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Influence of thermomechanical treatment on the corrosion behavior of Zr–1Nb–0.2Cu alloys

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Abstract

To investigate the effects of heat treatment and cold rolling on the corrosion of Zr–1Nb–0.2Cu alloy, the microstructure of aged specimens, which were manufactured by two different processes, was investigated to correlate it with the corrosion behavior. The corrosion characteristics of the alloy were remarkably dependent on thermomechanical treatment. The corrosion resistance was generally increased by aging and cold working possibly due to the promotion of precipitation. Good corrosion characteristics were observed for the specimens in which fine precipitates contain Nb as well as Zr and Cu. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A variety of Zr-based alloys containing Nb have been developed as the cladding material substitute for Zircaloy alloys and some alloys have been reported to show excellent corrosion performance under certain test conditions [1]. However, unlike Zircaloy alloys the optimized thermal processing for them have not been well established, partly because their sensitivity of corrosion characteristics to heat treatment varies with Nb content. For example, in the 427°C test for the 0.5 and 1%Nb binary alloys, the corrosion response was insensitive to heat treatment at the 0.5%Nb level, but very sensitive at the 1%Nb level [1]. Aging is generally reported to decrease the weight gain for Zr alloys with high Nb content, and this increased corrosion resistance was shown to be related to the formation of β-Nb [2–4]. β-Zr, a metastable phase, is known to increase the corrosion while β-Nb, a stable phase, decreases the corrosion [2–6].

In addition to heat treatment, cold working was also shown to affect corrosion behavior of Zr–Nb alloys [3,4,7]. Nikulina [7] reported that cold working (20%) following β-quenching significantly reduced the weight gain of Zr–Nb binary alloys with various Nb content in water at 350°C. Further increase in corrosion resistance was accomplished when aging was conducted following β-quenching and cold working.

As mentioned, the corrosion behavior of Zr–Nb alloys (with especially high Nb content) is greatly affected by both thermal processing and cold working. Therefore, the optimized processing should be established to maximize the corrosion resistance of Zr–Nb alloys. In this study the corrosion resistance of Zr–1%Nb–0.2%Cu in relation to heat treatment and cold working was evaluated and the microstructure of heat-treated specimens was investigated to correlate it with the corrosion behavior.

2. Experimental procedures

Zr–1%Nb–0.2%Cu alloy ingots were produced by vacuum arc remelting method (Table 1), and plates with about 1.5 mm thickness were manufactured by rolling and annealing the ingots as indicated in Fig. 1. Processing can be classified into two kinds, condition 1 and condition 2. The main difference between two conditions is that β-quenching is followed by aging in condition 1

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Table 1
Chemical analysis for Zr–1Nb–0.2Cu alloy

Alloying element	wt%
Nb	1.16
Cu	0.24

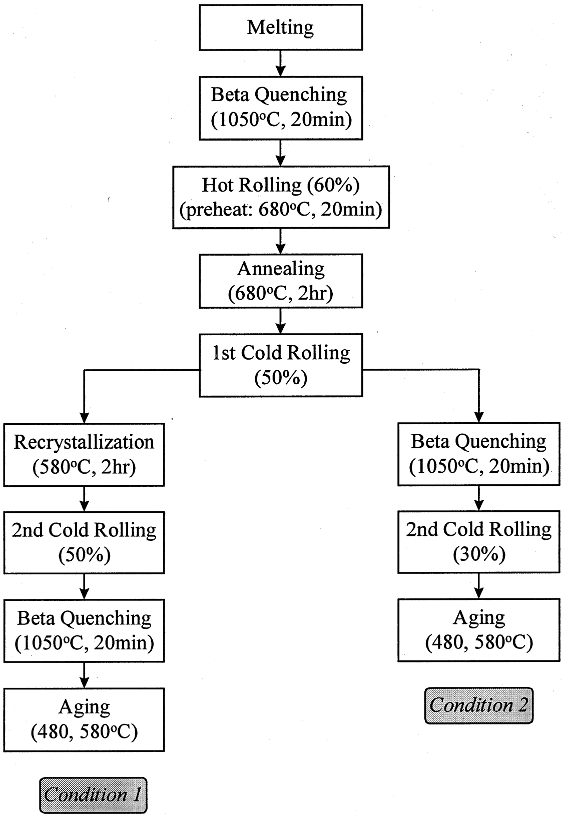

Fig. 1. Flow chart for heat treatment process.

while β-quenching is followed by cold rolling and aging in condition 2. Therefore, the effect of cold rolling before aging can be studied in condition 1. Final aging treatment was conducted at two different temperature, 480°C and 580°C for up to 500 h. After finishing the final heat treatment, specimens were prepared for corrosion test and microstructural analysis.

For the corrosion test, rectangular-shaped specimens, 15 by 25 mm in size, were cut from the plates and were mechanically ground using SiC paper (2400# in the final step) so that the same surface condition was used for all test specimens. The test was conducted at 400°C steam condition in the static autoclave under the pressure of 10.3 MPa. The corrosion resistance of the specimens were characterized by measuring their weight gains with the exposure time.

To investigate the precipitation during heat treatment, microhardness tests were carried out and precipitates were observed by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The microchemical analysis on the precipitate was conducted by energy dispersive spectroscopy (EDS) in the TEM.

3. Results and discussion

3.1. Influence of aging on the corrosion behavior

Autoclave experimental results of some specimens are shown in Fig. 2. Zircaloy-4 tube was also tested for the reference. β-quenched before aging (condition 1) specimens showed very large weight gain as compared to Zircaloy. β-quenched and cold-worked before aging (condition 2) specimens showed better corrosion resistance than specimens without final cold rolling before aging. In case of specimens aged at lower temperature (480°C) after cold rolling, better corrosion resistance than Zircaloy was observed. From this result, it was confirmed that Zr alloy with high Nb content are very sensitive to heat treatment.

The corrosion behavior of Zr–1Nb–0.2Cu alloy was indicated to be different from that of Zircaloy. The corrosion rate was changed at about 45 days (1st transition) and 90 days (2nd transition) while no sudden change of the corrosion rate was observed in Zr–1Nb–0.2Cu alloy. This means that the corrosion kinetics of two alloys are different.

Effects of aging temperature, aging time, and cold working on the corrosion can be more clearly shown in Fig. 3. The weight gain of all the specimens was generally observed to decrease as aging time was increased. However, long aging (100 h or longer) was not desirable for the cold-worked specimens. The improvement of

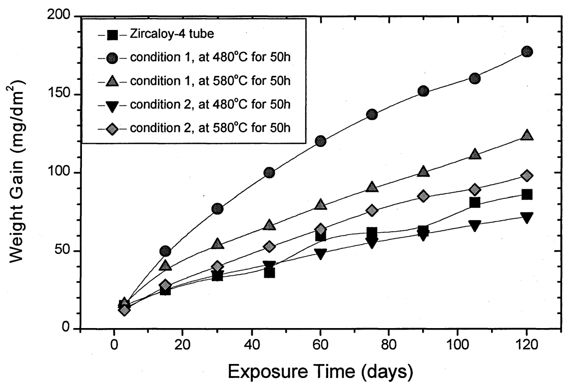

Fig. 2. Effects of aging and cold working on the corrosion behavior of Zr–1%Nb–0.2%Cu alloy.

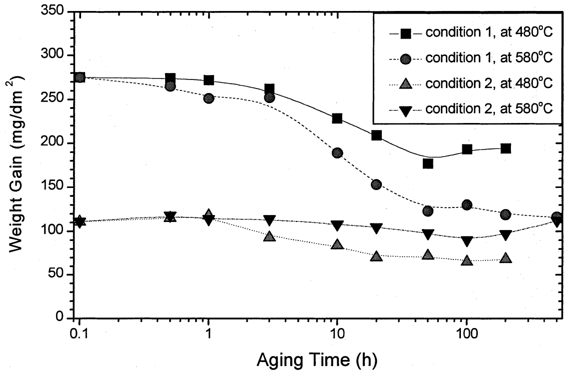

Fig. 3. Effect of thermal processing on the corrosion behavior of Zr–1%Nb–0.2%Cu alloy.

corrosion resistance during aging may be due to the effect of reducing the concentration of niobium in solid solution by the formation of precipitates [8,9]. According to Perovic et al. [10], the maximum solubility of Nb in α-Zr is 0.6 wt.%. So supersaturated Nb by β-quenching would be expelled from the matrix into the precipitate during aging. The weight gain was reduced more rapidly at higher aging temperature (580°C) probably because the formation of precipitates was more promoted. Cold working reduced weight gain significantly and its effect became small as aging time is increased. The best corrosion resistance was shown in the case that aged at 480°C for about 100 h following β-quenching and cold working (condition 2).

3.2. Precipitation and microstructural change during heat-treatment

Microhardness tests were conducted to confirm that precipitates were formed during heat treatment [11]. As indicated in Fig. 4 for specimens aged at 480°C, hardness peaks were observed during aging. Namely, in case of the β-quenched, cold worked, and aged at 480°C the hardness was measured to show the maximum at about 0.5 h and in case of the β-quenched, and aged at 480°C the maximum hardness was obtained at about 3 h. This implies that the precipitation was promoted by the introduction of cold working. The hardness peak was not shown for the aged at 580°C maybe because recovery and recrystallization process veiled the hardness change by precipitation.

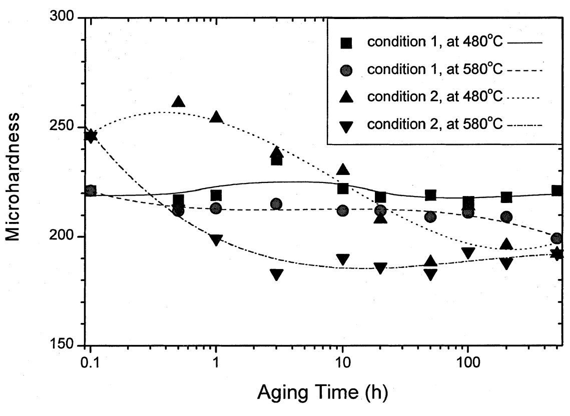

Fig. 4. Hardness change observed for Zr–1%Nb–0.2%Cu alloy during aging.

The precipitate formation during aging was observed by SEM as shown in Fig. 5. The promotion of precipitation by cold working is confirmed and more precipitates were formed by increasing aging temperature.

To identify precipitates formed, a transmission electron microscope was used. Typical microstructure of β-quenched and aged at low temperature (480°C) involves coarse martensite plates and twins as shown in Fig. 6(a). Twins disappeared and plates were changed into polygonized equiaxed shaped during aging at high temperature (b). This should be due to the rearrangement of dislocations reducing the stored strain energy. Since it was hard to recognize precipitates in unrecrystallized samples, only recrystallized specimens were analyzed by EDS.

In case of condition 2, recrystallization was completed after aging at 580°C for 30 min and at 480°C for about 50 h. No sudden change of the weight gain were observed by recrystallization.

Figs. 7 and 8 show the precipitates formed during aging at 580°C for 30 min and 50 h each. EDS spectrum indicated only the presence of zirconium and copper in the precipitates formed at the beginning of aging (Fig. 7). No niobium content was detected. The maximum solubility of Cu in α-Zr is 0.2 wt.%, but the solubility would be much smaller at lower temperature, therefore Cu would be emitted into the Cu-containing precipitate [12].

After aging for 50 h (Fig. 8), niobium as well as copper were detected in the precipitates. The precipitates at the grain boundaries showed the higher niobium content than in the grains. When aged at 480°C, very fine precipitates were observed as compared to those aged 580°C (Fig. 9). These fine precipitates involved copper and niobium but a few coarse precipitates did not show any niobium presence.

3.3. Correlation of microstructure and corrosion behavior

As discussed earlier, the increased corrosion resistance by aging was closely related to the precipitation. However, the improved corrosion resistance by the introduction of cold work cannot be directly explained by precipitation since no precipitates were observed in non-aged specimens with and without cold work. The beneficial effect of cold working may be attributed to that the

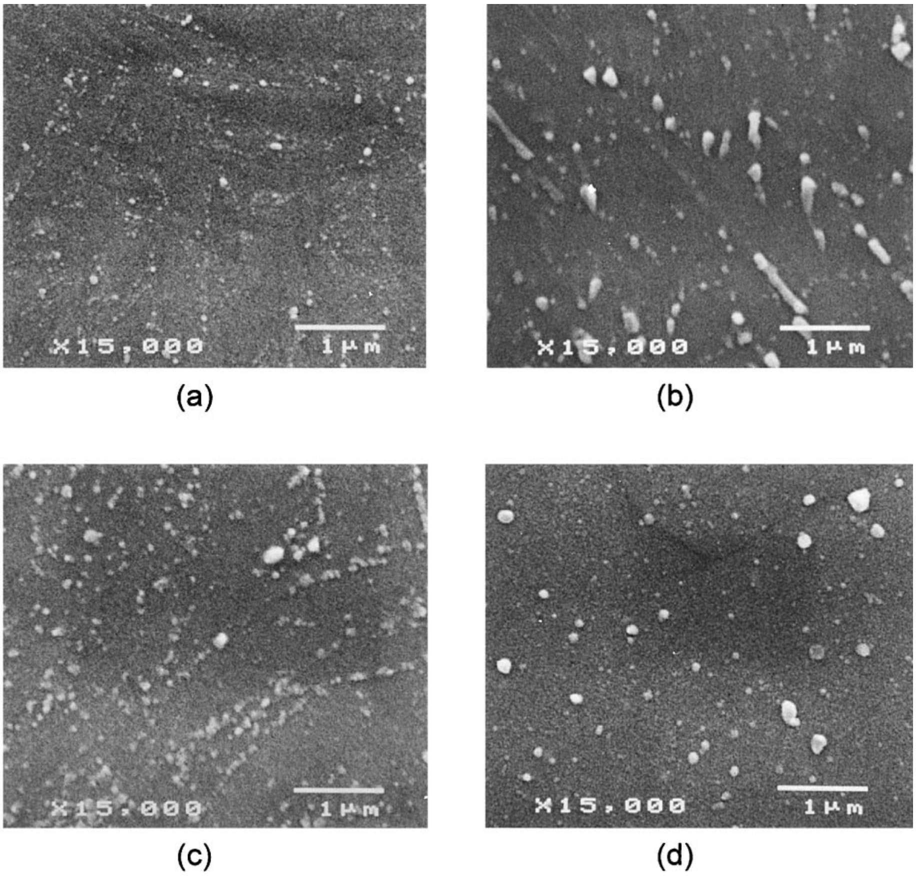

Fig. 5. SEM micrograph of precipitates formed during aging for 3 h.

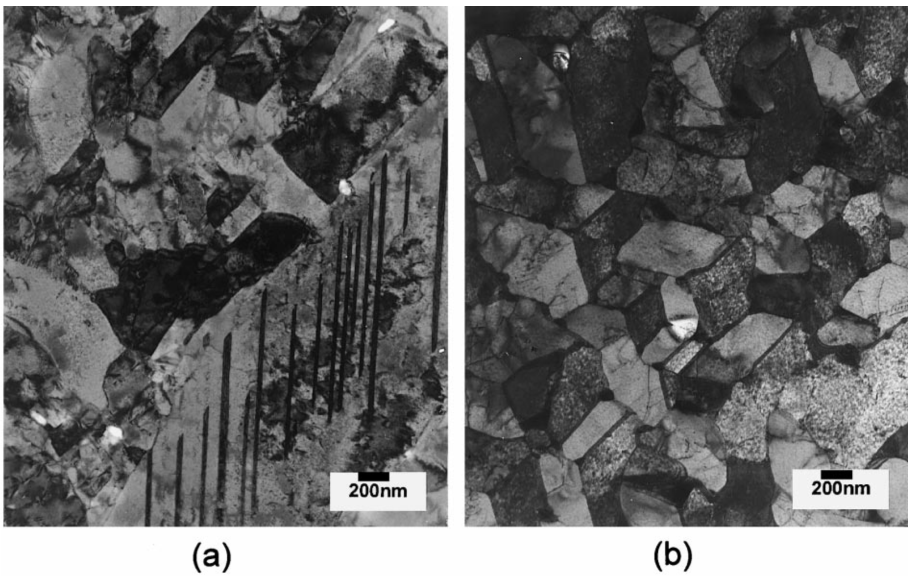

Fig. 6. TEM micrograph of specimens aged for 50 h following β-quenching.

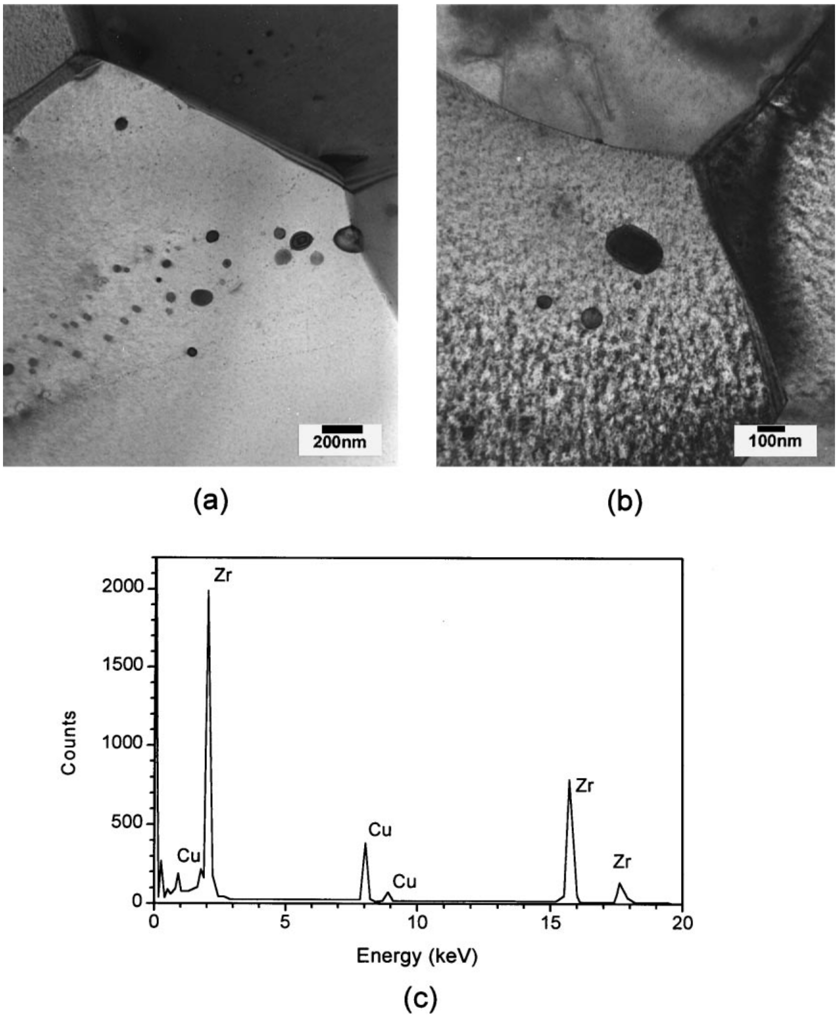

Fig. 7. Typical precipitates in the specimen aged at 580°C for 30 min (condition 2).

metal grains become oriented [13]. Because the oxide film grows on the base of crystal lattice of the matrix, the oxide grains on the oriented metal grains will posses a high degree of orientation. The good mutual orientation of the grains of the oxide film reduces the structural defects and ensures a high degree of crystallographic homogeneity in the oxide film, and lowers the oxidation rate. The studies of oxide morphologies are in need for clarification.

Based on the TEM analysis, generally two kinds of precipitates, the one with Nb and the other without Nb, were observed. Better corrosion resistance was obtained when precipitates involved Nb. In addition, fine precipitates are thought to be beneficial for corrosion resistance because specimens aged at 480°C for 50 h showed good corrosion behavior compared to that aged at 580°C for 50 h indicating somewhat coarse precipitates.

3.4. Influence of annealing parameter on the corrosion

In order to correlate thermal processing with the precipitate size or the corrosion behavior of Zircaloy alloys, annealing parameter have been used in many researches [14–16]. For Zircaloy alloys, it is known that the accumulated annealing parameter should be higher than certain value for good corrosion resistance at 400°C. In other words, there is a minimum precipitate size for good corrosion behavior.

In this study, aging was conducted at two different temperatures (480°C and 580°C) for up to 500 h. By using Q/R of 40,000 K [14], A-parameter varies from 10^{-24} to 10^{-18} h. The corrosion resistance was shown to generally increase as A-parameter was increased as indicated in Fig. 10. However, even though A-parameter was the same, the weight gain was quite different for process conditions. In addition, the relative effect of

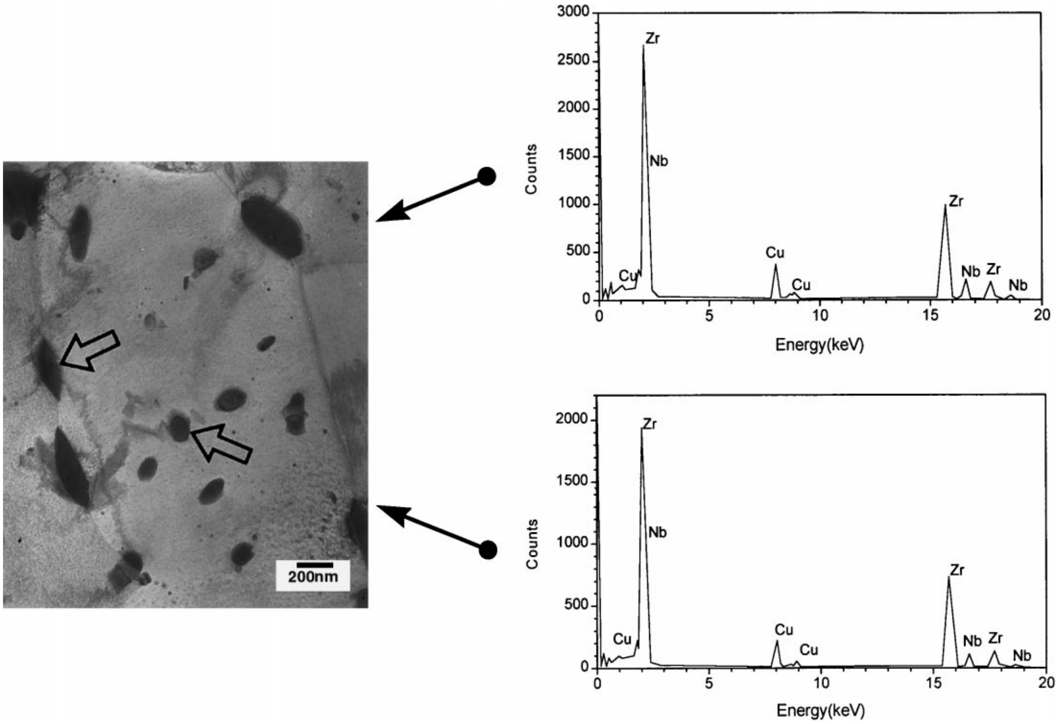

Fig. 8. Typical precipitates and their EDS spectrum in the alloy aged at 580°C for 50 h (condition 2).

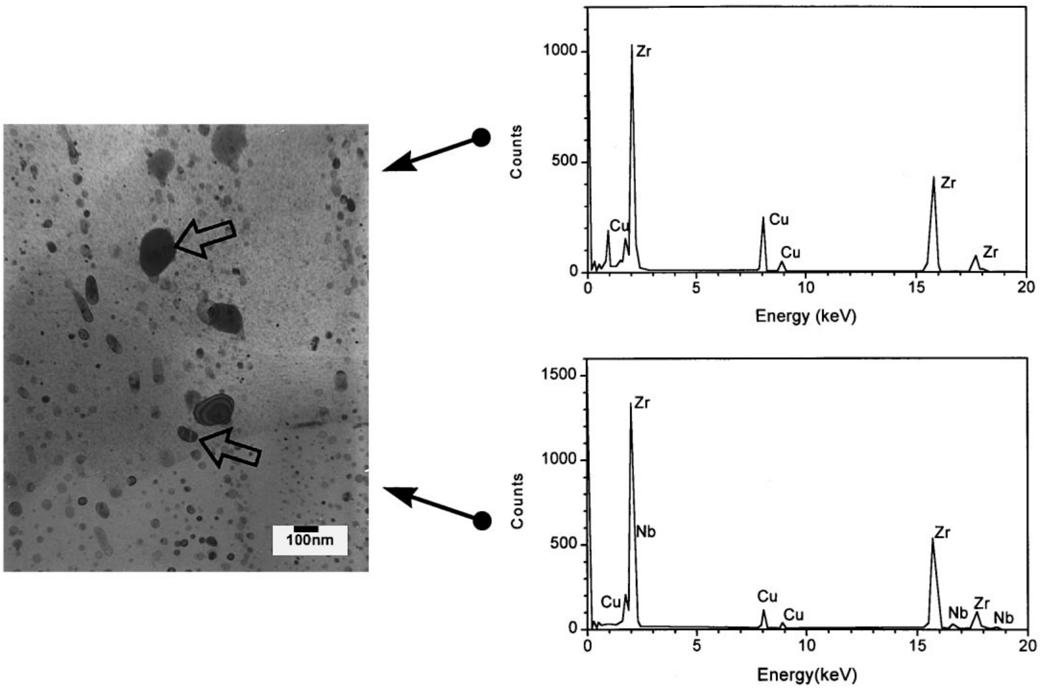

Fig. 9. Typical precipitates and their EDS spectrum in the alloy aged at 480°C for 50 h (condition 2).

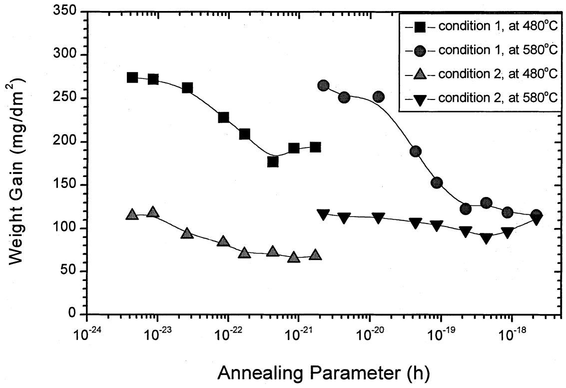

Fig. 10. Influence of annealing parameter on the corrosion behavior of Zr–1%Nb–0.2%Cu alloy.

temperature and time on the weight gain was very different for the same condition. Namely, for the same A-parameter of about 5×10^{-24} h, the low temperature aging (480°C) for a long time shows the much better corrosion resistance than the high temperature aging (580°C) for a short time.

4. Conclusions

The corrosion behavior of the Zr–1%Nb–0.2%Cu alloy is markedly dependent on heat treatment and cold working. Generally, aging and cold working increased the corrosion resistance possibly due to the promotion of precipitation. EDS spectrum in the TEM indicated generally two kinds of precipitates, the one with Nb and the other without Nb. Desirable corrosion behavior was observed for the case that fine Nb-containing precipitates are distributed in the matrix. Low temperature aging was found to be more beneficial than high temperature aging as far as the corrosion behavior was concerned.

Acknowledgements

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