Recrystallization Behavior of Zr-xNb Alloys

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The effect of Nb contents on the recrystallization behavior of a binary Zr-xNb was studied. The specimens of Zr-xNb alloys containing 0.2, 0.4, 0.8 and 1.0 mass % Nb were prepared under various heat-treatment conditions for a cold rolled sheet. The recrystallization behavior was evaluated by using a polarized optical microscope, TEM, and a Vickers hardness tester. The recrystallization temperature of the binary alloys was slightly increased with the Nb content. It was caused by an increment of the activation energy due to an increasing Nb content. The grain growth at the high temperature region was decreased with the Nb content, because the fraction of the beta-phase, which is determined by the Nb content, was increased by increasing the Nb content. Because the minimum hardness value was observed in the temperature range between 600 and 700°C, the annealing was performed in this range to obtain a good ductility in a high Nb-containing Zr alloy.

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1. Introduction

Zirconium-based alloys are being used as fuel cladding and structural materials for nuclear reactors since they have a good irradiation stability, corrosion resistance, and acceptable mechanical properties in a reactor environment. However, recently, more advanced Zr-based alloys are required for enhanced operating conditions such as an increased burn-up and higher operation temperatures. Therefore, the development of advanced Zr alloys for a fuel cladding is being progressed in various countries.1-3 The general properties of industrial materials are dependent on the microstructure of the materials and that of the materials is affected by the chemical composition and manufacturing process.4) The corrosion kinetics and mechanical properties of a Zr alloy are affected by the alloying element and the precipitates that were formed by adding various alloying elements. Since the corrosion behavior of a Zr alloy is largely affected by a Nb addition as an alloying element, most of the advanced Zr alloys for a fuel cladding contain Nb to improve their corrosion resistance.1-3 It has been reported that the corrosion behavior of a Nb-containing Zr alloy was very complex depending on the Nb content and annealing condition.5-7 From these reports, it was confirmed that a Nb addition to Zr alloys improved their corrosion resistance.

However, the fundamental data such as the recrystallization behavior and the hardness change with the Nb content are insufficient. Therefore, the purpose of this investigation is to obtain the recrystallization behavior for Zr-xNb alloys and this work will be useful for the manufacturing and design of Nb-containing Zr alloys as a fuel cladding.

2. Experimental Procedure

The binary Zr-xNb alloys shown in Table 1 were manufactured by a sequence of four vacuum arc re-meltings to promote a homogeneity of the alloying elements, and then these ingots were β solution treated at 1050°C for 30 min. The quenched ingot was hot-rolled after a preheating at 700°C for 30 min and cold-rolled three times to a final thickness of 0.6 mm. Between the rolling steps, the cold-rolled sheet was intermediate-annealed at 610°C for 2 h in a vacuum furnace and the final cold rolling reduction was 70%. The cold-rolled sheet samples were annealed at various temperature ranges from 400 to 800°C and for various times of 30, 60, 180, 600, 1200, and 5000 min in evacuated quartz tubes. The microstructural characteristics of the alloys were examined by using an OM and TEM equipped with an EDS. For the OM observation, the samples were cut from an annealed sheet and the observation surface was perpendicular to the rolling direction, and then etched with a mixed solution of 45 vol% H2O, 45 vol% HNO_3 and 10 vol% HF after a polishing. TEM specimens were prepared by using a twin-jet polisher with a solution of 10 vol% HClO_4 and 90 vol% C_2H_5OH after a mechanical thinning to 70 μm. The hardness variation with the annealing conditions was measured by using a Vickers tester for the OM observation samples.

3. Result and Discussion

3.1 Microstructural characteristics with annealing conditions

Figure 1 shows the optical microstructures of the Zr-xNb alloys after an annealing at various temperatures for 60 min. At the annealing temperature of 400°C for the binary alloys, a deformed structure was observed regardless of the Nb contents from 0.2 to 1.0 mass %. The fraction of the deformed structure was decreased with an increasing annealing temperature and the recrystallized grains were observed at an annealing temperature of 600°C for the binary alloys.
regardless of the Nb contents. However, the grain size in the recrystallized structure was decreased with an increasing Nb content for the binary alloy system. It was generally found that a grain growth was prevented by the resultant precipitates. It has been reported that the Nb solubility in Zr is about 0.2 mass %. Since Nb-containing precipitates were formed in some of the tested alloys, which contained Nb of more than 0.4 mass %, it could be postulated that the grain size was determined by the Nb contents in the alloys.

Figure 2 shows the TEM micrographs of the Zr-0.2Nb (a), Zr-0.4Nb (b) and Zr-1.0Nb (c) alloys annealed at 600°C for 60 min. Recrystallized grains were formed on the observed samples and precipitates were formed on the Zr-0.4Nb and Zr-1.0Nb alloys. It is related to the Nb solubility in Zr, because the alloys containing more Nb than their solubility such as the Zr-0.4Nb and Zr-1.0Nb alloys were found to have a two phase structure which consisted of an alpha-Zr phase and precipitates. Therefore, the grain growth was interrupted by the precipitates formed in the high Nb-containing alloys more than the solubility in the alpha-Zr phase.

Figure 3 shows the TEM micrographs for the precipitate analysis of the Zr-1.0Nb alloys. The precipitates formed at the grain boundaries designated as (A) and inside grains designated as (B) consisted of 85–90 mass % Zr and 10–15 mass % Nb from the EDS results, and the crystal structure of the precipitates was analyzed as a BCC from the SAD results. Therefore, the precipitates formed in the high Nb-containing alloys were defined as beta-Zr phase ones formed in both regions of grain boundary and inside grain. Therefore, the precipitates formed in the high Nb-containing alloys were defined as beta-Zr phase ones formed in both regions of grain boundary and inside grain. The area fraction of the beta-Zr phase in the Zr-1.0Nb alloy was increased with an increasing annealing temperature, to more than 600°C, because it was caused by a decrement of the Nb content in the beta-Zr phase. Generally, it could be explained by the lever rule. Since, the beta-Zr phase was formed in the high Nb containing alloys annealed at 600°C, it could be assumed that the monotectoid temperature was lower than 600°C. This result correlates well with a recent study which revealed a monotectoid temperature of about 585°C in commercial grade Zr-Nb alloys.

From the results of the microstructural observation of the OM and TEM, a partially deformed microstructure was observed in the alloys annealed at 550°C and an equiaxed microstructure was observed in the alloys annealed at 600°C after a cold working of 70%, in all the samples, regardless of the Nb contents. Thus, the recrystallization started at a temperature below 550°C and finished at a temperature above 600°C in the Zr-Nb alloys. The grain growth after a recrystallization was interrupted by the formation of the beta-Zr phase in the high Nb-containing alloys of more than 0.4 mass % Nb. Since the beta-Zr phase fraction was increased with an increasing Nb content, the grain size depended on the Nb content at a high annealing temperature.
Figure 4 shows the optical microstructures of the Zr-0.4Nb alloy after an isothermal and isochronal annealing. The microstructural characteristics were changed by changing the annealing time and temperature. The deformed structure was observed in the Zr-0.4Nb alloy annealed at 400°C from 30 min to 5000 min, whereas the equiaxed grains were observed in the alloy which was annealed at 500°C for 5000 min, annealed at 550°C for more than 180 min, and also annealed at 600°C for more than 30 min. Grain growth after a recrystallization was observed in the Zr-0.4Nb alloy annealed at 700°C for more than 180 min. Although the annealing temperature was increased to 800°C, the grain size was not increased that much, when compared with the annealing temperature of 700°C. From these results, the minimum temperature for recrystallization of the Zr-xNb alloys is suggested to be 500°C when the annealing time is extended to 5000 min. Bokros measured the grain size as a function of the temperature at the critical strains for sponge Zr and Zircaloy-3. He reported that the grain growth in the zirconium alloys with a second phase was much more restricted than in the unalloyed metal. Since the high Nb-containing alloy showed a similar grain size when annealed between 700°C and 800°C in this work, the reason for this behavior is the presence of a beta-phase which would inhibit a grain growth.

Figure 5 shows the mean grain diameter with the various annealing times and temperatures of the Zr-xNb alloys. With equal annealing conditions for the time and temperature, the mean grain size was decreased with an increasing Nb content. Since the grain size was significantly changed with the Nb content between 0.2 and 0.4 mass%, the formation of a beta-phase would remarkably affect the grain size.

### 3.2 Hardness behavior with the annealing conditions

Figure 6 shows the hardness variation with the annealing times and temperatures of the Zr-xNb alloys. The hardness for the equal annealing conditions was increased with an increasing Nb content. Since the hardness is usually determined by the solute atom contents and the precipitate fraction, both factors affect the tested Zr-xNb alloy system.

In a low Nb-containing alloy of 0.2 mass%, the hardness was mainly affected by the solute Nb content, whereas it was affected by the precipitate fraction as well as the solute Nb content in the high Nb-containing alloy ranges from 0.4 to 1.0 mass%.

From the result of the hardness variation with annealing conditions, the hardness was somewhat decreased when the Zr-xNb alloys were annealed at 500°C and it was clearly decreased when those alloys were annealed between 550 and 600°C, and maintained when those alloys were annealed at the temperature regions from 600 to 700°C regardless of the Nb content. However, at the annealing temperature of 800°C, the hardness was changed with the Nb content. It was assumed that the hardness variation was caused by the microstructural characteristics which were determined by the Nb content and the annealing temperature. When compared to the microstructural observation, the hardness variation with the annealing times and temperatures could be ex-
plained. In the Zr-0.2Nb alloy, the decrease of the hardness was caused by a grain growth resulting from a high annealing temperature of 800°C and an increment of the hardness in the Zr-0.4Nb, Zr-0.8Nb, and Zr-1.0Nb alloys was caused by an increment of the beta-phase fraction. Since the beta-phase fraction was increased with an increasing Nb content and temperature, the hardness was also increased with an increasing Nb content.

From this result, a correlation data between the annealing times and the annealing temperatures in the Zr-xNb alloys was obtained. Therefore the annealing condition for a suitable manufacturing process of Zr-xNb alloys could be determined from this work. Because the minimum hardness value was maintained in the temperature range from 600 to 700°C in the 0.4 to 1.0 mass % Nb-containing alloys, the annealing was performed in this range between 600 and 700°C to obtain a uniform recrystallization structure with a low hardness value in a high Nb-containing Zr alloy.

### 3.3 Activation energy of the Zr-xNb alloys

Generally, the rate of a phase transformation is related to the temperature and activation energy (Q). The Q value, which is based on the phase transformation time, is determined by an equation of the following form, \(\text{eq. (1)}\)

\[
\left(\frac{dy}{dt}\right) = [f(Y)]k_0 \exp\left(-\frac{Q}{RT}\right)
\]

Where, \(f(Y) = \text{Function of Y only}\)

\(Y = \text{Constant transformation rate (50%)}\)

\(k_0 = \text{Rate constant}\)

\(Q = \text{Activation energy}\)

\(R = \text{Gas constant}\)

\(T = \text{Temperature (K)}\)

The activation energy (Q) of the Zr-xNb alloys as shown in Table 2 was calculated from eq. (1). The value of the activation energy was increased with an increasing Nb content in the recrystallization region between 500 and 600°C. Particularly, the activation energy was significantly changed between 0.2 mass % and 0.4 mass % in this region. It could be assumed that the activation energy for a recrystallization was affected by the Nb solubility in the alpha-Zr phase.

Figure 7 shows a correlation between the logarithm time for a 50% recrystallization and the reciprocal of an absolute temperature for a recrystallization of the 70% cold rolled Zr-xNb alloys. Therefore, the slope change at 600°C in this figure was caused by a variation from a recrystallization to a grain growth behavior.

### 4. Conclusions

1. The recrystallization temperature of Zr-xNb alloys was increased with the Nb contents and the grain size after a recrystallization was decreased with increasing Nb contents.

2. The hardness increment of the high Nb-containing alloys of more than 0.4 mass % at a temperature of 800°C was caused by an increment of the beta-Zr phase fraction. To obtain a uniform recrystallization structure with low hardness value in a high Nb-containing Zr alloy, the annealing was performed at a temperature range between 600 and 700°C.

### Acknowledgements

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### REFERENCES


### Table 2: Activation energy of the Zr-xNb alloys.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Q (kJ/mol); recrystallization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-0.2Nb</td>
<td>84</td>
</tr>
<tr>
<td>Zr-0.4Nb</td>
<td>99</td>
</tr>
<tr>
<td>Zr-0.8Nb</td>
<td>108</td>
</tr>
<tr>
<td>Zr-1.0Nb</td>
<td>112</td>
</tr>
</tbody>
</table>

Fig. 7 Correlation of the logarithm time for a 50 percent recrystallization with the reciprocal of an absolute temperature for a recrystallization of the 70% cold rolled Zr-xNb alloys.