



Effect of oxygen content on the beta-quenched microstructure of modified Zircaloy-4

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Abstract

The effects of oxygen content on the beta-quenched microstructure of modified Zircaloy-4 were studied. The modified alloys were prepared by changing the chemical compositions of Zircaloy-4; the tin contents were decreased to 0.5 wt% while oxygen increased from 0.1 to 0.5 wt%, 0.1 wt% Nb was added and the amounts of Fe and Cr were kept 0.1 and 0.2 wt%, respectively. The beta-quenched structure for the cooling rate of 1000°C/s in the modified Zircaloy-4 alloys was composed of fine α laths and the α lath width did not change with oxygen content. The low dislocation density and no twins within the α lath interiors indicate that the β to α transformation for the cooling rate of 1000°C/s is governed by the non-martensitic transformation. Precipitates were not observed in any of the specimens, and thus the solute atoms were in supersaturation after beta-quenching, regardless of the oxygen concentration. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, a modified Zircaloy-4 alloy was developed by reducing the tin content from 1.0 wt% to zero and adding 0.1 wt% Nb and oxygen up to 0.8 wt% [1]. Oxygen was originally added to compensate for the decrease in strength resulting from the reduction of tin content. The oxygen addition showed a marked improvement in the mechanical strength. Furthermore, it was found that the modified Zircaloy-4 containing 0.2 wt% oxygen showed a better oxidation resistance than Zircaloy-4. The oxidation resistance in zirconium alloys is dependent on oxygen concentration and also on beta-quenching treatment. Beta-quenching at the final stage in the fabrication process of Zircaloy-4 has been an important process for advanced fuel cladding materials in recent years [2,3]. In the beta-quenched condition, the alloy contains a large fraction of low-soluble alloying elements in supersaturation. Supersaturation might be

one of the reasons for the improvement in the resistance of oxidation. Thus, in order to introduce the beta-quenching process to the modified Zircaloy-4 containing a high amount of oxygen, it is necessary to investigate the effect of oxygen on the beta-quenched microstructure. Some researchers investigated the effects of alloying elements, such as tin and titanium, on the beta-quenched microstructure [4,5], but little is known about the effect of oxygen on the beta-quenched microstructure. Furthermore, there is still a controversy with regard to the interpretation of the beta-quenched microstructure of zirconium alloys. In the present study, the beta-quenched microstructure of the modified Zircaloy-4 was studied by using an optical and transmission electron microscope and the effect of oxygen on the beta-quenched microstructure was investigated.

2. Experimental procedures

Reactor grade sheet-type pure Zr and alloying elements were arc melted into 20 g button type ingots. The oxygen content was varied from 0.10 to 0.49 wt%. In

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order to introduce oxygen of up to 0.49 wt%, predetermined amount of zirconium oxide powder were filled into the drilled holes in the premelted buttons, and the buttons were melted five times for homogenization of the alloying elements. Besides, 0.1 wt% Nb was added and the Fe/Cr ratio of Zircaloy-4 was reduced to 1/2 with the amount Fe and Cr fixed at 0.1 wt% and 0.2 wt%, respectively. The chemical compositions of the alloys are presented in Table 1.

All specimens with dimensions of 20 mm (L) \times 15 mm (W) \times 5 mm (t) were annealed in the air at 1300°C for 5 min and then water quenched. The cooling rate during water quenching was measured by using thermocouples attached to the specimen surfaces and it was about 1000°C/s. It was found that thermocouple remained attached to the specimen after quenching and the surface of the specimen was covered with oxide. The oxide layer could slower the cooling rate, however, it was considered that the oxide layer could not disturb the measuring method, if thermocouple was attached to the surface of the specimen. Thus, the cooling rate measured by the attached thermocouple represented the actual cooling rate of the specimen containing the surface oxide.

The cooling rate was measured in the temperature range of 1200–400°C where the temperature decreased linearly with the time. 400°C is far below the Ms temperature (martensite transformation start temperature) and the martensite transformation, if occurs, can be investigated in the temperature range.

The microstructural examination of the quenched specimens was conducted by using optical and transmission electron microscopy. For optical microscopy, the specimen was cut in half and the middle part of the cross-section was observed. Observations of upper and lower parts of the cross-section showed no difference of the microstructure in the three parts. The specimens were etched in a mixed solution of 5% HF, 45% HNO₃ and 50% H₂O.

Thin foils for transmission electron microscopy were prepared from the middle part of quenched buttons by mechanically thinning them to 0.05 mm thickness. Discs, 3 mm in diameter, were then punched out of these 0.05 mm foils and electropolished. Electropolishing was done in a solution of 85% methanol, 15% perchloric acid at below –20°C.

3. Results and discussion

Fig. 1 shows the optical microstructures of beta-quenched specimens at a cooling rate of 1000°C/s. The fine α lath structure was observed in all the specimens. The lath structure, different from the basketweave or parallel-plate structure, is considered to be developed due to fast cooling rate. It has been reported that in the basketweave structure formed at a slower cooling rate, the width of coarse α plates increased with increasing oxygen content, and in some cases, even the basketweave structure changed to parallel-plate structure with increasing oxygen content [6]. Okvist [7] discussed the influence of the carbon content and concluded that the carbon content was important in determining the type of the microstructures that would appear for a fixed cooling rate. He associated the presence of basketweave structure with a relatively high carbon content (100–200 ppm). On the other hand, for a low carbon content less than 50 ppm the structure would be parallel plate structure. Also, the formation of the basketweave structure or the parallel-plate structure is known to depend on impurity contents such as Si and P [8]. The precipitates containing the impurities act as effective nuclei for the β to α transformation. Basketweave structure development is associated with such nuclei on the phase transformation starts during cooling and the basketweave structure is favored as the number of nucleus increases. However, in the present study, no distinguishable changes in the width and shape of the fine α laths were found with increasing oxygen contents from 0.1 to 0.5 wt% as shown in Fig. 1.

TEM micrographs of the lath internal structure of the present specimens are shown in Fig. 2. All the internal structures of the α laths were similar regardless of oxygen content as shown in Fig. 2. The dislocation density was low, and no twins were found in the lath interiors. Controversy still exists with regard to the interpretation of the α lath formation mechanism. Rumball [9] considered that the α lath structure had martensitic characteristics. On the contrary, however, Bangaru [10] reported that the α lath structure had non-martensitic characteristics. It was concluded from the results that low dislocation density and no twins were found in the lath interiors. He suggested that the β to α

Table 1
Chemical compositions of the specimens (wt%)

Alloys	Alloying elements					
	Sn	Nb	Fe	Cr	O	Zr
1	0.55	0.07	0.09	0.16	0.10	Bal.
2	0.50	0.14	0.13	0.18	0.22	Bal.
3	0.52	0.12	0.12	0.18	0.31	Bal.
4	0.47	0.11	0.13	0.16	0.41	Bal.
5	0.52	0.13	0.12	0.18	0.49	Bal.

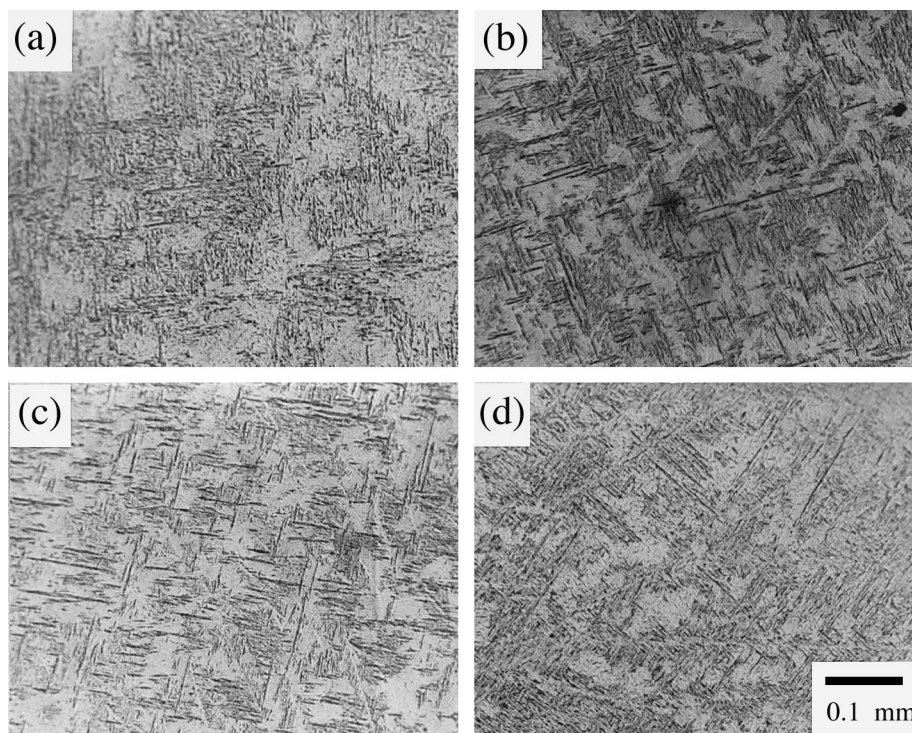


Fig. 1. Optical microstructure of beta-quenched specimens at the cooling rate of 1000°C/s (a) Alloy 1 (b) Alloy 2 (c) Alloy 4 (d) Alloy 5.

transformation during β -quenching occurred by massive transformation with shear characteristics. Accordingly, it was considered that the β to α transformation of the present specimens occurred by a non-martensitic mechanism with shear characteristics. Fig. 2(a) shows the α laths fragmented from the prior β grains, which is one of the evidences that involves shear mechanism as reported by Wadekar [5].

It was pointed out that at a cooling rate of slower than 1700°C/s, the β to α transformation in a Zr–Cr–Fe alloy was likely to be a non-martensitic transformation [11,12]. Perez [13] reported that an α phase microstructure was martensitic only for cooling rate exceeding 1500°C/s in Zircaloy-4. Therefore, it was considered that the cooling rate of 1000°C/s in the present study is not fast enough to induce martensitic transformation.

As shown in Fig. 2, precipitates were not observed in all of the specimens. In other words, atoms such as Fe, Cr and Nb, which are in excess of their solubility in the α phase during beta-quenching [14], were supersaturated in α phase after beta-quenching and no distinguishable difference in supersaturation of the solute atoms was found with increasing oxygen content.

A plot of the variation of lath width with oxygen content is shown in Fig. 3. The lath width exhibits little variation with oxygen content. It was known [15] that

plate width in the basketweave structure, which is formed by a nucleation and growth mechanism for low cooling rates slower than 400°C/s, increased with increasing oxygen content due to the widened ($\alpha + \beta$) two phase region. However, in the present cooling rate of 1000°C/s, the lath width was not affected by increasing oxygen content, which is in agreement that the formation of the α laths occurs through a shear mechanism of massive transformation.

4. Conclusions

1. The beta-quenched structure for the cooling rate of 1000°C/s in the modified Zircaloy-4 alloys was composed of fine α laths and the α lath width did not change with oxygen content.
2. The low dislocation density and no twins within the α lath interiors suggest that the β to α transformation for the cooling rate of 1000°C/s is governed by the non-martensitic transformation.
3. Precipitates were not observed in any of the specimens, and thus the solute atoms were in supersaturation after beta-quenching, regardless of the oxygen concentration in the present study.

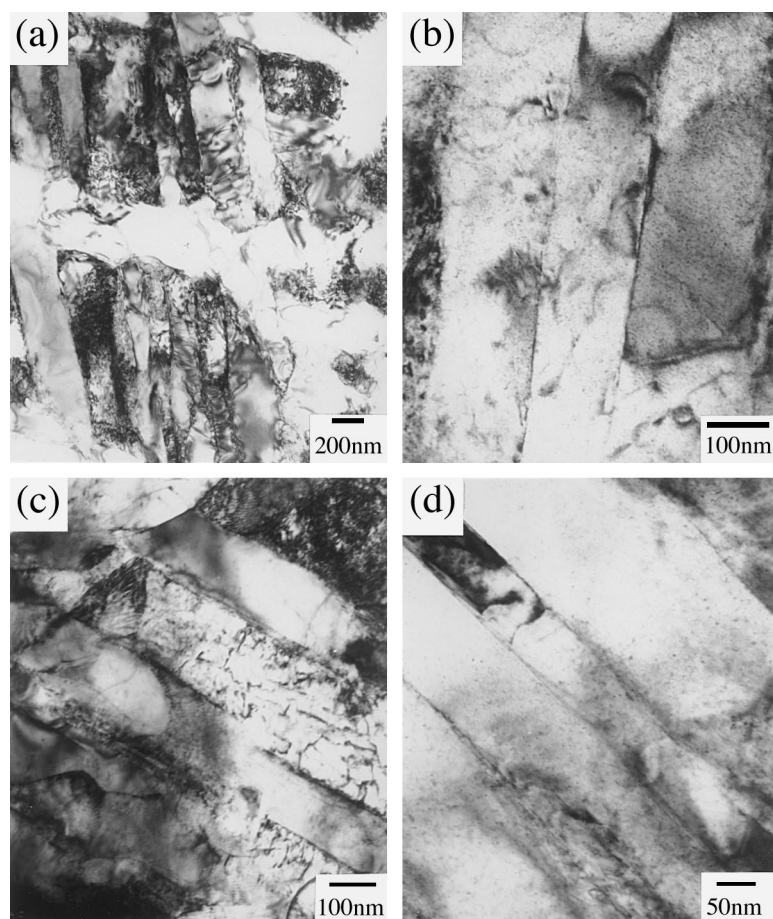


Fig. 2. TEM micrographs of beta-quenched specimens at the cooling rate of 1000°C/s (a) Alloy 1 (b) Alloy 2 (c) Alloy 4 (d) Alloy 5.

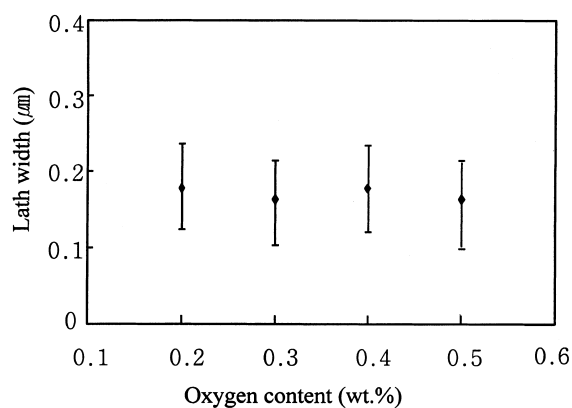


Fig. 3. Variation of lath width with oxygen content.

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