Nanocrystalline zirconium alloys obtained by severe plastic deformation

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Abstract. The structure and properties of commercial zirconium alloys Zr-2.5%Nb and Zr-1%Nb-0.3%Fe-1.2%Sn after severe plastic deformation (SPD) by high pressure torsion (HPT) at room-temperature under pressure of 4 GPa to N=5 (revolutions), which corresponds to a true deformation of $\varepsilon \approx 6$, and their thermal stability upon subsequent annealing have been studied. The alloys for HPT were taken in the two states: alloys were quenched from the single-phase $\beta$-region and from the two-phase $\alpha$-$\beta$ region. The structure formed in the Zr –2.5%Nb and Zr-1%Nb-0.3%Fe-1.2%Sn alloys after HPT is characterized by approximately similar nanograin sizes, 35– 55 nm and 30– 40 nm, respectively. The HPT of the alloys quenched from the two-phase region results in smaller grain sizes compared to those obtained from the alloys quenched from the single-phase region. It is shown that the HPT increases the microhardness of both alloys by a factor of 2.0– 2.5. Annealing at 350°C leads to an insignificant grain growth in the nanocrystalline matrix. The increase in hardness of the alloys after HPT remains after annealing at a temperature of 350–400°C.

1. Introduction
Zirconium alloys are promising materials for the manufacture of medical implants due to their good biocompatibility [1, 2]. However, the use of zirconium alloys for this purpose is limited because of their low strength in comparison, particularly with titanium alloys. Increased strength of zirconium alloys can afford to significantly expand their use in medicine.

One of the promising directions of improving the mechanical properties of zirconium alloys is the formation of nano- and submicrocrystalline structure by severe plastic deformation (SPD) [3, 4].

The purpose of this paper is to study the structure and properties of commercial zirconium alloys after severe plastic deformation by high pressure torsion (HPT). The Zr-2.5%Nb and Zr-1%Nb-0.3%Fe-1.2%Sn alloys, which are widely used to manufacture nuclear reactor core components, were selected for the study [5, 6]. HPT can use high pressure, which leads to the ultimate refinement of the structure and allows to study the possible phase transformation.
2. Experimental Procedure

High pressure torsion (HPT) was performed in Bridgman anvils at room-temperature under pressure of 4 GPa to N=5 (revolutions), which corresponds to a true strain of ~6. For HPT the specimens were cut into disks with a diameter of 10 mm and initial thickness of 0.6 mm. The alloys for HPT were taken in the following two states: the Zr-2.5%Nb alloy was quenched from the single-phase β-region (920°C, holding for 30 min, water-quenching, grain size of ~130 µm) and from the two-phase α+β-region (860°C, holding for 30 min, water-quenching, grain size of ~6 µm); the Zr-1%Nb-0.3%Fe-1.2%Sn alloy was quenched from the single-phase β-region (950°C, holding for 30 min, water-quenching, grain size of ~110 µm) and two-phase α+β-region (860°C, holding for 30 min, water-quenching, grain size of ~5 µm). Analysis of the structure was carried out using a JEM-100CX transmission electron microscope. Microhardness measurements were carried out by Vickers method using test machine MICROMET 5101 under a load of 100 g.

3. Results and Discussion

The structure and properties of commercial zirconium alloys Zr-2.5%Nb and Zr-1%Nb-0.3%Fe-1.2%Sn taken in two initial quenched states and their thermal stability after high pressure torsion (HPT) at room temperature and subsequent annealing at temperature of 550º C (1 hour, air cooling) have been studied.

The scheme of HPT deformation is inhomogeneous: it is minimal in the center of the specimen and maximum at the edges. To estimate the heterogeneity of the strain after HPT for Zr-2.5% Nb and Zr-1%Nb-0.3%Fe-1.2%Sn alloys the distribution of the microhardness values along the diameter of the samples was constructed (Fig. 1). For alloys quenched from the α+β-region, the microhardness along the diameter of the specimen is distributed more evenly. Structural studies and phase analysis were performed on the middle of the radius of the specimen.

![Figure 1](image1.png)  
**Figure 1.** Distributions of the values of Vickers microhardness along the diameter of the specimens of the Zr-2.5% Nb alloy: a - quenched from the two-phase region, 860°C; b - quenched from the single-phase region, 920°C

HPT provides a significant increase the microhardness of the both alloys by a factor of 2.0-2.5 compared to the initial state of the alloys (160-170 HV), but decrease the hardness of the center. Quenching of both alloys from the single phase β-region provides the maximum increase in hardness after HPT due to a higher supersaturation of the solid solution.

Electron microscopic analysis showed that the HPT of the Zr-2.5%Nb and Zr-1%Nb-0.3%Fe-1.2%Sn alloys leads to a nanocrystalline structure which is characterized by approximately similar nanograin sizes, 30–55 nm (Fig. 2, 3). The HPT of the alloys quenched from the two-phase region results in smaller grain sizes compared to those obtained from the alloys quenched from the single-phase region: 30–35 nm and 40–55 nm, respectively. It should be noted that, along with nanosized grains with high-angle boundaries there are small areas of subgrains of the same size with a low-angle boundaries.
Annealing at 350°C (holding for 1 h) leads to an insignificant grain growth in the nanocrystalline matrix. After annealing, the alloys quenched from the two-phase region exhibit a smaller grain size (of 35–45 nm) than that observed in the alloys quenched from the single-phase region, which after HPT exhibit a grain size of 70–75 nm.

![Figure 2. TEM micrographs of the Zr-2.5%Nb alloy, (quenched from 860ºC) after HPT: a - without annealing; b - after annealing at 350 ºC](image1)

![Figure 3. TEM micrographs of the Zr-2.5%Nb alloy, (quenched from 920ºC) after HPT: a - without annealing; b - after annealing at 350ºC](image2)

To study the thermal stability of the increase in hardness after HPT the dependence of the microhardness on the temperature of the annealing of the deformed alloys in the temperature range 50-550 °C was measured (Fig. 4). The increase in hardness of the alloys after HPT remains unchanged after annealing at temperature of 350–400°C, despite some increase in grain size (by a factor of 1.2-1.4). With a further increase in temperature above 400°C, the microhardness is significantly reduced due to the growth of grains in the matrix.
HPT leads to the formation of the $\omega$-Zr high pressure phase in $\alpha$-Zr matrix ($\alpha$-Zr-phase is partially preserved). During annealing the phase of $\omega$-Zr is transformed into $\alpha$-Zr. In the HPT-ed Zr-2.5% Nb and Zr-1%Nb-0.3%Fe-1.2%Sn alloys after annealing at 350 °C, some quantity of $\omega$-phase is preserved.

Thus, HPT zirconium alloys leads to the formation of nanocrystalline structure with the grain size of 30-55 nm and to increase of microhardness by a factor of 2.0-2.5 in comparison with the initial undeformed state. The increase in hardness after HPT remains unchanged during annealing at temperatures up to 350-400°C.

4. Conclusions
1. The structure formed in the Zr–2.5%Nb and Zr-1%Nb-0.3%Fe-1.2%Sn alloys after HPT is characterized by approximately similar grain sizes, 35–55 nm. The HPT of the alloys quenched from the two-phase region results in smaller grain sizes compared to those obtained from the alloys quenched from the single-phase region: 30–35 nm and 40–55 nm, respectively.
2. It is shown, that the HPT increases the microhardness of both alloys by a factor of 2.0-2.5. This effect is more pronounced in the alloys quenched from the single-phase region due to a higher supersaturation of the solid solution in spite of somewhat larger grain size. The increase in hardness of the alloys after HPT is remains unchanged after annealing at temperature of 350-400°C.
3. Annealing at 350°C (holding for 1 h) after HPT leads to an insignificant grain growth in the nanocrystalline matrix. After annealing, the alloys quenched from the two-phase region exhibit a smaller grain size (of 35–45 nm) than that observed in the alloys quenched from the single-phase region, which exhibit a grain size of 70–75 nm.
4. The Zr-2.5%Nb alloy upon HPT undergoes the $\alpha'_{Zr} \rightarrow \omega_{Zr}$ transformation. A partial reverse $\omega_{Zr} \rightarrow \alpha_{Zr}$ transformation occurs upon annealing.

References

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