Corrosion Behavior and Oxide Properties of Zr-Nb-Cu and Zr-Nb-Sn Alloy in High Dissolved Hydrogen Primary Water Chemistry

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Outlook

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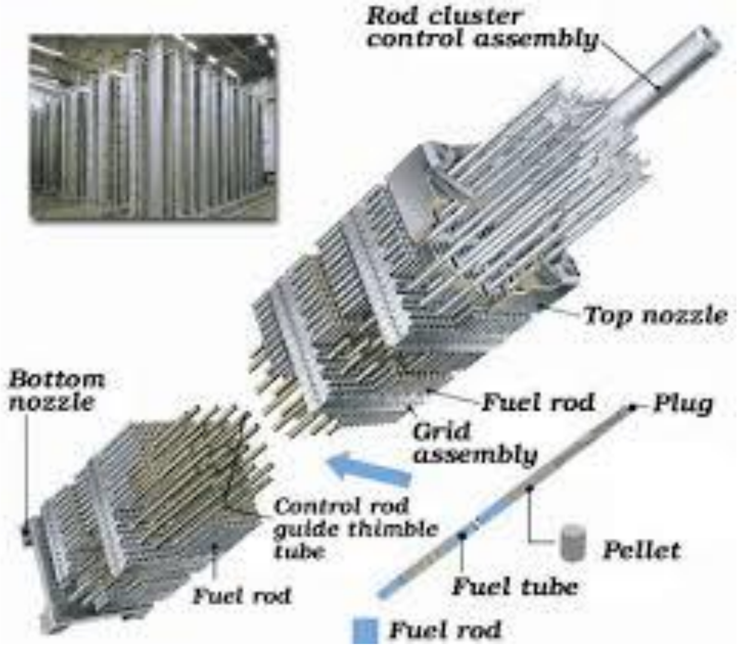
Development of zirconium alloys

- Zirconium alloy characteristic
- Zirconium alloys were commercially developed primarily for use in nuclear reactors as fuel rod cladding and other core components.
- Very low thermal neutron capture cross section as well as desirable mechanical properties.

- A burn-up extension is desirable in context of economics of reactor operation, but it is hard to get without an improvement of zirconium fuel cladding corrosion resistance.



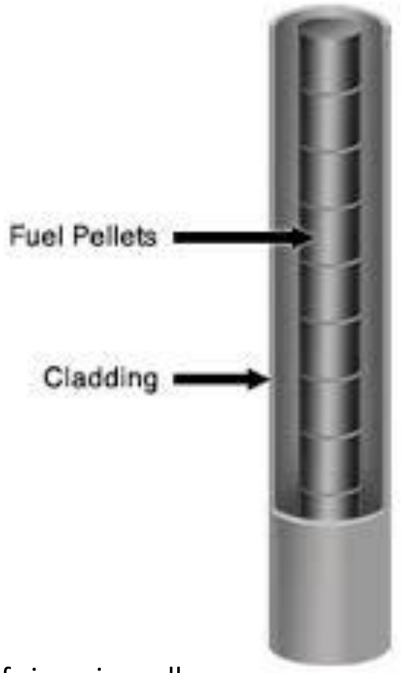


Fig. 1 Fuel assembly of PWR whose cladding is made of zirconium alloy

Corrosion of zirconium alloy

- Zirconium corrosion mechanism

1) Zr corrosion

- $Zr + 2H_2O \rightarrow ZrO_2 + 4H^+$
- Growth of oxide layer on the waterside of Zr cladding during the reactor operation.

2) Hydrogen pick-up behavior in zirconium alloys

- The formation of an oxide layer and the release of hydrogen gas in the coolant according to following equation
- $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$

- Zr oxidation mechanism does not show the pitting or grain boundary corrosion, so the anodic reaction occurs along the oxide/metal interface, generating oxygen vacancies that move through the oxide scale.

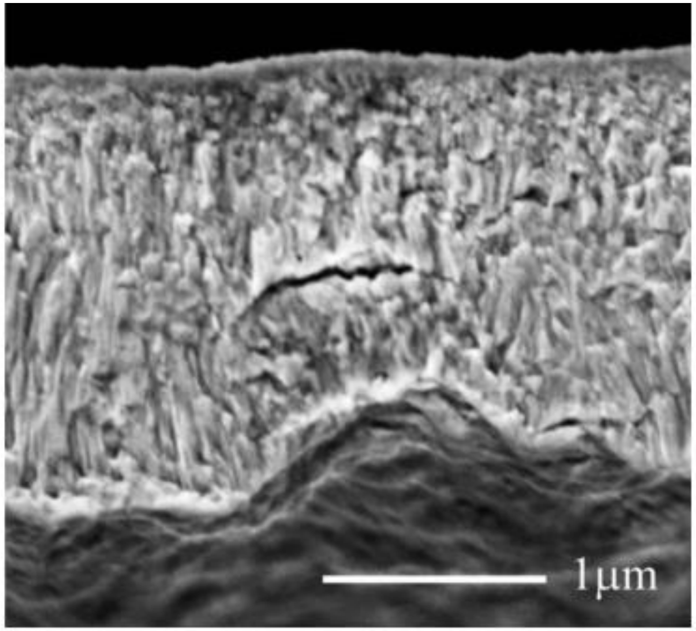


Fig. 2 Details of the microstructure of the oxide pre-transition

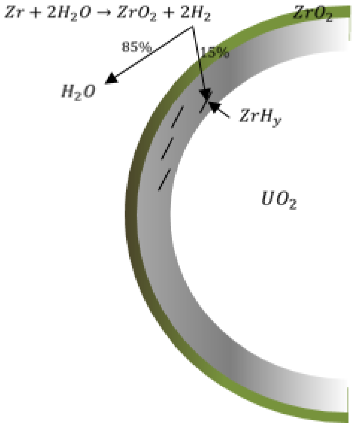


Fig. 3 Hydride formation mechanism in Zr alloy

Characteristic of zirconium oxide

- Tetragonal phase zirconium oxide can be stabilized at lower temperatures (under 1100 ℃) in the presence of high compressive stresses(about 2 GPa).

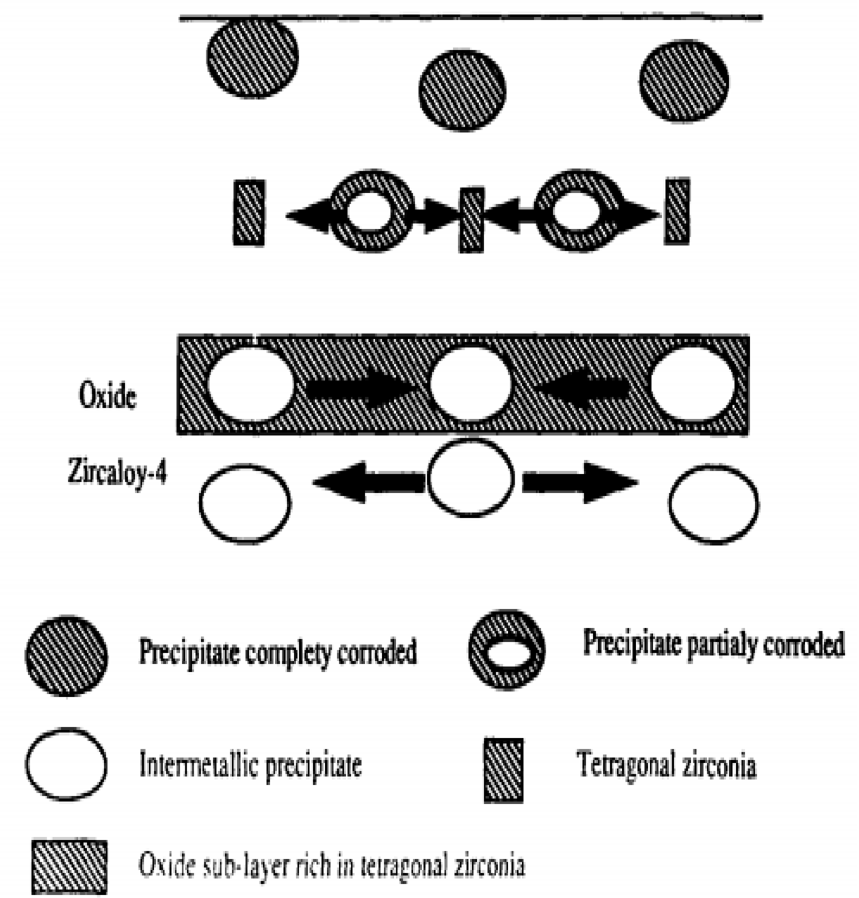


Fig. 4 Procedure that compressive stress occur in oxide layer

- When the zirconium is oxidized to zirconium oxide, stresses are formed due to the volume difference between initial zirconium oxide and newly formed zirconium oxide.
- Some precipitates remain at non-oxidized state.

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- Tetragonal phase zirconium oxide is maintained by the stress which is formed when the precipitates become oxidized .

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- When the precipitates oxidation is over, there are no additional stress so, stress field disappears.

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- The tetragonal zirconium oxide changes into the monoclinic oxide so the stress released. (t→m transformation)

Effects of the transformation on corrosion resistance

- The oxidation of zirconium occurs at oxide/metal interface.
- Oxygen and hydrogen diffuse into oxide/metal interface and oxidize zirconium metal matrix.

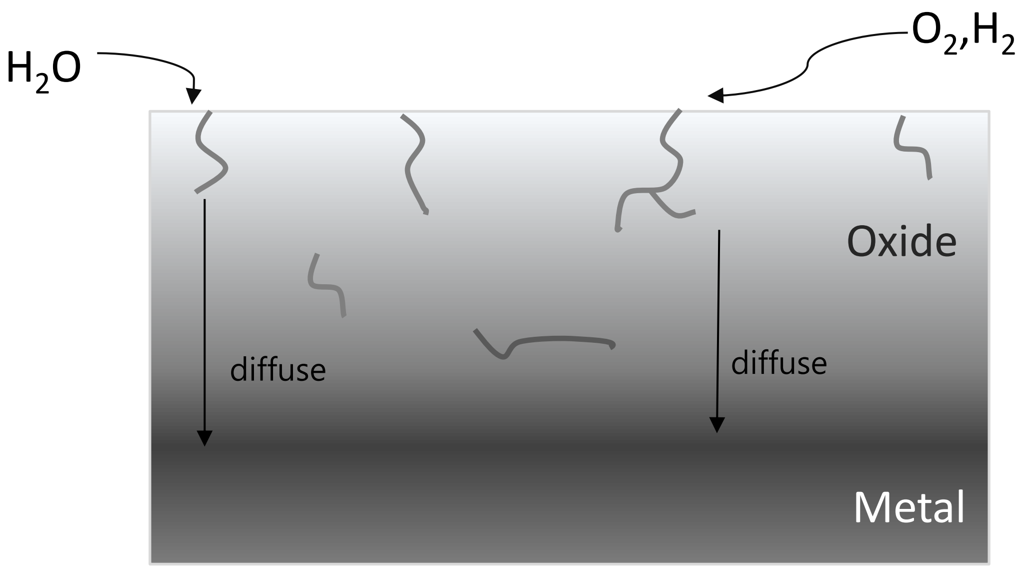

Fig. 5 Schematic diagram of crack and corrosion mechanism of zirconium

- The transformation from tetragonal phase to monoclinic phase makes cracks, and cracks can help diffusion of oxygen and hydrogen.
- The more the transformation from tetragonal phase to monoclinic phase happen, the worse the corrosion resistance is.

Investigation of Zr-Nb-Cu alloy and corrosion resistance

- In many previous results obtained from advanced Zr alloys, a Nb addition was proven to be very beneficial for increasing the corrosion resistance of Zr alloys.
- More recently, Cu addition was reported to be effective for improving corrosion resistance of Nb-containing Zr alloys.
- The effect of dissolved hydrogen on zirconium alloy is floating topic in the research about corrosion of zirconium.
- It is well known that corrosion rate of zirconium alloy is greatly affected by its microstructure.
- By previous researches, the **distribution of tetragonal phase and monoclinic phase of zirconium oxide can be good indicator of corrosion resistance** of the alloy.

[1] Park et al., Journal of Nuclear Materials 340 (2005) [2] Kim et al., Corrosion Science 99 (2015)

Research objective

- Importance of investigation of zirconium alloy corrosion

1) A higher fuel discharge burnup to reduce fuel cycle costs
2) A higher temperature of inlet coolant to increase plant thermal efficiency

→ The corrosion mechanism of zirconium alloy is still not fully understood as yet, and the main factors determining its corrosion rate are the metallurgical characteristics of the zirconium alloy, alloy composition, and water chemistry.

- Investigation of the effect of Cu addition on zirconium alloy corrosion resistance.

- Research on **the effects of Cu addition on Nb containing zirconium alloy corrosion resistance** were not fully being established.
- The purpose of this investigation is to provide additional insight on the relationship between structure of the oxide layer formed by particular chemical composition and corrosion resistance.

[1] Park et al., Journal of Nuclear Materials 340 (2005)

Experimental

- Oxidation environment
  - Primary water chemistry: 360 °C, 19 MPa, DO < 5 ppb, LiOH: 2 ppm, H_3BO_3: 1200 ppm
  - Oxidation time: 20 days
  - Dissolved hydrogen : 50 cm^3/kg

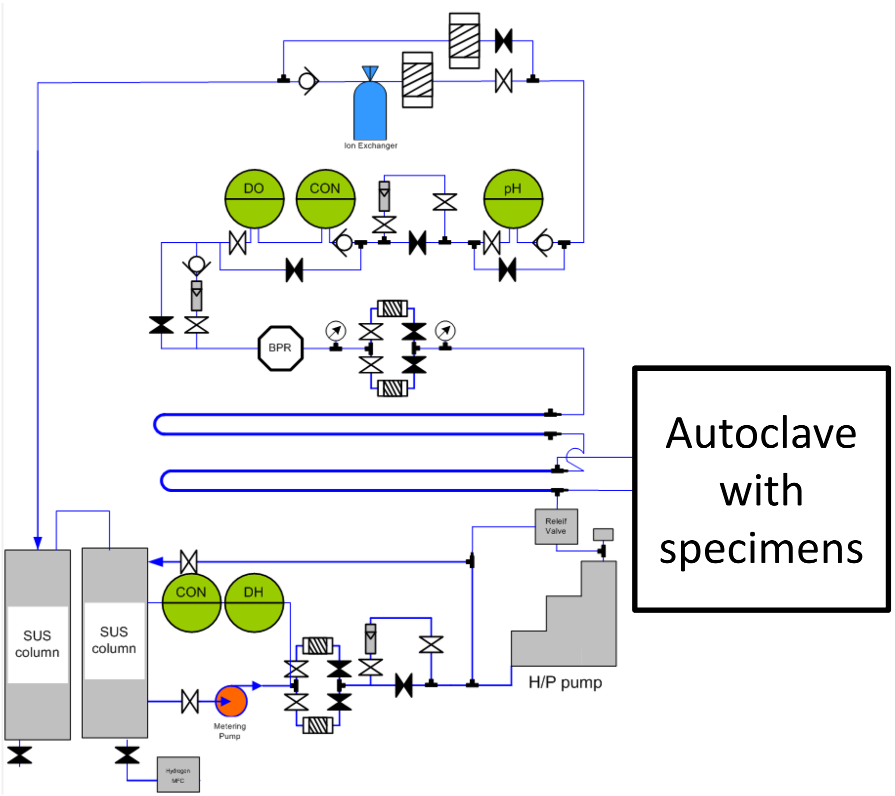

Fig. 6 Schematic diagram of oxidation loop

Fig. 7 Oxidation system which can simulate primary water chemistry of nuclear power plant

Experimental

- Alloy
- Zr-Nb-Cu alloy and Zr-Nb-Sn alloy

Table. 1 composition of two different zirconium alloys (w.t.%)

Alloy	Nb	Sn	Hf	Cu	C	O	N	Fe	Zr
Zr-Nb-Sn	0.96	0.76	0.002	-	0.1	0.62	0.03	0.18	Bal.
Zr-Nb-Cu	0.55	0.06	-	0.12	0.01	-	-	0.07	Bal.

- Specimens size
- Zr-Nb-Cu alloy : 10 mm × 10 mm × 0.75 mm
- Zr-Nb-Sn alloy : 10 mm × 10 mm × 0.6 mm

- Analysis
- Weight gain measurement
- Focused ion beam (FIB) – Scanning electron microscopy (SEM) analysis
- Raman spectroscopy

Weight gain analysis & FIB-SEM analysis

- Weight gain of two zirconium alloys

Table. 2 weight gain of two zirconium alloys

Alloys	Zr-Nb-Cu alloy	Zr-Nb-Sn alloy
Weight gain [mg/dm^2]	18.02	21.69

- FIB-SEM image of two zirconium alloy

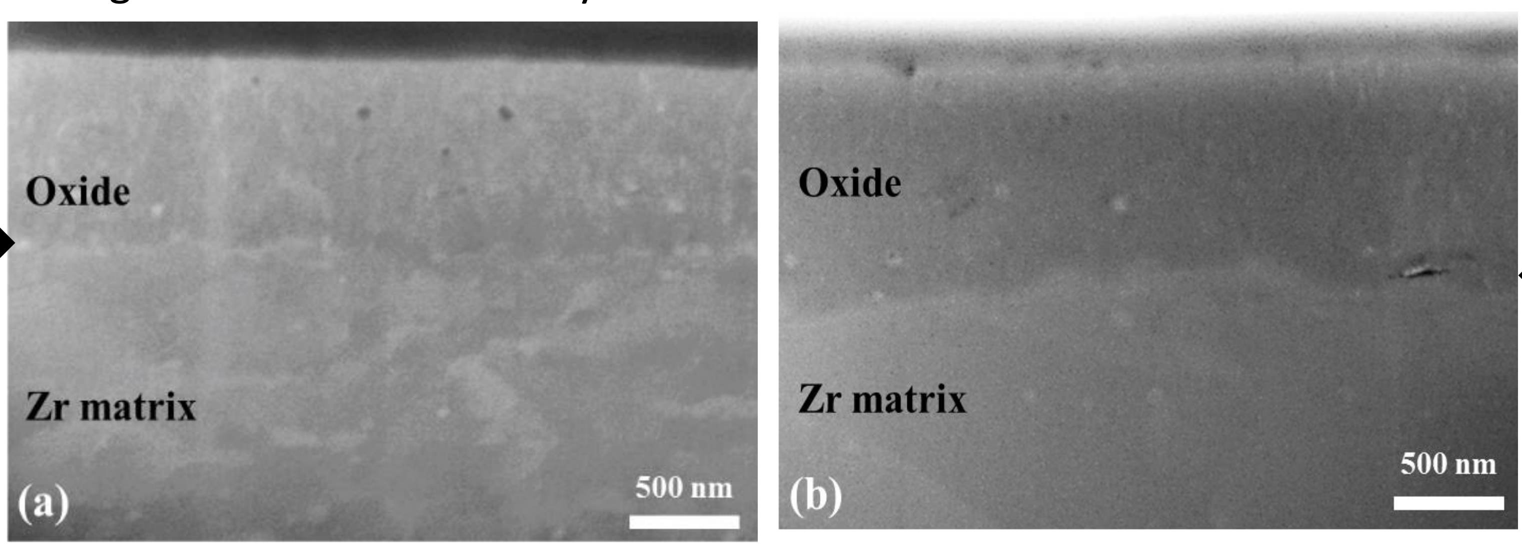

Fig. 8 FIB-SEM image of (a) Zr-Nb-Cu alloy and (b) Zr-Nb-Sn alloy.

- Relatively, Zr-Nb-Cu alloy has thinner and regular oxide layer than Zr-Nb-Sn alloy.

Oxide thickness analysis & Raman spectroscopy analysis

Table. 3 Summarized oxide thickness data of zirconium alloy

Material	Calculated oxide thickness (μm)	Measured oxide thickness (μm)
Zr-Nb-Cu alloy	0.93	1.06
Zr-Nb-Sn alloy	1.45	1.15

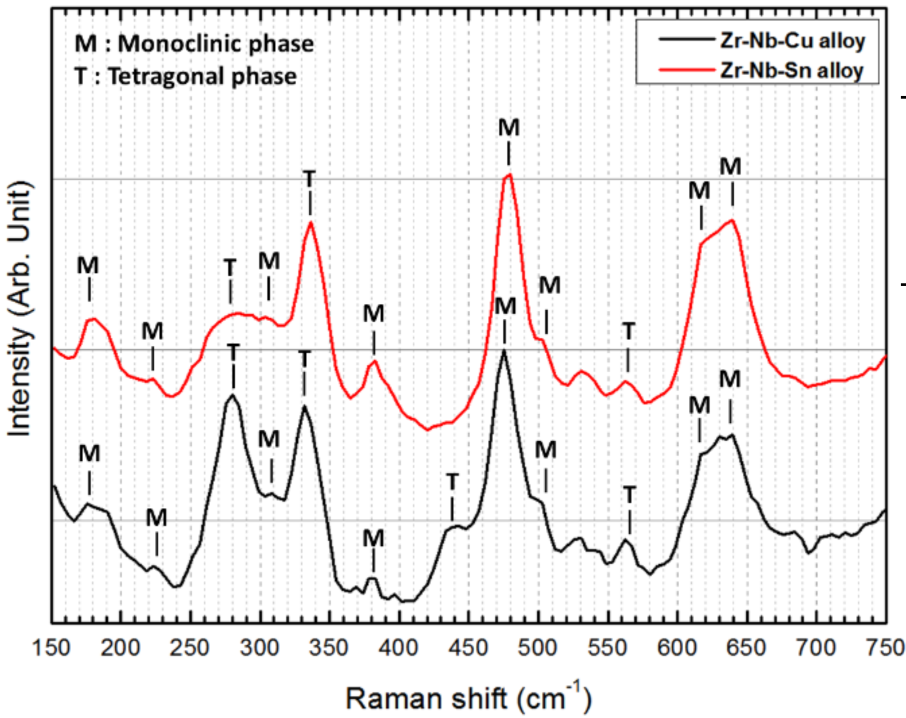

Fig. 9 Measured Raman spectrum of Zr-Nb-Cu alloy and Zr-Nb-Sn alloy oxide excited by a laser at 532 nm at room temperature in air.

Table. 4 Specification of Raman peak position obtained from the two specimens(in cm^{-1})

Zr-Nb-Cu alloy		Zr-Nb-Sn alloy	
Monoclinic	**Tetragonal**	**Monoclinic**	**Tetragonal**
177		179	
224	279*	223	279*
308*	331*	306*	335*
380*		383*	
474	439*	479	
503*		503*	
616	562*	616	562*
639		639	

Oxide phase fraction analysis

- Oxide phase fraction analysis

- With using the following equation, the fraction of each oxide phase can be calculated.

$$\%\mathbf{ZrO_2}_{(T)} = \frac{\sum \boldsymbol{Intensity}_{(T)}}{\sum \boldsymbol{Intensity}_{(T)} + \sum \boldsymbol{Intensity}_{(M)}} \times \mathbf{100}$$

Table. 5 Calculated percentage of tetragonal phase zirconium oxide.

Alloy	Zr-Nb-Cu alloy	Zr-Nb-Sn alloy
% Tetragonal zirconium oxide	41.2	13.8

- Both the fraction of tetragonal and the compressive stress gradient affect to the corrosion resistance of zirconium alloy.

Precipitates of Zr-Nb-Cu alloy and Zr-Nb-Sn alloy

- The distribution and morphology of precipitates have great effects on the compressive stress gradient, and make compressive stress distribute regularly.
- In the previous research, both the oxide of Zr-Nb-Cu and Zr-Nb-Sn alloy have two precipitates. One is β-Nb precipitates and the other is ZrNbFe precipitates.
- β-Nb precipitates show small and roundish shape, and ZrNbFe precipitates show long and facet C-14 Laves phase structure or fcc structure.
- β-Nb precipitates is smaller and observed more frequently than ZrNbFe precipitates.

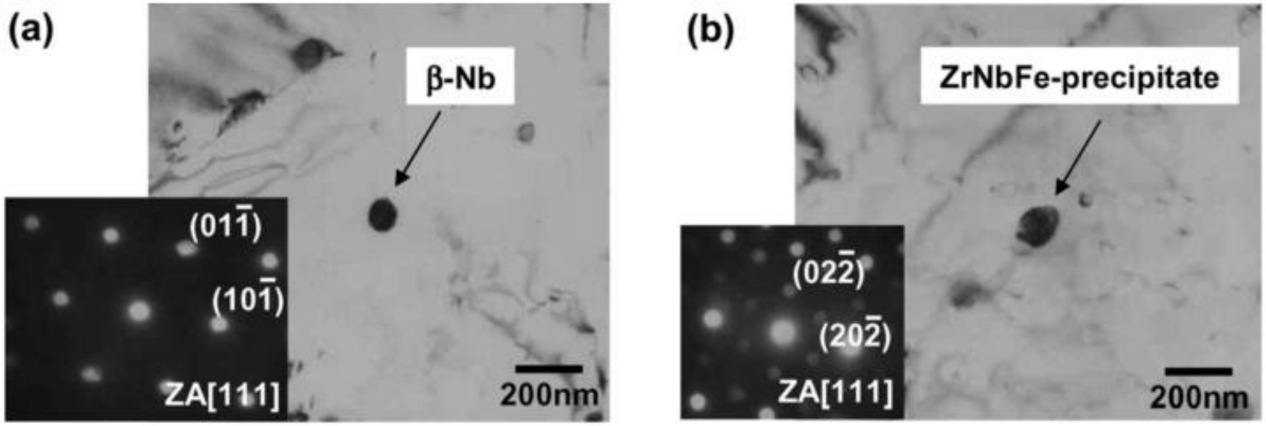

Fig. 10 β-Nb precipitates and ZrNbFe precipitates in Zr-Nb-Cu alloy

Discussion

- Effects of precipitates on compressive gradient

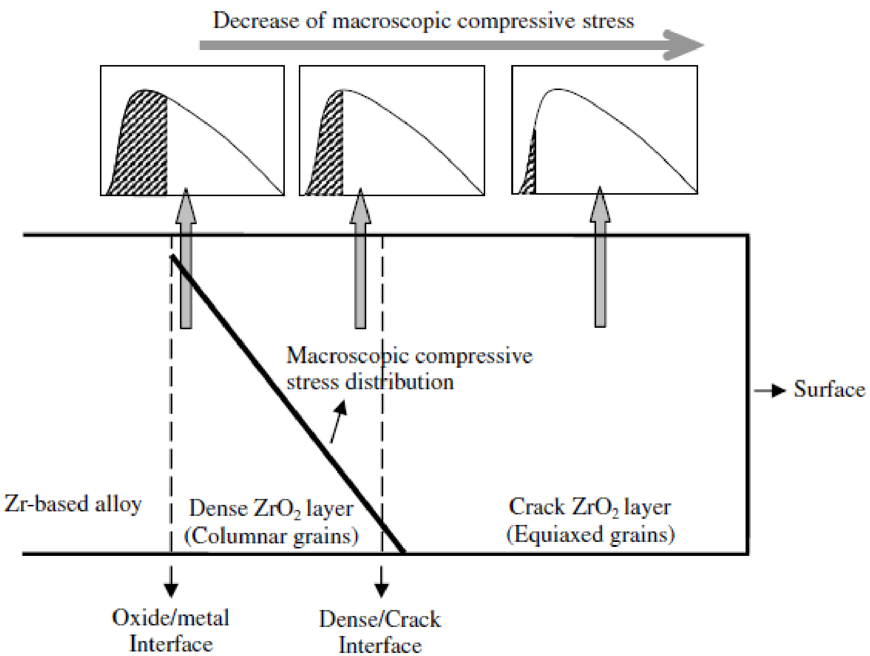

Fig. 11 Fraction of tetragonal phase change according to compressive stress.

- By previous research, the precipitates make compressive stress distributed regularly and make additional compressive stress when it is oxidized, and the compressive stress gradient becomes gradual.
- The lower gradient of compressive stress may reduce the t→m transformation due to the small size precipitates.

- As compressive stress gradient is small, the amount of t→m transformation decreases.
- As the fraction of small size of β-Nb precipitates increase the corrosion resistance increases.

[1] Qin et al. Acta Materialia 55 (2007)

Discussion

- Effects of intermetallic precipitates on the internal stress
  - The internal stress, produced in the t→m transformation can be effectively relaxed through the deformation of precipitates.
  - Due to intermetallic precipitates, the strain energy will be reduced because elastic moduli of metals are generally smaller than that of oxide.
  - The oxidation of β-Nb precipitates is slower than ZrNbFe precipitates.
  - As the quantity of β-Nb precipitates is larger, the corrosion resistance of the alloy increases.
- Effect of solute element on corrosion resistance
  - Solute elements like Sn and Nb cause segregation when it oxidized.
  - Oxidization of solute elements causes the cracking.
  - Most of Nb elements exist as β-Nb precipitates.
  - Sn-containing zirconium alloy shows higher corrosion rate than Nb-containing zirconium alloy.

[1] Qin et al. Acta Materialia 55 (2007) **[2] Park et al., Journal of Nuclear Materials 340 (2005) [3] Park et al., Journal of Nuclear Materials 359 (2006)**

Conclusion

- **Corrosion resistance of zirconium alloy is greatly affected by phase transformation** from tetragonal phase to monoclinic phase of zirconium oxide.
- The **corrosion resistance of Zr-Nb-Cu alloy was better** than that of Zr-Nb-Sn alloy.
- The compressive gradient is affected by morphology and distribution of precipitates in zirconium oxide.
- The fraction of **tetragonal phase is larger at Zr-Nb-Cu alloy than that of Zr-Nb-Sn alloy**, but the compressive stress gradient is steeper at Zr-Nb-Sn alloy, because of precipitates distribution.
- **β-Nb precipitates effectively make the distribution of compressive stress regularly** and **form additional compressive stress** when it oxidized, it is helpful to form a gentle slope of the compressive stress gradient.
- **Zr-Nb-Cu alloy shows higher fraction of β-Nb precipitates** than Zr-Nb-Sn alloy.
- **Sn addition on zirconium alloy shows low corrosion resistance** because it is segregated when it oxidized.

Thank you for your attention!