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(Ⅲ)

# Effects of Alloying Elements on Nodular and Uniform Corrosion Resistance of Zirconium-Based Alloys

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ABSTRACT: The effects of alloying and impurity elements (tin, iron, chromium, nickel, niobium, tantalum, oxygen, aluminum, carbon, nitrogen, silicon, and phosphorus) on the nodular and uniform corrosion resistance of ziconium-based alloys were studied. The improving effect of iron, nickel and niobium in nodular corrosion resistance were observed. The uniform corrosion resistance was also improved by nickel, niobium and tantalum. The effects of impurity elements, nitrogen, aluminum and phosphorus were negligibly small but increasing the silicon content seemed to improve slightly the uniform corrosion resistance. Hydrogen pick-up fraction were not changed by alloying and impurity elements except nickel. Nickel addition increased remarkably hydrogen pick-up fraction. Although the composition of secondary precipitates changed with contents of alloying elements, the correlation of composition of secondary precipitates to corrosion resistance was not observed.

*KEY WORDS: zirconium, Zircaloy,* nodular corrosion, uniform corrosion, alloying elements, impurities, hydrogen absorption, precipitates

## 1. INTRODUCTION

Zirconium alloys, called Zircaloy-2 and Zircaloy-4, have shown good in-reactor corrosion performance as cladding tube materials for light water reactor fuels. However, under extended in-reactor exposure conditions, their corrosion resistance is regarded as a potential and important life-limitting factor of fuels.

At the earliest stage of the development of Zircaloys, extensive works about the effects of alloying elements on the uniform corrosion properties were done and reported[1]. To develop candidate cladding materials for the extended *burn-up fuels, further* basic corrosion data about the effects of chemical compositions on the nodular and uniform corrosion resistance of zirconium based alloys are needed.

In this study, the effects of chemical composition on corrosion resistance of zirconium-based alloys were studied by out-of-pile autoclave tests in steam and water at elevated temperatures.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Specimens

Zirconium-based alloy specimens were prepared by non-consumable arc melting followed by hot rolling, cold rolling and annealing. The range of contents of alloying and impurity elements for these specimens were shown in Table-1.

Table 1- Composition of test specimens

| Type of Alloys | Element | Range of Content |
|---|---|---|
| Zircaloy | Sn | 0.1 - 2.2 wt.% |
| | Fe | 0.11 - 0.35 |
| | Cr | 0.01 - 0.28 |
| | Ni | 0.01 - 0.18 |
| | Nb | 0.00 - 1.0 |
| | O | 0.10 - 0.28 |
| | N | 40 - 170 ppm |
| | Si | 67 - 170 |
| | Al | 82 - 150 |
| | P | 40 - 95 |
| Binary Alloy | V | 0.01 - 1.02 wt.% |
| | Nb | 0.10 - 1.03 |
| | Ta | 0.10 - 0.95 |

### 2.2 Testing

Nodular and uniform corrosion resistance were tested using autoclave furnaces in static conditions *with high pressure steam* at 773 K *or water at* 633 K, respectively. Test durations were 24 hours for nodular corrosion tests and 7200 hours totally for uniform corrosion tests. The appearnaces of test specimens and weight gains were evaluated. Hydrogen concentration of specimens which were tested at 633 K for 7200 hours were analysed by the vacuum extraction technique.

## 3. RESULTS AND DISCUSSION

### 3.1 Nodular Corrosion Resistance

The effects of variation of alloying elements contents in Zircaloy-2 and the addition of niobium to Zircaloy-2 and Zircaloy-4 on the nodular corrosion resistance were shown in Fig.1. Tin and oxygen had slightly harmful effects on the nodular corrosion resistance and chromium had little effect. Remarkable effects of iron and nickel were observed. The addition of iron and nickel in amounts to 0.05% and 0.1 % improved the nodular corrosion resistance. The addition of iron and nickel in amounts over 0.1 to 0.2%, respectively, was not so usufu l. The modification of alloy contents in Zircaloys to improve the nodular corrosion resistance could be do ne by both lowering the content of tin and by increasing the contents of iron, chromium, and nickel within the specification limits.

The addition of niobium to Zircaloys was also effective in improving the nodular corrosion resistance. The effect in Zircaloy-4 was more remarkable than in Zircaloy-2. The difference of this effectiveness was attributed to the lack of nickel as an alloying element in Zircaloy-4. Although the addition of niobium to Zircaloys is effective in improving the nodular corrosion resistance, adding in amounts over 0.5% seemed to deteriorate the uniform corrosion resistance. The optimum content for better resistance to both nodular and uniform corrosion would be from 0.05 to 0.3 %.

### 3.2 Uniform Corrosion Resistance

The effects of alloying and impurity elements on the uniform corrosion resistance in 633 K water were evaluated by the corrosion rate exponent( n ) before and after transition defined as a following equation:

$$Wg = Wo \cdot t^{n} \quad (mg/dm^2)$$

where Wg is weight gain, Wo is a constant, t is test duration, and n is the corrosion rate exponent. The effects of alloying elements were shown in Fig.2. The corrosion rate exponents before transition remained constant, approximately 0.3, regardles of the contents of alloying elements for all alloys.

In the post-transition region, the corrosion rate exponents increased with tin content for both Zircaloy-2 and Zircaloy-4. Iron and chromium had no effects and the exponents were around one. The alloy without nickel(similar composition to Zircaloy-4) had a slightly larger corrosion rate exponent but the alloys containing nickel over 0.05 wt.% had the same exponents, approximately one, as other alloys.

The effects of oxygen and impurity elements were shown in Fig.3. The corrosion rate exponents before and after transition increased with oxygen contents. The effects of other elements were comparably small. Among these impurities, silicon seemed to be an attractive and potential element to improve the uniform corrosion resistance of zirconium-based alloys. Although it has been reported that nitrogen had detrimental effect to the corrosion properties of zirconium alloys, negligible effect of nitrogen was observed within the amount upto 200 ppm in this study.

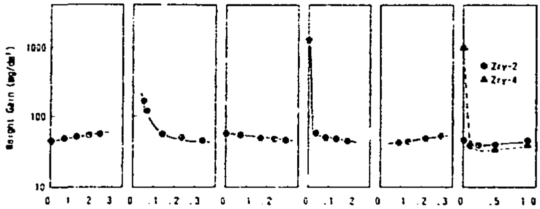

Fig.1- Effect of tin, iron, chromium, nickel, and niobium on nodular corrosion in Zircaloys.

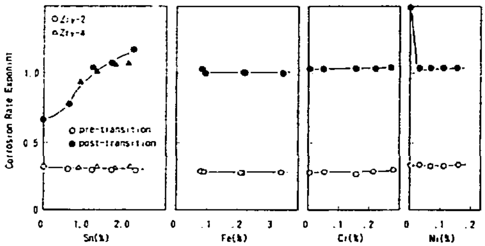

Fig.2- Effect of tin, iron, chromium, and nickel on corrosion rate exponents in 633 K water.

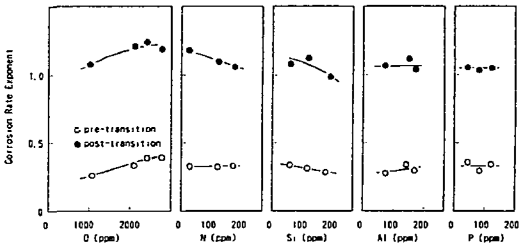

Fig.3- Effect of oxygen and impurity elements on corrosion rate exponent in 633 K water.

The effect of vanadium, niobium and tantalum in the zirconium-based binary alloys were shown in Fig.4. Niobium and tantalum had improving effects in uniform corrosion resistance, but not for vanadium. Tantalum is a very interesting element for the improvement of long term uniform corrosion resistance by eliminating the rate transition from cubic or palabolic to linear. As Zr-1%Ta alloy corroded with parabolic law rate through the testing, this alloy would show the lower weight gain after a long term exposure than Zircaloys which had the clear corrosion rate transition from cubic to linear.

### 3.3 Hydrogen Pick-up

The effects of alloying elements on hydrogen pick-up fraction for Zircaloy-2 and Zircaloy-4 after 7200 hours test in 633 K water were shown Fig.5. The effects of variation of contents of tin, iron and

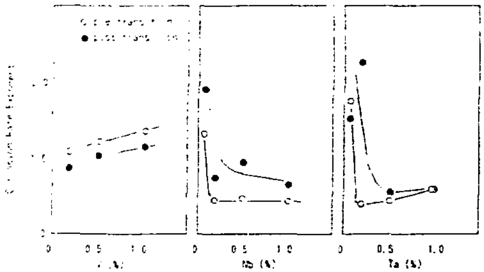

Fig.4 Effect of vanadium, niobium, and tantalum on corrosion rate exponent in 633 K water.

chromium were negligibly small. On the other hand, hydrogen absorption remarkablly increased with nickel contents(Fig.5-d). These results were consistent with the earlier studies[1]. The reason for the larger hydrogen pick-up fraction in Zircaloy-2 than Zircaloy-4 was the presence of nickel as a alloying element.

### 3.4 Second Phase Particle

It is recognized that there are essentially two kinds of precipitates in Zircaloy-2, namely $Zr(Fe,Cr)_2$ and $Zr_2(Fe,Ni)$[2]. The ratios of iron to chromium (Fe/Cr ratio) and iron to nickel (Fe/Ni) for the precipitates, respectively, were determined by Analytical Transmission Electron Microscopy and their relation to the uniform corrosion resistance was studied.

The Fe/Cr and Fe/Ni ratios for standard Zircaloy-2 were approximately 0.9 and 1.1 respectively. These ratios changed systematically with the change of contents of iron, chromium and nickel, except that Fe/Ni ratio decreased with chromium contents. The possible explanations of this result are many fine precipitations of un-detectable $Zr(Fe,Cr)_2$ and/or preferential precipitation of iron as $Zr(Fe,Cr)_2$ than as $Zr_2(Fe,Ni)$.

Although there were considerablly large and systematic variations in the compositions of secondary particles with contents of alloying elements, systematic variations in the corrosion resistance corresponding to the compositions of secondary particles was not observed. The corrosion resistance of these zirconium based alloys is thought to be affected by solute elements but not by the compositions of secondary precipitates.

### 3.5 Oxide Morphology

The oxide transformation from tetragonal to monoclinic structure near the metal/oxide interface and its correlation to the corrosion rate transition were reported[3]. The oxide structure formed during the corrosion tests of Zircaloys containing different contents of tin was examined by X-ray diffraction and transmission electron microscopy. In the low tin alloy which showed better uniform corrosion resistance, small amounts of cubic and un-identified zirconium oxides other than monoclinic structure were observed at the metal/oxide interface. Further, tetragonal oxide on

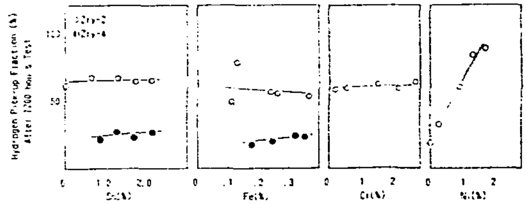

Fig.5- Effect of tin, iron, chromium, and nickel on hydrogen pick-up fraction in 633 K water.

the outer surface of specimen was also detected. On the other hand, in the high tin alloy which showed poor corrosion resistance, no other oxide than monoclinic structure was observed in the oxide.

The stability of oxides, transformation behavior of oxide, seems to be an controling factor of the corrosion behavior of zirconium based alloys. Further research on the transformation mechanism of the oxide is required.

## 4. CONCLUSIONS

The summary of this study are as follows:

(1) The effects of alloying element (tin, iron, chromium, and nickel) on the nodular corrosion resistance of Zircaloys were comparatively small within the limit of ASTM standards. For the improvement of nodular corrosion resistance, lower tin content and higher iron and nickel contents are preferable. The addition of small amounts of niobium is effective to improve the nodular corrosion resistance of Zircaloys.

(2) The effect of alloying elements(iron, chromium and nickel) on the uniform corrosion resistance were negligible within the specification limits. Tin, however, increased the post-transition corrosion rate, and oxygen seemed to increase the post transition corrosion rate too. Nickel increased the hydrogen pick-up fraction. The effects of impurity elements on the uniform corrosion resistance in Zircaloys were also negligible.

(3) Zirconium-based binary alloys with niobium and tantalum were resistant to uniform corrosion and Zr-Ta alloys, especially, seened to be potentially resistant to uniform corrosion without showing the corrosion rate transition.

(4) Although the compositions of secondary particles in Zircaloys changed with the contents of alloying elements, their correlation to the uniform corrosion resistance was not observed. The corrosion behavior is thought to be related to the properties of oxide films, but the clear relation between the oxide structure and corrosion resistance was not observed in this study.

## REFERENCES


[1] Kass,S. in Corrosion of Zirconium Alloys, ASTM STP368, 3 (1963)

[2] Inagaki, M. et al. J. Atomic Energy Soc. of Japan, Vol.32, No.5, 498 (1990)

[3] Bradley, E. R. and Perkins, R. A., IAEA Technical Committee Meeting, Portland, Ore., Sep. (1989)