Low temperature annealing of a cold worked Zr-Nb alloy

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Abstract. When typical Zr-Nb alloys undergo thermomechanical processing, they form additional Nb nanoclusters during the irradiation. This suggests Nb remains slightly supersaturated in the α-Zr matrix. To confirm it, assuming that the defect generated during irradiation stimulates the additional formation of these Nb nanoclusters, and the diffuse path is very short, cold worked ZIRLO with a high dislocation density is annealed at a similar temperature of the nuclear power plant to see if Nb precipitation will form. The XRD was used for indirect detecting the Nb precipitation formation. The result shows that Nb may precipitate at a temperature around 400℃, the stored energy from processing and aging at a slightly higher temperature to the operating temperature of nuclear power plants can also stimulate the precipitation of Nb nanoclusters.

1. Introduction
Zirconium alloys are important structural materials in nuclear power reactors as they have a small thermal neutron absorption cross-section, good corrosion resistance and high temperature mechanical properties [1]. The accurate maximum solubility of Nb in the Zirconium alloy is always controversial, but it is regarded as around 0.1 wt.% to 0.5 wt.%. When typical Nb-containing Zr-alloys like ZIRLO and M5 undergo the thermomechanically process, they generate Nb-containing precipitates or β-Nb particles [2].

In the study of microstructural evolution of M5 Alloy irradiated in PWRs up to high fluences, the β-Nb natural particles present in the M5 alloy remained completely crystallized after the irradiation process. After the dose of $11 \times 10^{25} \text{n} / \text{m}^2$, the natural particles reached 55 wt.% Nb of the equilibrium composition under the irradiation. Irradiation-enhanced acicular precipitation results in a significant decrease in the Nb content in the matrix [3]. It means that although undergoes thermomechanical processing and aging treatment, Nb is still supersaturated in the matrix. It is assumed defects generated during the irradiation stimulate the additional Nb nanoclusters formation, and it requires a very short diffusion path.

This paper focuses on exploring the driving force of additional Nb nanoclusters formation during irradiation. Heat treatments at temperatures similar to reactor operating temperature will be carried out to investigate whether Nb nanoclusters can be formed without irradiation. X-ray diffraction (XRD) is described for detecting lattice parameter change of the zirconium matrix, which can predict possible Nb nanocluster formation. The width of peaks is used to investigate dislocation density changes as a result of possible recovery. Hardness testing is used to explore the effect of the Nb precipitation on the mechanical properties of Zr alloys. The results will then be discussed in the context of previous literature.
2. Experimental methods

2.1. Materials and Sample Preparation

In this project, ZIRLO alloy was utilized as it contains Nb, it was produced by cold working and contains a very high dislocation density, which is similar to the M5 alloys after irradiation in the previous studies. A long ZIRLO tube was separated into several small pieces. Then they were annealed by furnace technique. Aging temperatures were set as 250℃, 300℃, 350℃, 400℃, aging time lengths were set as 1h, 16h, 100h, so 12 annealed samples can be obtained. During the annealing, they were under an argon atmosphere to minimize the sample surface oxidation during the heat treatment [4].

2.2. X-Ray Diffraction

As the size of Nb atom is smaller than Zr atom and it is a kind of substitutional solid solution in the Zr alloys, the lattice parameter will decrease with the Nb content increasing in the Zr matrix. The precipitation of Nb from the matrix should cause a loss of the Nb, then the lattice parameter of the α-Zr matrix should increase, so the possible Nb nanocluster formation can be detected indirectly by XRD. Machine and analysis parameters of XRD are shown in Table 1.

| Machine and analysis parameters of XRD | Proto AXRD |
|---------------------------------------|------------|
| Source                                | Cu K-α with nickel K-β absorber (Kα1=1.540598Å, Kα2=1.544426Å) |
| Generator voltage                     | 30 kV      |
| Tube current                          | 20 mA      |
| Receiving slit                        | 0.1 mm     |
| Scan range                            | 20 range of 25˚-125˚ |
| Filter                                | incident soller slit of 0.4mm, receiving soller slit of 0.6mm |
| Detector                              | Dectris Mythen 1K |
| Data handling                         | Bruker AXS TOPAS 4.2 (Pawley refinement) |
| Step size                             | 0.02 2θ/˚ |
| Scan time per step                    | 8s         |
| Data acquisition rate                 | 11.5h      |
| Reference pattern                     | α-Zr P63/mmc lattice parameter a=3.232Å c=5.147Å [5] |
| Analysis                              | 23 α-Zr peaks identified from reflections 010–032 |

2.3. Hardness testing

Microhardness testing is a kind of micro static test methodology. The most popular microhardness testing methods include Vickers and Knoop microhardness testing. In the project, the Vickers hardness testing is utilized [6, 7].

During the Vickers hardness testing, the diamond pyramid indenter is pressed into the sample by a certain test load and a certain compress time, the remaining indentation can be found by the optical amplification (10×, 40×), then the hardness can be obtained by measuring the diagonal length of the indentation [8]. Test parameters during the project are shown in Table 2.

| Test parameters of Microhardness | Vickers EN ISO 6507 |
|----------------------------------|---------------------|
| Microhardness instrument model   | MMT-X7A             |
| Ser. No.                          | MM6110X             |
| Manufacturer                      | Matsuzawa Co., Ltd.-Japan |
| Test load                         | 0.5kg               |
| Compress time                     | 10s                 |

3. Results and Discussion

3.1. Lattice parameter
Lattice parameters (a and c) of annealed samples measured by XRD are shown in Figure 1. The a lattice parameters of annealed samples are lower than those of as-received sample, a lattice parameter of the 400℃ annealed sample increases with the aging time, and at 350℃ it decreases with the aging time, for other temperatures it fluctuates with the aging time, and all figures tend to concentrate on a middle value as the aging time increasing. For the c lattice parameter, it increases with the aging time at 400℃, for other temperatures it fluctuates with the aging time, all figures fluctuate around the as-received sample value.

The change in lattice parameter measured by XRD shows a lower value of the lattice parameter a than that of the as-received sample, which is contrary to the theoretical result of the Nb precipitation. Both the a and c lattice parameter increase with the aging time during the 400℃ heat treatment, precipitation of Nb might be the reason for this phenomenon.

### 3.2. Cell volume and c/a ratio

Cell volumes and c/a ratios of annealed samples calculated by lattice parameters are shown in Figure 2. All cell volumes of annealed samples are lower than that of as-received sample, the cell volume of the 400℃ annealed sample increases with the aging time, and at 350℃ it decreases with the aging time, for other temperatures it fluctuates with the aging time, and all figures tend to concentrate on a middle value as the aging time increasing.

The analysis of annealed samples by XRD shows a lower cell volume than that of the as-received sample, which is contrary to the theoretical result of the Nb precipitation. Then at a high enough temperature (400℃), Nb may precipitate gradually and it causes the increasing of lattice parameters and cell volumes.
If this is the case, then it is likely that the defect and supersaturated Nb are the factor that stimulates the additional formation of Nb nanocluster during the irradiation, but dislocations of the cold worked ZIRLO need more energy to make the Nb diffuse through.

The residual stress development caused by annealing may result in the elongation in the c direction and the contract in the a direction, so that all c/a ratios of annealed samples are higher than that of the as-received sample. The higher the temperature, the more residual stress is removed, the higher the c/a ratio. In total, this change causes the decrease of cell volume.

After the long aging time, it is likely that almost all Nb elements are precipitated, c/a ratio and cell volume tend to concentrate on a middle value which might be the value of the α-Zr unit cell with no Nb elements.

3.3. Full width at half maximum of XRD peaks

The full width at half maximum (FWHM) of 002 (0002) and 110 (11-20) peaks obtained from Fityk are shown in Figure 3. All FWHM of annealed samples is lower than that of the as-received sample, and almost all figures decrease with aging time increasing.

During the recovery, the movement of dislocations and point defects causes the dislocation density to decrease, the dislocations are reordered, and the number of point defects decreases, thereby making the material performance to be restored to some extent [9]. The change of the dislocation density obtained from FWHM measurements can be utilized to prove recovery happening.

3.4. Hardness

The hardness of annealed samples measured by the hardness testing is shown in Figure 4. All figures fluctuate around as-received sample value with aging time increasing, but 250℃ and 300℃ annealed samples have a bigger fluctuation than others.
The analysis of hardness shows just a small change; fluctuations of 250℃ and 300℃ annealed samples are bigger than the other two, precipitation may cause the increase of the hardness, but during the annealing recovery may occur and offset the effect of precipitation in hardness, and the dislocation density decreases as reordering occurs by recovery, so FWHM of peaks is lower than that of the as-received sample and decreases with aging temperature increasing as more recovery may occur at a higher temperature.

Pawley fitting may be affected by the change of the dislocation density, then it causes the contrary result of the lattice parameter and cell volume. Residual stresses may also be the reason for that.

4. Conclusions
(1) Nb may precipitate at a temperature around 400℃, which means it is still supersaturated after intensive thermomechanical processing and aging treatment.

(2) The assumption is valid, the supersaturated Nb and the defect generation during irradiation stimulate the additional formation of Nb nanoclusters, the stored energy from processing and aging at a slightly higher temperature to the operating temperature of nuclear power plants can equally stimulate the precipitation of Nb nanoclusters.

(3) During the annealing, recovery may occur and cause a decrease of the hardness which is opposite to the effect of precipitation.
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