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Effects of copper addition on the tensile properties and microstructures of modified Zircaloy-4

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Abstract

The effects of the copper content on tensile properties and microstructures of modified Zircaloy-4 (Zry-4) were investigated. The modified alloys were prepared by changing the chemical composition of Zry-4; the Fe/Cr ratio of Zry-4 was reduced from 2 to 0.5 and the Cu content was varied from 0 up to 0.5 wt%. The ultimate tensile strength (UTS) and the yield stress (YS) of the modified Zry-4 increased significantly with the increase in copper content. 0.1 wt% copper could make up the decrease in strength resulting from the reduction of tin content. Three types of precipitates, $Zr(Fe,Cr)_2$, $Zr(Fe,Cr,Cu)_2$ and Zr_2Cu, were found in the present study. The average size and the area fraction of precipitates increased as the copper content increased. The higher tensile strength is believed to be due to the higher precipitate fractions. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Zircaloy (Zry-4) is used as a nuclear fuel cladding material due to its satisfactory oxidation resistance under current PWR operating conditions. However, recent trends toward extended fuel-burnup and high-pH operation have led to the need of improving oxidation resistance of the Zry-4 cladding. Considerable efforts are devoted to the development of advanced cladding materials, especially by modifying the chemical composition of Zry-4 [1–5]. It is well known that the oxidation resistance of Zry-4 is improved by reducing the tin content [1,2]. However, the reduced tin content decreases ultimate tensile strength and yield strength [3,4]. Recently, a modified Zry-4 alloy has been developed by reducing the tin content from 1.0 to 0 wt% and by adding oxygen up to 0.8 wt% [3]. Oxygen has originally been added to compensate for the decrease in strength resulting from the reduction of the tin content. The oxygen addition has shown a marked improvement in the mechanical strength, but it has degraded the oxidation resistance. Some studies on adding copper to zirconium alloys have been performed [6,7]. Copper has been reported to improve the oxidation resistance in Fe–Cu–Zr alloys [7]. However, no systematic study of the effect of copper on the oxidation has been performed and little is known about the effect of copper on the mechanical properties.

The objective of this work is to investigate the effect of copper on the tensile properties and to find the optimum copper content to compensate the loss of strength due to the reduction of tin content that improves the oxidation resistance. Also, the effect of copper content on the microstructure has been investigated.

2. Experimental

2.1. Specimens

Two classes of modified Zry-4 specimens were prepared by changing the chemical composition of Zry-4. Both types of specimens have the standard tin content (1.5 wt%). In the first class, the Fe/Cr ratio of Zry-4 was reduced to 0.5 and the copper content was varied from 0 up to 0.5 wt%. In the second class, the Fe/Cr ratio of Zry-4 was maintained at 2. In addition, the copper

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content was increased up to 0.5 wt%. The chemical compositions of the modified Zry-4 alloys are presented in Table 1.

The specimens for tensile tests were prepared by the procedures as shown in Fig. 1. Reactor grade pure Zr and alloying elements were arc melted into 200 g button type ingots. The buttons were remelted seven times for homogenization of the alloying elements. The homogenized ingots were beta forged at 1010°C and quenched into water. After beta quenching, procedures for hot rolling at 700°C and cold rolling were followed. The tensile test specimens were machined from the plates that were cold rolled and annealed at 700°C. The oxide scale formed on the plates during the thermomechanical treatments was removed by mechanical polishing and pickling in a mixed solution of 10% HF, 45% HNO_3 and 45% H_2O before the test specimens were machined.

2.2. Tensile tests

Tensile tests were performed at room temperature at a strain rate of 5.2×10^{-4} s^{-1} by using a SATEC tensile testing machine with the maximum load capacity of 10 000 kg. The tensile test specimens were made along the rolling direction with a gauge length of 25 mm, a width of 6 mm and a thickness of 1 mm. The specimens were mechanically and chemically polished in a solution of 10% HF, 45% HNO_3 and 45% H_2O in order to remove any surface defects. A total of three runs per each specimen were carried out and both of the ultimate tensile strength and the yield stress were measured. The standard deviation of the results was ±5 MPa.

2.3. Microstructural analysis

The size and the distribution of precipitates in the specimens were observed by SEM and TEM. Thin foils for TEM were prepared from the plates that were cold rolled and annealed at 700°C by mechanically thinning to 0.05 mm in thickness. Discs, 3 mm in diameter, were then punched out of the 0.05 mm foils and electropolished. Electropolishing was done in a solution of 85% methanol and 15% perchloric acid below −20°C. For optical microscopy, the sample was etched in a mixed solution of 5% HF, 45% HNO_3 and 50% H_2O.

Table 1
Chemical composition (in wt%) of the modified Zry-4 alloys

Specimen number	Alloying elements				
	Sn	Fe	Cr	Cu	Zr
1	1.5	0.2	0.1	0.0	Balance
2	1.5	0.2	0.1	0.1	Balance
3	1.5	0.2	0.1	0.5	Balance
4	1.5	0.1	0.2	0.0	Balance
5	1.5	0.1	0.2	0.1	Balance
6	1.5	0.1	0.2	0.5	Balance

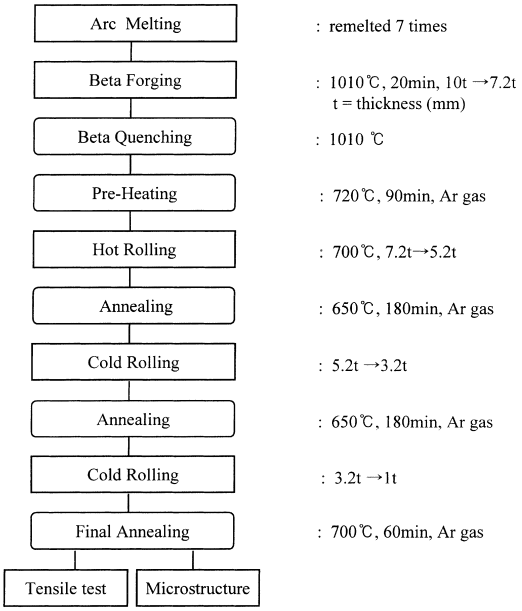

Fig. 1. Flow chart of the sample preparation.

3. Results and discussion

3.1. Tensile tests

Changes of ultimate tensile strength (UTS) and yield stress (YS) as a function of copper content for the specimens are presented in Fig. 2. As the copper content increased from 0 to 0.1 and 0.5 wt%, the UTS of the

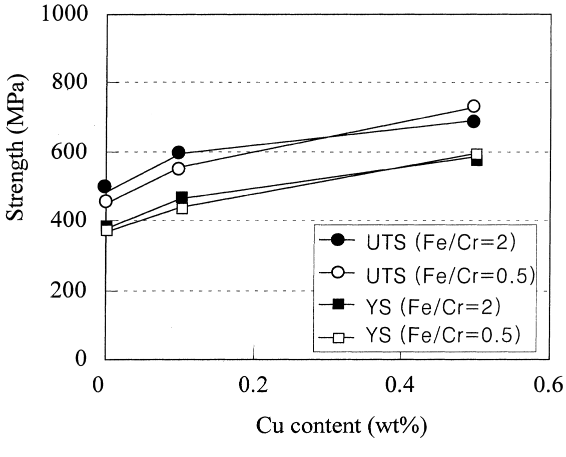

Fig. 2. UTS and YS as a function of copper and tin contents at room temperature.

specimens with the Fe/Cr ratio of 2 increased from 484 to 593, and 689 MPa, respectively. The YS increased from 376 to 466 and 584 MPa. The specimen with a Fe/Cr ratio of 0.5 showed similar results to those of the specimen with a ratio of 2. The UTS and the YS of the modified Zry-4 generally increased with the copper content. As the Fe/Cr ratio decreased from 2 to 0.5, the UTS of the 0 and 0.1 wt% copper specimens slightly decreased, but increased in the 0.5 wt% copper specimen. The change in UTS with the Fe/Cr ratio is about 6%, which is found to be much smaller than that with the present copper contents (42% change in UTS).

Hong et al. [3] suggested in the previous study that the UTS of the 0.2Cr–0.1Fe–0.1Nb–*x*Sn–Zr alloy increased from 384 to 419 MPa and 463 MPa, respectively, when the tin content increased from 0 to 0.5 wt% and 1.0 wt%. According to Isobe [4], the UTS of 0.2Fe–0.1Cr–0.5Nb–*x*Sn–Zr specimen increased from 410 to 490 MPa as the tin content increased from 0.5 to 1.5 wt%. Although the contents of Fe, Cr, and Nb of the previous specimens are different from Isobe's, the previous results are in good agreement with Isobe's. Therefore, it was found that the effect of copper in increasing the UTS was greater than that of the tin. For example, when the tin content increased from 0 to 1.0 wt%, the UTS increased from 384 to 463 MPa. The UTS of the specimen with a Fe/Cr ratio of 2 increased from 484 to 593 MPa with increasing copper content from 0 to 0.1 wt%. Thus, it appears that the increase in strength due to the addition of 0.1 wt% copper is sufficient to compensate for the

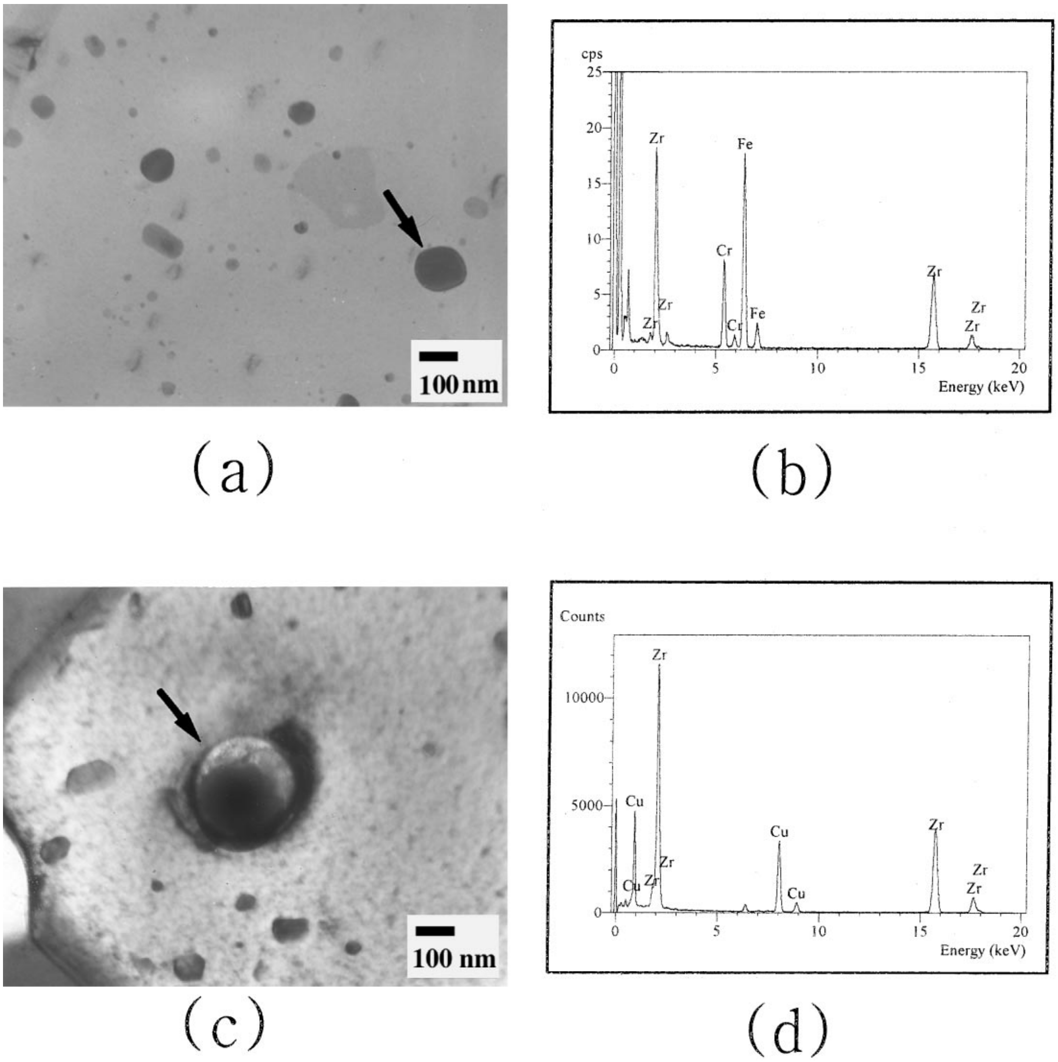

Fig. 3. Micrographs of precipitates in the specimen before the oxidation test (wt%): (a) TEM micrograph of $Zr(Fe,Cr)_2$ precipitate; (b) EDS spectra of $Zr(Fe,Cr)_2$ precipitate; (c) TEM micrograph of $ZrCu_2$ precipitate; (d) EDS spectra of $ZrCu_2$ precipitate.

decrease in strength due to the reduction of tin content from 1.0 to 0 wt%.

The strengthening role of tin in Zry-4 is well known [4,8], however, few studies have been reported about the effect of copper on the mechanical properties of zirconium alloys. The phase diagram of zirconium–copper system has been extensively studied [9–13]. The solubility of copper in α-Zr at room temperature has not been clarified up to now. However, it can be estimated by using the terminal solubility equation, $C = C_0 \exp(-\Delta H/RT)$. The solubilities of copper at 822°C and at 803°C are reported to be 0.2 and 0.1 wt%, respectively [9]. From these data the ΔH and the C_0 values can be determined, and the solubility of copper at room temperature is calculated to be about 5×10^{-47} wt%. Therefore, the lowest copper content (0.1 wt%) used in this study is considered to be far above the solubility limit of copper at room temperature. Accordingly, the increase in strength with increased copper content is believed to be due to precipitation hardening effect of copper.

3.2. Characteristics of microstructure

Precipitates in the present specimens were studied using transmission electron microscopy and energy dispersion spectroscopy. It was observed that many precipitates were homogeneously distributed either along α-Zr grain boundaries or within the grains. Three types of precipitates were found, namely, (i) $Zr(Fe,Cr)_2$ precipitates in both the copper-added and the copper-free specimens; (ii) $Zr(Fe,Cr,Cu)_2$; and (iii) Zr_2Cu precipitates in the copper-added specimens. $Zr(Fe,Cr)_2$ Laves phase precipitates with hexagonal structure have been found in the previous studies [14–18]. Some of these $Zr(Fe,Cr)_2$ precipitates were also found in the present study as shown in Fig. 3(a)–(d). The $Zr(Fe,Cr,Cu)_2$ precipitate was identified to be a C14 type hexagonal structure, and the Zr_2Cu precipitate shown in Fig. 3(c) and (d) was found to have a tetragonal structure. It can be seen that the Zr_2Cu precipitate is larger than the $Zr(Fe,Cr)_2$ precipitate.

Fig. 4 shows the size distribution of precipitates in the 0.2Fe–0.1Cr–0.5Sn–Zr specimen. The sizes of $Zr(Fe,Cr)_2$ and $Zr(Fe,Cr,Cu)_2$ precipitates were measured to be around 0.1 µm and were always less than 0.3 µm, and these precipitates are not as large as the largest Zr_2Cu precipitates. The size of Zr_2Cu precipitates ranges from 0.3 to 0.55 µm, and the number of the precipitates is much smaller than that of the $Zr(Fe,Cr)_2$ precipitates as shown in Fig. 4.

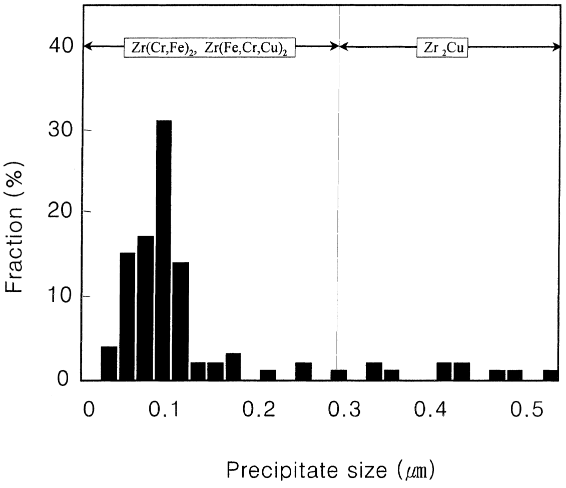

Fig. 4. Size distribution of precipitates in the modified Zry-4 alloys.

Table 2
Particle size and area fraction of the precipitates

Specimen number	Particle size (µm)			Area fraction (%)
	Ave.	Min.	Max.	
1	0.12	0.04	0.29	1.27
2	0.14	0.03	0.53	2.31
3	0.16	0.05	0.54	3.86
4	0.10	0.04	0.25	1.13
5	0.13	0.05	0.53	2.23
6	0.16	0.03	0.57	3.92

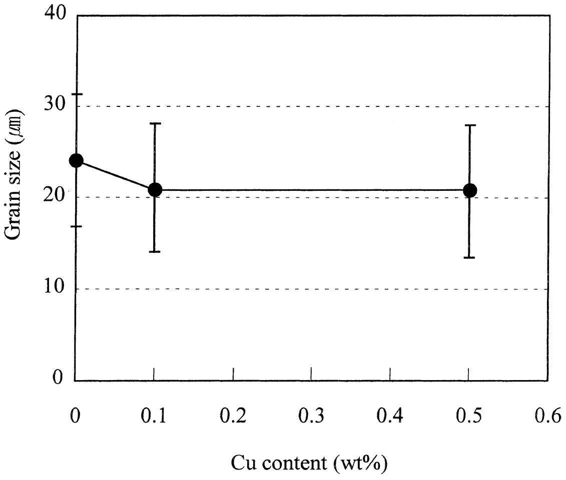

Fig. 5. Grain size variation as a function of copper content.

The average size and the area fraction of the precipitates increased as the copper content increased in the present study as shown in Table 2. The size of the precipitates increased from 0.12 to 0.16 µm, and the fraction from 1.27% to 3.86% as the copper content increased from 0 to 0.5 wt% in the specimen with a Fe/Cr ratio of 2. Specimens with the Fe/Cr ratio of 0.5 showed similar results to those of specimens with the ratio of 2. The size increased from 0.1 to 0.16 μm, and the fraction from 1.13% to 3.92% as the copper content increased from 0 to 0.5 wt%. It is believed that higher amounts of copper result in higher tensile strengths due to a higher fraction of precipitates. The stress needed to force the passage of a dislocation line through a precipitate array can be obtained by $\sigma_s = 2Gb/\lambda$ [19,20], where G is the shear modulus, b the Burgers vector and λ is the average spacing between precipitates. The spacing is given by $\lambda = (2rN)^{-1/2}$ where r is the radius of the precipitate and N is the number of the precipitates per unit volume. The yield stress increase, calculated using $G = 35$ GPa [21], $b = 0.32$ nm [22] and using the average radius of precipitate and the area fraction of precipitate shown in Table 2, ranged from 29 to 38 MPa as the copper content increased from 0 to 0.5 wt% in the specimens with the Fe/Cr ratio of 2. Precipitates less than 0.03 μm in diameter were not included in calculating the stress (σ_s) due to difficulties in observation. Thus, it is thought that the increase in the calculated σ_s with copper content is smaller than that in YS.

The grain size in the Zr–Cu binary alloys was reported to decrease by 12 μm as the copper content increased from 0 to 0.3 wt% [23]. It was speculated that grain growth was restrained by the grain boundary pinning effect of Zr_2Cu precipitates. Therefore, the grain size was smaller in the specimens containing higher copper contents. In the present study, the grain size exhibits little variation with the copper content as shown in Fig. 5. The same grain size is obtained probably because the pinning effect of Zr_2Cu precipitates is much less effective than that of $Zr(Cr,Fe)_2$ precipitates. $Zr(Fe,Cr)_2$ precipitates were also present as well as Zr_2Cu precipitates in the present specimens and the Zr_2Cu precipitates are much less numerous than $Zr(Fe,Cr)_2$ precipitates as shown in Fig. 4. Therefore, it is considered that the addition of copper to the modified Zry-4 alloys can enhance the tensile strength by the formation of precipitates rather than by refinement of grain size.

4. Conclusions

The UTS and the YS of the modified Zr alloys strongly depended on the copper content. About 0.1 wt% copper content was sufficient to compensate for the decrease in strength due to the reduction in tin content from 1.0 to 0 wt%. Precipitates found in the present specimens were identified as hexagonal $Zr(Cr,Fe)_2$, $Zr(Cr,Fe,Cu)_2$ and tetragonal Zr_2Cu. Increasing the copper content, the average size and the area fraction of the precipitates increased, but the grain size of the modified Zry-4 alloy was not changed.

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