) for 3 hours to obtain a fully recrystallized
structure. Transmission electron microscopy (TEM) and
composition analysis were performed using a JEM TECHNA C2 20
transmission electron microscope equipped with energy dispersive
X-ray (EDX) analyzer. TEM foils were mechanically thinned to
50 μm in thickness and further reduction was carried out using a
Tenupal-5 twin-jet electrolytic polisher in a solution of 10% perchloric acid and 90% ethanol (volume fraction).

3. Results

Fig. 1 shows the changes in the micro-hardness with annealing
time at 600 °C and 700 °C respectively. Generally the samples
annealed at 600 °C had higher micro-hardness than that at 700 °C.
In the first hour the micro-hardness of both samples increased. After
2 h annealing at 600 °C or 3 h annealing at 700 °C, the micro-
hardness for the annealed samples became constant. Thus the
samples annealed at 600 °C for 3 h (60°C/3 h-AC) and at 700 °C for
3 h (70°C/3 h-AC) were chosen for detailed TEM study.

Fig. 2 shows the typical bright-field TEM microstructure of the
600 °C/3 h-AC sample. The spherical precipitates were uniformly
distributed within the equiaxed α grains. The diameter was
30–65 nm and the volume fraction was 2.5%, as shown in Fig. 2a
and b. The selected area electron diffraction (SAED) pattern
revealed that the precipitates were β phase with body-centered
cubic crystal structure, as shown in Fig. 2c. EDX analysis under
TEM indicated that the precipitates contain ~68 wt.% Nb.

Fig. 3 shows the typical bright-field TEM microstructure of the
700 °C/3 h-AC sample. The morphologies of the precipitates were
obviously different from that in the 600 °C/3 h-AC sample. The
precipitates had a stick-shaped morphology ~150 nm in diameter
and ~300 nm in length. The volume fraction was ~88%, as shown
in Fig. 3a and b. Selected area electron diffraction (SAED) revealed
that the precipitates were β phase with body-centered cubic
structure, as shown in Fig. 3c. The TEM-EDX analysis indicated
that the precipitates contained ~10 wt.% Nb. In this case, through
the combination of bright- and dark-field imaging with the consider-
ation of magnetic rotation, it was noticed that the βf (βf boundary
of the needles corresponded to the (010) plane of the β phase, and this
βf particle plane is also parallel to the (0001) plane of the α–Zr matrix. When a dark-field image was taken using the
(010)βf diffraction spot from a βf precipitate, almost all precipi-
tates containing the same axial direction were highlighted in the
DF image, which suggested that these precipitates maintained
an orientation relationship with the α–Zr matrix.

4. Discussions

Comparing the characteristics of precipitates in the 600 °C/3 h-AC
and 700 °C/3 h-AC samples, one noted that when the annealing
temperature changes from 600 °C (below monotectoid temperature)
to 700 °C (above monotectoid temperature), the volume fraction increased from ~2.5% to ~8.8%, while the Nb content
decreased from ~68 wt.% to ~10 wt.% At the same time, the size increased and the morphology changed from spherical to stick-
shaped. The changing trends in volume fraction and composition are consistent with the lever rule of the Zr–Nb binary phase
diagram. The Zr–Nb phase diagram shows that at 600 °C and the Nb
content of ~10 wt.% the Nb (Nb-enriched) phase exists. The Nb content of ~68 wt.% and the volume fraction is ~2.5% At 700 °C and the Nb
content of ~10 wt.% the Nb (Nb-enriched) phase is ~8.8%. The distinctions between the experimental and theoretical data may result
from several factors. On the one hand, the inhomogeneities, such as
Fe, O, or H, etc. will change the phase boundaries in Zr–Nb binary
phase diagram. On the other hand, the annealing time was not long
enough to reach full equilibrium. Because the compositions of α, βf
(Nb-impositional), and βf (Nb-enriched) phases are substantially
different, the growth rate of βf precipitates will be mainly controlled
by the diffusion coefficients of Nb and Zr atoms.

Fig. 4 shows the HRTEM image of the boundary between α–Zr matrix
and βf precipitate in Zr–1Nb alloy with annealing of 700 °C
for 3 h-AC. The outline of the stick-like βf precipitates is composed of
straight and curved interfaces from the lateral sectional point of view. As shown in Fig. 4, the orientation relationship between
α and stick shaped βf phase precipitate for a straight interface is (021)α//(1010)βf and the [11̅2]α cone axis of the βf phase precipitate is parallel to the [11̅2]α cone axis of α–Zr matrix, so the
orientation relationship between α matrix and βf phase precipitate satisfies Burgers orientation relationship, i.e., (01T 02T//1T 2βf)
for the broad face, (0001)βf//(11̅0)α for the side facet and (11̅2 02T//1T 1)α for the edge, just like the orientation relationship of phase
transformation from βf-matrix to α lamell [15]. Therefore the broad
faces and side facets together form the straight interface perpendicular to the S-axis, and the edges form the curved one parallel
to the L-axis, as shown in Fig. 5.

The distinction in the morphologies of βf phase precipitates indicates
that at 600 °C the growth rate of βf (Nb-enriched) is isotropic while at 700 °C the growth rate of βf (Nb-impositional) is significantly
anisotropic. A lot of studies have revealed that the migrating rate of
the phase interface is intensely influenced by the interfacial
structure. The more disordered the arrangement of atoms in the
interface is, the faster migrating rate of the phase interface is.
With the extent of disorder can be reflected by the lattice misfit. As the
increase of Nb content of βf phase, the lattice parameter of βf phase
gets larger. We calculate the lattice misfits of different interfaces at 600°C and 700°C. For β$_1$ (Nb-enriched) with Nb content of 68 wt.% and α phases the lattice misfits of broad face, side facet and edge are 27.7%, 8.4% and 32.1%, respectively at 600°C. While for β$_2$ (Nb-impoverished) and β$_3$ (Nb-enriched) are always intensely disordered, while the arrangements of atoms in the broad face and side facet for β$_2$ (Nb-enriched) are more disordered than that for β$_3$ (Nb-impoverished). The misfit dislocation observation on straight and curved interfaces also supports the calculated results as shown in Fig. 6, which is from the inverse FFT in the curved and straight interface areas of the stick-shaped particle in the 700°C CT3 h-AC condition in Fig. 4c and d, respectively. It is well known that when the lattice misfit is larger than 5% the coherent interfacial structure will be destroyed. This means that as the Nb content of β phase increasing, the lattice misfits on broad face and side facet increase and their interfacial

Fig. 2. (a and b) Bright-field TEM images of precipitates in Zr–1Nb alloy after annealing at 700°C for 3 h followed by air cooling, showing spherical precipitates. (c) the selected area electron diffraction (SAED) pattern of the precipitate along the [110]$_b$ zone axis.

Fig. 3. (a and b) Bright-field TEM images of precipitates in Zr–1Nb alloy after annealing at 700°C for 3 h followed by air cooling, showing stick-shaped precipitates. (c) the selected area electron diffraction (SAED) pattern of the precipitate along the [110]$_b$ zone axis and the corresponding SAED pattern of α-Zr matrix.

Fig. 4. HRTEM image of the boundary between α-Zr matrix and β precipitate in Zr–1Nb alloy with annealing at 700°C for 3 h/AC. a) and b) display the crystal orientation of α-Zr matrix and β precipitate, respectively.

Fig. 5. A diagram illustrating the boundaries of α precipitate in Zr–1Nb alloy with annealing at 700°C for 3 h/AC.
structures change from coherent (obtained at 700 °C) into incoherent (obtained at 500 °C), and the edge is always incoherent. Therefore, the edge interface has a higher movement rate than the broad face and side face at 700 °C and stick-shaped β particle forms. While the three interfaces have a comparable movement rate at 600 °C and spherical β particle forms.

5. Conclusions

1) After annealing at 600 °C for 3 h the precipitate in Zr-1Nb alloy is spherical β phase with the diameter of 30–60 nm, volume fraction of -2.5% and Nb content of -68 wt.%.

2) After annealing at 700 °C for 3 h the precipitate in Zr-1Nb alloy is stick-shaped β phase with ~100 nm in diameter and ~300 nm in length, volume fraction of -2.8% and Nb content -10 wt.%.

3) The changing trends in volume fraction and composition are accordant to the lever rule in Zr-Nb binary phase diagram.

4) The distortion in the morphologies of β phases results from the change in the interfacial structure.

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References


Formation and fine-structures of nano-precipitates in ZIRLO
Formation and fine-structures of nano-precipitates in ZIRLO

Gaihuan Yuan a,6, Guoqin Cao a,6, Qiangu Yue a, Qi Yang b,6, Yifan Yun b,6, Guosheng Shao a,6, Junhua Hu a,6

a Institute for Renewable Energy and Environmental Technologies, University of Bolton, Bolton, BL3 5AB, UK
b School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China
c State Key Laboratory of Metal Matrix Composites for Advanced Deep Low-Carbon and Environmental Engineering, Zhejiang University, Hangzhou, 310027, China
d State Nuclear Fuel Uranium Industry Co., Ltd (SNFI), Beijing, 100124, China

1. Introduction

Nuclear energy has been considered as an effective means to power the modern world without the emission of carbon dioxide. Currently, almost 15% of the world’s electricity consumption is generated from nuclear power. Zr-based alloys, or ZIRLO, have been used for fuel cladding tubes in nuclear reactors due to their low absorption cross-section for thermal neutrons, good mechanical properties, and high corrosion resistance. There has been a continuing effort in prolonging the service life of the fuel-cladding materials, in order to meet the challenging request for ever-increasing burn-up of nuclear reactors [1]. This can be achieved through the introduction of alloying elements with low absorption cross-section of thermal neutrons to induce solution and/or precipitate strengthening while maintaining good corrosion resistance. Therefore, only a limited number of alloying elements are suitable for cladding Zr alloys, with their acceptable contents being fairly low. So far the recognized alloying elements for such materials include Nb, Sn, Fe, Cr, O etc. The ZIRLO alloy is one of the few successfully developed and commercially applied alloys, which was introduced to pressurized water reactors in 1987 [2]. The nominal ZIRLO composition (wt%) contains 12% Nb, 1% Sn, and 0.1% Fe. In addition to the improvement of corrosion resistance achieved by ZIRLO cladding with respect to that of the Zircaloy-4 material, the in-service growth and creep were also significantly slower, resulting in an improved dimensional stability [3]. The compositions and crystalline structures of precipitates in ZIRLO are reckoned to be influenced by the solubility of Nb and Fe in α-Zr, as well as by the empirical ratio R = Fe/[Fe + Nb] = 0.38 [4]. As the solubility limit of Sn, Tofilon-Mascl et al. updated the Zr-Sn binary phase diagram through experimental investigation together with first-principle calculation, and thus reevaluated the Sn solubility limit in α-Zr [5]. Based on their work there would be no Sn containing precipitates in ZIRLO. According to the parameter R proposed by Shishov, the precipitates should be the body-centered-cubic β-Nb and the hexagonal Zr-Fe-Nb phase. For the Zr-Fe-Nb phase, Granovsky [6], Ration [7], Barberis [8], and Tofilon-Mascl et al. [9] independently performed some Zr-Sn-Nb-Fe alloys, and carried out structural study of precipitated phases. They concluded that the Zr-Nb-Fe particles could be divided into FCC and HCP structures, the former space group was Fm 3m (Ia3d type), while the latter had...
When serving in nuclear reactors, the inner surface of cladding tubes is in contact with fission products at high temperature while the outer surface endures high temperature and high pressure water (200–350 °C, 10–16 MPa), in such a harsh working environment, the corrosion resistance of Zr alloys is very important. Numerous experiments have shown that the size distribution and type of second phase(s) affect the penetration of oxygen ions and associated nodular corrosion. The optimized corrosion performance of Zr alloys was achieved when the fine second-phase particles were uniformly precipitated in α-Zr matrix. Rudling et al. showed that the SPP's distribution and chemical composition heavily affected the corrosion behavior, since the barrier layer (dense zirconia) which influence the diffusion of oxygen ions was closely related to the SPPs [10]. On the other hand, the defects of precipitates make them prone to amorphization and elemental migration, which would change the stability of precipitates and chemical compositions of the matrix thereby lowering the working performance of Zr alloys [11,12].

While moderate incorporation of alloying elements such as Fe, Cr, and Ni etc within the α-Zr matrix may help strengthen the materials without evident negative impact on corrosion resistance, the precipitation of intermetallic compounds will occur when their concentrations are above the lower solid solubility. The formation of such second phases in alloying elements will affect their mechanical properties, corrosion resistance and as well as possible hydrogen pickup process in service. It is therefore important to understand the precipitation process and associated crystallographic phenomena and compositional redistribution [13-16]. In spite of years of investigation, such data, particularly defect evolution and crystallographic details, are yet lacking for Zr alloys containing Nb and Fe as the main alloying element. This work is focused on the refined structural/crystallographic characteristic of nano-precipitates in a thermomechanically processed ZIRLO alloy, with particular interest in orientation relationship, compositional redistribution across phases, defects formation and phase interfaces.

2. Experimental methods

Ingots of alloys with the typical ZIRLO composition (Zr – 1 wt%; Nb – 1 wt%; Sn – 01 wt%; Fe) were prepared by vacuum arc melting, using a self-consuming electrode of the same composition to avoid impurity pickup. Each ingot was then forged at 1070 °C (in the β phase field) into forging blocks for subsequent thermal mechanical processing. The forged blocks were water-quenched down to room temperature. After surface cleaning each forging block was subjected to hot rolling at 600 °C into sheets of 3.8 mm in thickness. After annealing at 900 °C for 2 h, they were then cold rolled down to 0.8 mm in thickness. Finally, the sheets were annealed at 600 °C for 3 h to obtain a fully recrystallized structure.

Thin foils for transmission electron microscopy (TEM) were mechanically polished to about 60 μm in thickness, and then the central region of each disc was dimple-polished down to about 20 μm in thickness. Twin-jet electro-polishing was then followed, using an electrolyte consisting of a solution of 15% perchloric acid and 90% ethanol. The working temperature for the electrolyte was maintained at −40 °C and the working voltage was 45 V. Finally, the foils were polished by ion milling at 5 eV, with a liquid nitrogen cooling stage. TEM and energy dispersive X-ray spectrometry (EDS) were carried out at 200 kV, using a JEM 2100 microscope equipped with an energy dispersive X-ray (EDX) detector (Oxford UTW Isis).

3. Result and discussion

Fig.1 shows bright field (BF) image typical of the microstructure of the ZIRLO alloy. The equiaxed morphology of α-Zr grains indicate complete re-crystallization, and nano-precipitates are shown to distribute largely across the grains of the matrix phase. The precipitates can be classified into two size groups, the larger precipitates (SPP1) above 60 nm (mostly 60–80 nm) in size and ultrafine nano-crystals below 30 nm in size (SPP2). EDS analysis showed that the larger precipitates (SPP1) contained similar atomic levels of Zr, Fe and Nb without evidence of Sn, and is thus a ternary Zr–Fe–Nb phase. While the size of the ultrafine precipitates (SPP2) are below the limit of the spatial resolution for EDS, EDS quantification with 1 nm electron probe centered on such ultrafine precipitates did indicate that even under the influence of the matrix composition, they were significantly richer in Nb than the former. This offers strong indication that the two kinds of precipitates are of different type of phases. This is consistent with the work of Tafsson-Masclet [3], as the Zr-rich ZIRLO alloy is located within the three phase region (α-Zr – 1Cr – 1Nb) on the isothermal section at 550 °C of the Zr rich corner of the Zr-Nb-Fe phase diagram, as show in Fig. 2. This leads to Zr being the major phase of matrix and the other two phases being minor precipitates formed through precipitation from the Zr solid solution.

![BF images: (a) equiaxed grains with nano-precipitates; (b) image at higher magnification with relatively larger (SPP1) and significantly smaller (SPP2) precipitates indicated. Note the presence of dislocations in the matrix phase.](image-url)
3.1 \( \beta \)-Nb

Ultrafine spherical precipitates were observed within the grains of the matrix \( \alpha \)-Zr phase (Fig. 3(a)). EDS result shows that it contained more than 44 at.% Nb, considering the influence of the matrix phase composition. The solubility limit of Nb in \( \beta \)-Zr is about 36 at.%, which is lower than the tested Nb content in the spherical phase, indicating that the spherical phase should be \( \beta \)-Nb [6]. Due to the low diffusion coefficient and low content of Nb in \( \alpha \)-Zr, most Nb would be kept in the matrix phase to form supersaturated \( \alpha \)-Zr, during quenching the alloy from the forging temperature in the \( \beta \)-Zr phase field. The precipitates including the ultrafine \( \beta \)-Nb particles were formed via a solid state precipitation process during thermomechanical processing and annealing at 600 °C when the alloy was in the three-phase field (\( \alpha \)-Zr + C4M + \( \beta \)-Nb).

HRTEM study was carried out to study the refined crystallographic characteristics between the precipitates and the matrix phase. Fig. 3(b) shows a HRTEM image corresponding to the [0001] zone axis of the matrix phase, revealing excellent coherency at the interface, owing to small lattice mismatches between the hcp and bcc structures involved. The corresponding orientation relationship was [0001]//\( \{110\} \), and \( \langle 100\rangle \), //\( \langle 112 \rangle \), which satisfies the so-called Burgers orientation relationship between hcp and bcc solid solution phases. Such typical Burgers orientation relationship is generic for alloys based on the group IV transition metals, such that it also holds in \( \beta \)/\( \beta \) alloys [12].

3.2 The ternary \( \text{Zr-Fc-Nb} \) precipitate

Selected area electron diffraction (SAED) showed that the larger ternary \( \text{SFP1} \) particles were of the hexagonal \( \text{C41} \) Laves phase structure, being consistent with the alloy phase diagrams near the \( 600 \) °C thermomechanical processing temperature (Fig. 2). Fig. 4 shows the orientation relationship between the \( \text{SFP1} \) C41 compound and the matrix, with a SAED pattern from the region of Fig. 4(a) containing two sets of low-index diffraction patterns from the matrix and a spherical \( \text{SFP1} \) precipitate, respectively. The diffraction pattern from the matrix is at the \( \text{SFP1} \); [0001] zone axis, and that from the precipitate corresponds to the \( \text{SFP1} \); [1010] zone axis of the C41 phase. The orientation relationship is therefore near: \( \{2\langle 1010\rangle_{\text{SFP1}}\} \langle 111\rangle_{\text{SFP1}} \text{C}41 \langle 111\rangle_{\text{C}41} \langle 10\rangle_{\text{SFP1}} \). Fig. 4(c) shows the corresponding atomic illustration for such an orientation relationship. Using the \( \text{SFP1} \); C41 pattern as an in situ reference, the lattice parameters of the precipitate was calculated to be \( a = 0.559 \text{ nm, } c = 0.842 \text{ nm} \). The orientation relationship is only approximate, from the evidence that the precipitate was somewhat off the corresponding zone axis. This could be attributed to geometric relaxation in reducing interface stress.

There was evidence for the existence of stacking faults in the C41 compounds, as is shown in Fig. 5(a), which reveals parallel planes corresponding to the traces of the habit planes for the faults. Corresponding diffraction pattern, Fig. 5(b), shows streaking in some spots along the \( \langle 10\rangle_{\text{SFP1}} \) vector, owing to the presence of stacking faults in the \( \langle 10\rangle_{\text{SFP1}} \) plane. The stacking fault was found before \([18,19]\), but the researchers did not specify the stacking fault plane. Usually, the formation of stacking fault is related with the moving of dislocation. The dislocations in alloys generally start at the most close-packed crystal plane. In a hexagonal phase with the \( \sqrt{3} \) ratio being the ideal 1.536 value, the close-packed plane is [0001]. If the phase is not close packed, the [0001] plane may not be the most close-packed plane any more. Dislocations can then move preferentially on the prism (1010) plane when it is the most closely packed. Even for the \( \alpha \)-Zr phase, its \( \sqrt{3} \) ratio is 1.503. Interestingly, even for pure \( \alpha \)-Zr, the spacing of the prism plane [100] is 2.798 Å, while the spacing of its basal plane [0002] is only 2.573 Å. So the prism plane for \( \alpha \)-Zr is most closely packed in the \( \alpha \)-Zr [20,21].
Fig. 4. (a) BF image showing a spherical Zr-Fe-Nb precipitate in the α-Zr matrix; (b) corresponding SAED pattern; (c) illustration of orientation relationship.

Fig. 5. (a) BF image showing a Zr-Fe-Nb precipitate exhibiting contrast of parallel lines; (b) Corresponding diffraction pattern showing streaking in strong spots from the phase.

Fig. 6. The Zr-Fe-Nb precipitates and related compositions.
the other hand, the \(c/a\) ratio of C14 Zr-Fe-Nb phase is only about 1.5, making the prism planes the most closely packed. The orientation relationship between the C14 Zr-Fe-Nb phase and α-Zr is, as noted above, (2\(\bar{1}\)T0)\textsubscript{C14}//(10\(\bar{1}\)0)\textsubscript{α-Zr}. Presumably, dislocations could move from a matrix (10\(\bar{1}\)0) plane to a SPP (2\(\bar{1}\)T0) plane. However, because the (2\(\bar{1}\)T0) plane is not the close-packed plane, dislocations tend to transfer to the (10\(\bar{1}\)0) planes of the Zr-Fe-Nb phase. The dislocations can then cross slip between intersecting (10\(\bar{1}\)0) planes in a way similar to that between the closely packed (11\(\bar{1}\)) planes in a face centered cubic phase, thus leading to dissociation of dislocations into partials with stacking fault in between. The trace of the habit planes will then exhibit as parallel lines such as observed in Fig. 5(a).

EDS was used to quantify the contents of Nb and Fe in the Zr-Fe-Nb SPPs with different sizes (Fig. 6). Because SPPs are very small and embedded into the matrix, the characteristic X-rays generated from the matrix will also contribute to the results, with the high concentration of Zr in the matrix leading to most serious error in the analysis. We therefore only quantified the ratio of Fe/Nb for the C14 phase, with the consideration that the rather low contents of Nb and Fe in the matrix would not lead to evident errors. A second phase with different sizes could represent different growth stages. The Fe/Nb ratio of Zr-Fe-Nb phase varied with the increase of particle size (Fig. 7). The bigger the particle size the smaller the ratio of Fe/Nb became. When the particle size increased beyond 100 nm,

![Image](72x23 to 595x779)

**Fig. 7.** Fe/Nb ratio against particle size of C14 precipitates.

![Image](a)

**Fig. 8.** (a) Zr-Nb-Fe ternary isothermal section calculated at 900 °C. (b) XRD pattern of the prepared C14 type Zr-Fe-Nb alloy. Rietveld plot of C14 phase reported by Ref. was put as reference [5].

![Image](a)

**Fig. 5.** TEM analysis of the prepared C14 type Zr-Fe-Nb alloy.
the ratio of Fe/Nb is close to what Barberis et al. reported [22], meaning that the SPPs were then largely in the stable state. This phenomenon confirmed that during the growth of Zr-Fe-Nb phase, 

elemental evolution was controlled by solid state diffusion. Due to the fact that Fe diffuses orders faster than Nb in \( \alpha-Zr \) \( \left( D_{Nb} = 10 \times 10^{-10} \times 10^{-15} \text{ m}^2/\text{s} \right) \), the surrounding Nb atoms would diffuse into the Zr-Fe-Nb nucleus prior to Nb. This led to higher Fe content than Nb in the initial growth state. Fig. 7 shows the relationship between Fe/Nb ratio and particle size from data of this work and reported data from the literature [24–26]. Although different manufacturing processes were adopted, all data showed the same trend that the Fe/Nb ratio decreases with increasing particle size in all samples.

As a class of phase structures due to geometrical packing of atoms of rather different sizes, the atomic configurations of Laves phases are dependent upon the relative atomic radii of the constituents. The atomic radii for Zr, Fe and Nb are \( R_Zr = 0.216 \text{ nm} \), \( R_{Fe} = 0.208 \text{ nm} \), and \( R_{Nb} = 0.172 \text{ nm} \), respectively. In the \( \alpha-Zr \) stoichiometry of the C14 Laves phase, Zr occupies the 4f site due to its large atomic radius, and Fe as the smaller atom occupies the 2a and 6h sites. In the Zr-Fe-Nb system, it has been debatable however about the position of Nb atoms in C14 Laves phase. In the late 1960s, Kanematsu [27], Tanaka [28], Affrati [29], Petkov [30] proposed that laves phase (C14, C15, C16) were of the atomic formula of \( (Zr_2 + \alpha_2)\alpha_2Fe_3 \) with the 2a site being partially occupied by Nb. On the basis of the valence electron concentration, they reported a cubic C15-type structure for \( x < 0.35 \) and a hexagonal C14-type structure for \( x > 0.5 \). However, recent experimental work by Ramos et al. showed that Nb mainly substitute Fe in the \( 2a \) 6h site in the C14 laves phase instead [7]. Ramos et al. obtained different compositions of the C14 compound by adjusting the contents of alloying constituents Fe and Nb. The Zr content of the compound phase was found to be largely constant and the content of Fe and Nb varies inversely. This suggests that Nb prefers to occupy the positions of Fe atoms instead, which is consistent with the calculated phase diagram by Toftolien–Masclet et al. [5].

An effort was made in this work to test the latest phase equilibrium data [5,7], with the preparation of an alloy close to the C4 composition in the \( \left( \alpha-Zr + C14 + \beta-Nb \right) \) region at 550 °C. [10] Toftolien–Masclet [31] observed that at 550 °C in the three-phase region \( \left( \alpha-Zr + C14 + \beta-Nb \right) \) for the ternary Zr-Fe-Nb system, the atomic composition was nearly constant at 33.5Zr-38.5Nb-28Fe (at.%) as this three-phase region is of particular interest to the ZIRLO alloy, here we prepared the alloy with the nominal composition of the melted alloy being 34Zr-38 Nb-28Fe (at.%), on the tip of the C14 ternary phase (marked as a black dot on the isothermal section of Zr-Nb-Fe ternary system at 900 °C [5], Fig. 8(a)). The XRD spectra of the as-cast C14 compound and the referred standard PDF pattern are shown in Fig. 8(b) [5]. It can be seen that single C14 Zr-Fe-Nb phase was obtained.

Fig. 9 shows three diffraction patterns from different areas. It was found that the only alloy consisted of the C14 type Zr-Fe-Nb phase with composition being close to the nominal composition, indicating the great accuracy in the latest phase diagram. Fig. 10 shows a HRTEM image between two Zr-Fe-Nb grains. From the HRTEM of Fig. 10(b, d) it can be seen that both grains (A and B) had the hexagonal C14 structure and the zone axes are C14-[0110], C14- [0001], respectively. Fig. 10(c) clearly shows the two grains are
coherently related, and the orientation relationship between two particles is a \((0002)/(\beta\{10\overline{1}0\})\); \((0\overline{1}1\overline{0}\{\overline{1}1}\overline{2}\overline{0})\). It can be determined that \(d_{(0002)} = 4\gamma (10\overline{1}0)\). However, in the C14 structure, the spacing of \((0002)\) planes is slightly smaller than that of \((1\overline{1}0\overline{1})\) planes. Thus, we conclude that the spacing of \((0002)\) plane in grain A \((0.425 \text{ nm})\) is larger than that in grain B \((0.400 \text{ nm})\), and the corresponding lattice constant of grain A is larger than grain B. From the perspective of components, grain A has more Nb but less Fe compared with grain B, while the content of Zr is largely unchanged in both grains. Taking into account the atomic radius of Fe, Nb, Zr \((R_{\text{Fe}} = 0.216 \text{ nm}, R_{\text{Nb}} = 0.208 \text{ nm}, R_{\text{Zr}} = 0.172 \text{ nm})\), we can conclude that the chemical composition of C14-type \(\beta\text{-Fe-Nb}\) phase should be \(Zn(Fe,Nb)\), which means that the lattice constant will increase when Nb atoms replacing Fe. Thus it is reasonable to conclude that the formation of \(\beta\text{-Fe-Nb}\) precipitates can be attributed to the substitution of Fe at 2a, 5h site by Nb in C14 lives phase.

The fact that the Nb and Fe contents could be swapped between two neighboring grains, while maintaining a constant Zr content, offers strong evidence that Nb and Fe can be easily mixed on the B sublattice site of the \(\alpha\text{-Fe}\) stoichiometry of the C14 phase. As this phase structure does not exist as a stable phase in either the \(\beta\text{-Fe}\) or the \(\beta\text{-Nb}\) system, their coexistence is essential to stabilize such a structure in the \(\beta\text{-Fe-Nb}\) system. It is reasonable that the two later transition metals, Nb and Fe, take the same B sublattice sites of the C14 phase, as both play a similar role in stabilizing the same crystal structure of the \(\beta\) phase and thus are of different electronic nature from that of the group IV element Zr.

4. Conclusion
This work shows that a \(\beta\) alloy with the typical 2B0 composition lies in a three-phase equilibrium region containing the ground state phases of \(\alpha\text{-Zr}, \beta\text{-Nb}\), and a ternary C14 Laves phase, which does not exist as an equilibrium phase in the constituent binary systems.

In the current thermomechanically processed material, the \(\beta\text{-Nb}\) and a ternary C14 Laves phases presented in the \(\alpha\text{-Zr}\) matrix as nano-precipitates. Unlike spherical \(\beta\text{-Fe}\) particles about 30 nm in size, these particles were found to precipitate within the \(\alpha\text{-Zr}\) grains, with the \(\beta\) interface being crystallographically coherent, with a Broggi orientation relationship between the two phases. This provides a basis for the unique mechanical properties of the \(\beta\text{-Zr}\) alloy.

Intermetallic nano-particles with the C14 Laves phase structure were found to be the coarser precipitates typically larger than 60 nm in sizes, with the \(Zr(Fe,Nb)\) stoichiometric formula wherein Fe and Nb are mixed on the second sublattice site. Stacking faults were also observed in the typical Laves phase orientation. The orientation relationship between the Laves phase and the matrix was close to \((10\overline{1}0)_{\alpha} m / (2\overline{1}0\overline{1})_{\text{C14}}\) and \((0\overline{1}\overline{1}0)_{\alpha} m / (0\overline{1}1\overline{0})_{\text{C14}}\). The significant difference in the diffraction coefficients of \(\beta\) and \(\gamma\) in the \(\beta\text{-Zr}\) solid solution led to delayed enrichment of \(\beta\) in the C14 phase, with the \(\gamma\text{-Nb}\) rate increasing during the coarsening of the Laves phase.

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