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DEVELOPMENT OF NEW ZIRCONIUM BASED ALLOYS FOR BURN-UP EXTENSION OF LIGHT WATER REACTOR FUELS
(I)
Development of Highly Corrosion Resistant Zirconium-Base Alloys

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Abstract : Steam corrosion tests and tensile tests were conducted to investigate the effects of alloying elements such as Sn, Nb, Fe, Cr, Mo and V, and the mechanical properties of Nb-containing Zr-base alloys. The corrosion resistance of Zr-base alloys in comparison to Zr'y-4 was significantly improved by the reduction of the Sn content by 0.5wt% and by a small addition of Nb (about 0.05 to 0.2wt%). However, the decrease in solute Sn atoms degraded mechanical properties. The increase of the total content of Fe and Cr from 0.3 to 0.7wt% improved the mechanical properties without affecting the corrosion resistance. The decrease of the Fe/Cr ratio from 6.0 to 0.5 increased the corrosion resistance. Small addition of Mo and/or V resulted in a further improvement of mechanical properties. Based on these experiments, three Nb-containing Zr-base alloys with equivalent mechanical properties and superior corrosion resistance to Zr'y-4 were developed.
Key words : Zr alloys, Sn, Nb, Fe, Cr, Mo, V, uniform corrosion, corrosion resistance, tensile property

1. INTRODUCTION

Zr'y-4 has been used extensively as a cladding material in PWRs. However, the recent trend toward extended burn-up in PWR fuel has led to the need for improved waterside corrosion resistance of Zr'y-4 fuel claddings. Many studies on the corrosion behavior of Zr'y-4, especially uniform corrosion, have been performed by in-pile and out-of-pile corrosion tests. The test data have shown the beneficial effect of the added Nb on the corrosion resistance of Zr-base alloys.[1,2,3] In this work, autoclave corrosion tests and tensile tests were performed on the Nb-containing Zr-base alloys to investigate the effects of alloying elements such as Sn, Nb, Fe, Cr, Mo and V. Subsequently, alloys for the high performance cladding material were developed.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

The materials used in this study were melted into about 300g button ingots by nonconsumable Ar arc melting. As input materials, sponge Zr(nuclear grade), Zr'y-4 sheets(ASTM B-353) as Sn source, and Fe(purity:99.9%), Cr(99.9%), Nb(99.9%), Mo(99.9%), and V(99.7%) flakes were used. Table 1 summarizes the studied chemical composition ranges of the alloying elements. The button ingots were converted to about 0.5mm-thick sheets by means of a standard Zr-alloy processing sequence (fig.1). Sheet materials were finally annealed in either stress relieved or fully recrystallized conditions.

2.2 Experiments

Corrosion tests - Long-term corrosion tests were performed on the stress relieved materials in steam at 673K for 300 days at a pressure of 10.3Mpa in static autoclaves. The general procedures were in accordance with the ASTM Practice for Aqueous Corrosion Testing of Samples of Zr and Zr Alloys (G2).

Tensile test - Materials for tensile testing were cut from the sheets, with the longitudinal direction perpendicular to the rolling direction, and then fully recrystallized. Tensile tests were conducted at room temperature using Instron-type testing machine in accordance with the ASTM Methods of Tension Testing of Metallic Materials (E8).

Table 1 · Composition range of materials

Element	Studied Range (wt%)	Zr'y-4 nominal
Tin	0.5 to 1.5	1.5
Iron + Chromium	0.3 to 0.7	0.3
Niobium	0.05 to 1.0	-
Molybdenum	0.05 to 0.5	-
Vanadium	0.1 to 0.5	-

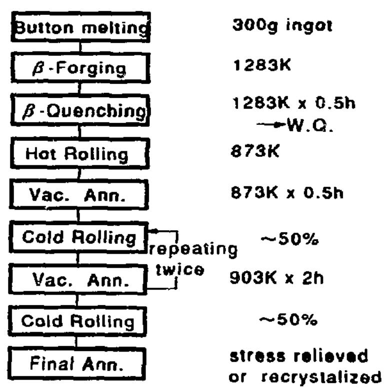

FIG. 1 - Processing sequence of sheet materials investigated

3. RESULTS AND DISCUSSION

3.1 Effect of Nb

Fig.2 shows the effects of the Nb content on the weight gains in steam at 673K for 300 days as a function of the Sn content. Corrosion tests on Nb free Zr-1.0Sn-0.2Fe-0.1Cr and Zr-1.5Sn-0.2Fe-0.1Cr alloys were abandoned in 120 days because of the heavy corrosion. Small additions (0.05 to 0.2%) of Nb reduced the weight gains to a significant extent, while additions of Nb more than about 0.2% lead to an increase in weight gain. As shown in fig.2, this tendency is observed in the range of Sn from 0.5 through 1.5%. And with decreasing Sn content, weight gains generally decreased, that is, corrosion resistances increased. Thus the corrosion resistance of Zr-base alloys, especially Zr'y-4, could be significantly improved by the reduction of the Sn content to 0.5% and a small addition of Nb (about 0.05 to 0.2%).

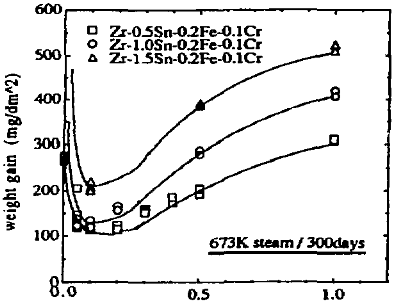

FIG. 2 - Weight gains as a function of Nb content at 673K for 300days as a parameter of Sn content

The tensile properties at room temperatures are plotted as a function of Sn and Nb contents in figs.3(a) and 3(b), respectively. Ultimate tensile strength (U.T.S.) and 0.2% yield strength (0.2%Y.S.) decreased with decreasing Sn content.

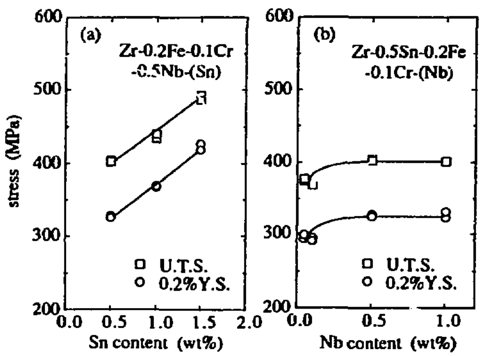

FIG. 3(a) (b)- Tensile strength as a function of (a) Sn and (b) Nb content at room temperature

The tensile strength increased with increasing Nb content up to 0.5%, but didn't change with further additions of Nb. The saturation of strength seems to relate to the precipitation of Nb. Moreover, it was found that the increase in strength by the addition of Nb was not enough to compensate for the decrease in strength due to the reduction in Sn content.

3.2 Effects of Fe and Cr

Fig.4(a) and 4(b) indicate the effects of the total content of Fe and Cr on the corrosion and tensile properties, respectively. With increasing total content of Fe and Cr from 0.3%, the nominal content of conventional Zr'y-4, to 0.7%, weight gain decreased slightly; however, its effect on corrosion was smaller than those of Sn and Nb. On the other hand, tensile strength was considerably improved with increasing total content of Fe and Cr. Fe and Cr addition compensate mechanical properties without affecting the corrosion resistance.

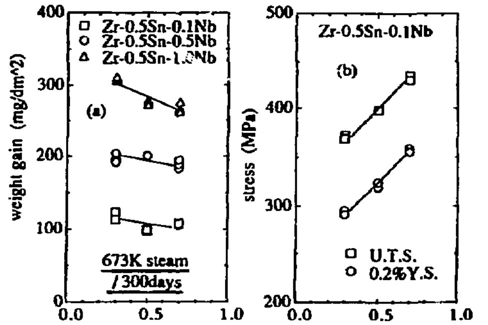

FIG. 4(a) (b) - (a)Weight gains and (b)Tensile strength as a function of total content of Fe+Cr

Fig.5(a) indicates a dependence of weight gains on Fe/Cr ratio in the alloy. The weight gain increases with increasing Fe/Cr ratio from 0.5 to 6.0. As shown in fig.5(b), when either Fe or Cr content was increased independently, Cr increased the strength but Fe had no effect.. These results seem to be related to the microstructure.

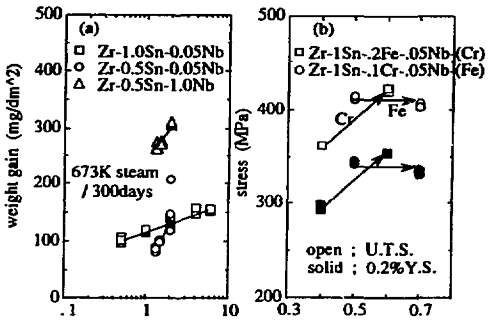

FIG. 5(a) (b) - (a)Weight gains as a function of Fe/Cr ratio (b)Tensile strength for alloys increased either Fe or Cr

3.3 Effects of Mo and V

The effects of Mo and V on the weight gain are shown in fig.6(a). The addition of Mo and V increases the weight gains. In the case of Mo, the degradation of corrosion behavior saturates at higher Mo contents. Tensile strengths increase with increasing content of Mo and V as shown in fig.6(b). The strengthening effect of Mo seems to saturate at a concentration of about 0.5%. Since these elements are generally harmful for corrosion resistance, the addition of these elements should be limited to 0.1%.

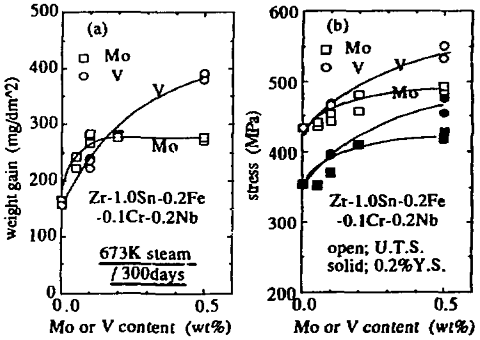

FIG. 6(a) (b) - (a)Weight gains and (b)tnsile strengthes as a function of either Mo or V content

3.4 Candidate alloys for high corrosion resistance

On the basis of the experimental results, three Nb-containing Zr-base alloys were designed in order to develop an alloy with superior corrosion resistance and equivalent mechanical properties to conventional Zr'y-4. Their compositions are listed in table 2. These three alloys were vacuum arc melted into about 5kg-ingots and were fabricated into sheets (about 1.0mm thickness) in accordance with the industrial Zr'y-4 processing. The sheet and Zr'y-4 tube specimens were subjected to the corrosion tests in steam (673K) and tensile tests at room temperature and at elevated temperature (658K) under the same testing conditions as described above. The corrosion and tensile test results for these alloys are compared in fig.7 and table 3, respectively, with those of standard Zr'y-4 tubes manufactured by our company.

Corrosion weight gains for 300 days of the candidate alloys were lower by about 20 to 50% than that of standard Zr'y-4. Moreover, as to the mechanical properties, 0.2% yield strengths (0.2%Y.S.) were nearly equal to those of Zr'y-4 at room and elevated temperatures. Thus the desired alloys were obtained.

Table 2 - Ingot chemical analysis

Element	Alloy compotision wt%		
	VAZ-01	VAZ-02	VAZ-03
Sn	0.99	0.55	0.73
Fe	0.17	0.18	0.20
Cr	0.089	0.089	0.36
Nb	0.21	0.21	0.21
Mo	----	0.090	----
V	----	0.094	----

Table 3 - Tensile properties of Candidate alloys

Alloy	Room Temp. 298K		Elevated temp. 658K	
	Yield Strength MPa	Elong. %	Yield Strength MPa	Elong. %
VAZ-01	405	30.4	130	37.2
VAZ-02	432	31.3	131	32.8
VAZ-03	431	28.4	130	35.7
Zircaloy-4 *	~392	~35	~137	~48

* manufactured by this company
Tensile test ; Recrystallized
Corrosion test ; Stress relieved

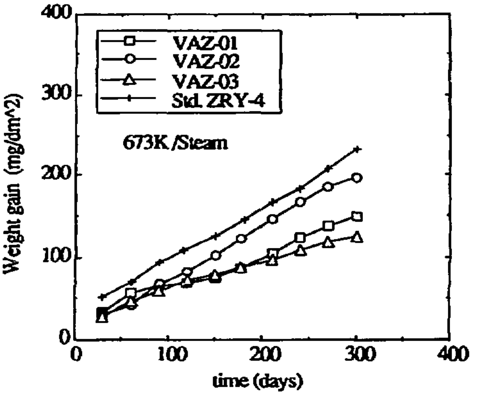

FIG.-7 Weight gains as a function of exposure time for candidate alloys

4. CONCLUSIONS

—The corrosion resistance is improved to a significant extent by the reduction of the Sn content down to 0.5wt% and a small addition of Nb (about 0.05 to 0.2%) ,but the mechanical property is degraded.

—The increase of the Fe and Cr contents results in the improvement of the tensile strength without affecting the corrosion resistance.

—With the increase of the Fe/Cr ratio, corrosion resistance tends to decrease in the Nb-containing Zr-base alloys, different from the conventional Zr'y-4.

—The small addition of Mo and V results in a further improvement of the mechanical properties without a considerable degradation of corrosion resistance.

—The data obtained in this work have led to the design of Nb-containing Zr-base alloys with superior corrosion resistance and equivalent mechanical properties to Zr'y-4.

Acknowledgments

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