THE STRUCTURE AND PROPERTIES OF ULTRAFINE-GRAINED ZIRCONIUM ALLOYS

Ph.D. Rogachev S., Prof., d.t.s. Nikulin S., Prof., d.t.s. Dobatkin S., Prof., d.t.s. Terentev V., Ph.D. Kopylov V.
National University of Science and Technology "MISIS"¹, A.A. Baikov Institute of Metallurgy and Materials Science", Moscow, Russia, Physicotechnical Institute, Belarusian Academy of Sciences², Minsk, Belarus

Abstract: Severe plastic deformation (SPD) of zirconium alloys Zr-2.5% Nb and Zr-1% Nb-0.3% Fe-1.2% Sn by torsion under room-temperature hydrostatic pressure (HTP) and equal channel angular pressing (ECAP) leads to significant grain refinement of the structure and strengthening. ECAP of the Zr-2.5 Nb alloy substantially increases the ultimate tensile strength (by a factor of 1.4) and yield strength (by a factor of 1.6). The fatigue strength of the Zr-2.5 Nb alloy after ECAP reaches ~420 MPa. In spite of significant strengthening of the Zr-2.5 Nb alloy after ECAP, material retains a sufficiently high reserve of ductility and toughness upon both static and fatigue loading.

KEYWORDS: ZIRCONIUM ALLOYS, SEVERE PLASTIC DEFORMATION, ULTRAFINE-GRAINED MATERIALS

1. Introduction

To achieve ultrafine-grained (UFG) materials with high strength and reasonable ductility, a great attention has been allocated to the application of severe plastic deformation (SPD) [1-6]. Despite the numerous researches for SPD processing of different pure metals and alloys, there are limited reports for Zr-based alloys. In this paper, UFG state of commercial zirconium alloys Zr-2.5% Nb and Zr-1% Nb-0.3% Fe-1.2% Sn was obtained by two methods of SPD: torsion under room-temperature hydrostatic pressure (THP) and equal channel angular pressing (ECAP). The Zr-2.5% Nb and Zr-1% Nb-0.3% Fe-1.2% Sn zirconium alloys selected for the study is widely used for the critical elements of the active zone of atomic power reactors [7].

THP was held to select the mode of ECAP, studying the regularities of formation of UFG structure during SPD and obtain the limit of the structural states of the material at maximum pressure. Mechanical properties of the materials studied in the specimens after ECAP.

The alloys for THP were taken in the following two states: the Zr-2.5% Nb alloy was quenched from the single-phase region (920°C, holding for 30 min, water-quenching) and from the two-phase region (860°C, holding for 30 min, water-quenching); the Zr-1% Nb-0.3% Fe-1.2% Sn alloy was quenched from the single-phase b region (950°C, holding for 30 min, water-quenching) and two-phase region (860°C, holding for 30 min, water-quenching) (Fig. 1). HPT was performed at room-temperature under pressure of 4 GPa to N=5 (revolutions), which corresponds to a true deformation of ~6.

Bars of 20 mm in diameter of the Zr-2.5% Nb alloy (alloy E125 in Russian standard) containing (wt. %) 97.25 Zr, 2.7 Nb, 0.05 Fe after cold rolling and annealing at 530°C (1 h) were used for ECAP. After annealing, the structure of the alloy is partially polygonized (with a subgrain size of 100-300 nm) and partially recrystallized (with a grain size of 1-5 µm). Pieces 120 mm long were cut from the bars of the alloy in the as-received condition and milled by hard-alloy head to a size of 14x14 mm, which corresponds to the size of the working channel of the tool for isothermal ECA pressing.

ECA pressing of Zr-2.5% Nb alloy was performed under isothermal conditions at a temperature of 420°C with an angle of 90° between channels by the route close to Bc by 4 passes corresponding to a true (logarithmic) strain of 2.1 [8].

Before ECAP, the Zr-2.5% Nb alloy after cold rolling and annealing at 530°C (1 h) has a mixed structure, which is partially polygonized (with a subgrain size of 100-300 nm), and partially recrystallized (with a grain size of 1-5 µm) (Fig. 1). The structure of the Zr-2.5% Nb alloy contains the b-Nb particles of 0.015-0.05 µm in size are arranged predominantly inside the a-Zr grains.

2. Experimental and results

2.1 Experimental procedure

Analysis of the structure was carried out using an AxioScop 40 optical microscope and transmission electron microscope JEM-100CX.

Microhardness measurements were carried out by Vickers method using microhardness MICROMET 5101 under a load of 100 g (exposure time 15 s).

The static mechanical properties were determined with a 10-ton 3380 Instron mechanical testing machine. The fatigue tests under the conditions of repeated tension at a constant minimum stress of 30 MPa were performed with an E3000 Instron Electro Puls pulser at a frequency of 30-40 Hz. Flat samples with a gage part of 1x3.5x16 mm² in size were spark cut from the billets. These samples were used for static and fatigue tests. The gage part surfaces of the samples were subjected to mechanical and chemical polishing, which ensured the mean arithmetic deviation of the profile irregularities (roughness) Ra = 0.29 µm.

The fractography analysis was carried out in an HITACHI S800 scanning electron microscope.

A comparative study of resistance to stress corrosion cracking (SCC) of the Zr-2.5% Nb alloy with UFG structure, and the same alloy in coarse-grained state (annealing at 530°C) was performed. Additionally, for comparison, specimens of the Zr-2.5% Nb alloy after cold rolling (grain size 4 ... 6 µm) were tested. Comparative SCC-tests on the Zr-2.5% Nb alloy specimens in all three states have been carried out by a specially developed original method of "express" SCC-tests with quantitative assessment of corrosion damage of the specimens after testing (measuring the number and size of pits and cracks). SCC-tests were performed on sheet specimens (size 20.0 x 4.5 mm and a thickness of 0.6 mm) using loading by bending at the exposure time to corrosive solution (1 % iodine solution in methanol) 100 and 200 hours and the same level of stress (~ 0.8 YS for the alloy of the state). Corrosive environment of 1 % iodine solution in methanol was chosen as the most aggressive for zirconium alloys, and allowed for a relatively short period of time trials to observe the various stages of corrosion damage.
2.2 Structural state

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 nanograin sizes. 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 40-50 nm, respectively (Fig. 2).

Heating to 350°C (holding for 1 h) leads to an insignificant grain growth in the nanocrystalline matrix. After heating, the alloys quenched from the two-phase region exhibit a smaller grain size (of 40-60 nm) than that observed in the alloys quenched from the single-phase region, which after HPT exhibit a grain size of 70-80 nm. It was found that the Zr-2.5% Nb alloy upon HPT undergoes the α’Zr→ωZr transformation. The reverse ωZr→αZr transformation occurs upon heating.

The ECAP of the Zr-2.5% Nb alloy formed the predominantly submicrocrystalline grained-subgrained structure (Fig. 3). The structure is somewhat oriented as a consequence of the formation of elongated subgrains at the stage of unsteady polygonization and/or shear bands at the early stages of ECAP [9].

Upon low-temperature ECAP, the ultrafine-grained (UFG) structure is formed by the recrystallization mechanism similar to the Cahn-Burgers mechanism [10], i.e., through the coalescence of subgrains with some structure features characteristic of cold deformation, upon which, in addition to the cellular structure and subgrains, the oriented structure elements such as twins, deformation bands, shear bands, kink bands, etc. appear in the deformed grains [11], and the diffusion processes occur due to high pressure and high degree of deformation rather than at the expense of thermal activation [12]. In our case, the transformation of the oriented subgrained structure into equiaxed grains (subgrains) can be multiple. The transverse size of the oriented structure elements in the Zr-2.5% Nb alloy after ECAP was 30-150 nm, and the size of the equiaxed grains (subgrains) was 50-200 nm. The presence of high-angle boundaries, i.e., the grained structure, was judged from the presence of the rings of point reflections in the electron diffraction patterns and the banded contrast at the boundaries.

2.3 Mechanical properties upon static tensile tests and fatigue tests

It is shown that the HPT increases the microhardness of both alloys by a factor of 2.0-2.5 (~400 HV) (Fig. 4). 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 strain hardening of the Zr-2.5% Nb and Zr-1% Nb-0.3% Fe-1.2% Sn alloys after HPT is retained after heating to a temperature of 350-400°C due to the precipitation of the β-Nb particles in spite of a certain grain growth (Fig. 5).

The static tension curves of the Zr-2.5% Nb alloy are represented in Fig. 6, and the mechanical properties are given in Table 1.

<table>
<thead>
<tr>
<th>Initial state</th>
<th>YS, MPa</th>
<th>UTS, MPa</th>
<th>EL, %</th>
<th>σR, MPa</th>
<th>σR/UTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>States</td>
<td>377</td>
<td>569</td>
<td>26,1</td>
<td>340</td>
<td>0,60</td>
</tr>
<tr>
<td>After ECAP</td>
<td>622</td>
<td>771</td>
<td>9,7</td>
<td>420</td>
<td>0,54</td>
</tr>
</tbody>
</table>

Note: σR - the fatigue limit based on 107 cycles.
It is evident from Table 1 that the yield strength and ultimate tensile strength of zirconium alloy after ECAP substantially increases, but the ductility decreases more than by a factor of two. The yield strength after ECAP increases by a factor of 1.6. The fatigue curves of the materials are represented in Fig. 7. The fatigue limit $\sigma_R$ of the Zr-2.5% Nb alloy samples after ECAP is 420 MPa, i.e., it increases by 80 MPa (or by a factor of 1.2) in comparison with that of the initial state. The limited fatigue life of the Zr-2.5% Nb alloy samples after ECAP increases in several times in comparison with that of the samples in the initial structural state. The endurance ratio $\sigma_R/UTS$ of the zirconium alloy is 0.54 after ECAP and 0.60 for the initial state.

2.4 Fractographic studies

Figure 8 shows the failure fracture surfaces of the Zr-2.5 Nb alloy samples in the initial state and after ECAP. The macroscopic picture of the fatigue failure in both cases consists of two clear regions, i.e., the flat surface of fatigue fracture and quasi-ductile static rupture area. The regions of intergranular fracture at the boundaries of blocks (granules) of are observed 23 $\mu$m in size with the traces of significant plastic deformation are observed in the initial zone of the fatigue crack propagation (Figs. 8a and 8d). At a high magnification, fatigue micro-grooves with submicron-size spacing between them are observed on the surface of the blocks.

At the stage of the stable fatigue crack propagation, quasi-ductile grooved relief with the secondary cracking at the front of the crack advance (Figs. 8b and 8e) is observed both in the initial material and in the samples subjected to ECAP; however, the relief in the ECAP samples is flatter (Fig. 8e).

A mixed fracture surface with alternating regions of quasi-ductile and ductile fracture with a dimple size of 1-3 $\mu$m is observed in the zone of the accelerated fatigue crack growth (Figs. 9c and 9f). However, the relief is flatter in the ECAP samples. The static rupture area of the samples of both series exhibits quasi-ductile fracture (Figs. 8c and 8f).

2.5 CSS-tests

On the surface of the specimens after cold rolling after 2-4 h exposure during SCC-tests there have been observed cracks with length up to 1.5 mm, extending from the edges of the specimen, as well as pits with radiating from them small cracks with length of about 20-200 microns. On the surface of the specimens after annealing there were observed pits, and only some of them depart some few cracks with length of about 20 microns. Large cracks, as in cold rolling specimens, in this case were not observed (Fig. 9).

Formation of submicrocrystalline structure at ECAP Zr-2,5% Nb alloy does not change the characteristic of coarse-grained zirconium alloys mechanisms of SCC associated with pits formation, but leads to increased resistance to corrosion damage under stress compared with the alloy with the initial CG structure: at the same time of exposure in a solution, the number of pits are 2-4 times smaller, and their average size is 4-7 times less, compared with the alloy with the coarse-grained structure. The increase in test time from 100 to 200 hours does not lead to a significant increase of pits size. For the alloy with UFG structure after ECAP during testing at the time of exposure to 200 hours there no cracks were observed comparing to the coarse-grained alloys. For the UFG alloy in the local areas there are concentrations of very fine pits with a diameter of about 2 microns. The accumulation of corrosion
damage with increasing exposure time from 100 to 200 hours is mainly due to the appearance of new pits, but not of their growth.

Fig. 9. Corrosion defects on the surface of the samples of Zr-2.5% Nb after exposure in a corrosive solution for 100 hours: a - after the cold deformation, b - after annealing, c – after ECAP

3. Conclusion

1. The structure formed in the Zr-2.5% Nb and Zr-1% Nb-0.3% Fe-1.2% Sn alloys after THP is characterized by nanograin sizes: 30-35 nm for the alloys quenched from the two-phase region and 40-50 nm the alloys quenched from the single-phase region.

2. The THP increases the microhardness of both alloys by a factor of 2.0-2.5.

3. The strain hardening of the Zr-2.5% Nb and Zr-1% Nb-0.3% Fe-1.2% Sn alloys after THP is retained after heating to a temperature of 350-400°C.

4. The Zr-2.5% Nb alloy upon THP undergoes the α’Zr→ωZr transformation. The reverse ωZr→αZr transformation occurs upon heating.

5. The ECAP of the Zr-2.5% Nb alloy formed the predominantly submicrocrystalline oriented grained-subgrained structure. The transverse size of the oriented structure elements in the Zr-2.5% Nb alloy after ECAP was 30-150 nm, and the size of the equiaxed grains (subgrains) was 50-200 nm.

6. ECAP of the Zr-2.5 Nb alloy substantially increases the ultimate tensile strength (by a factor of 1.4) and yield strength (by a factor of 1.6); however, their ductility decreases more than by a factor of two.

7. The ECAP of the Zr-2.5 Nb alloy after ECAP reaches ~420 MPa, and their σR/UTS ratios after ECAP are approximately similar (0.54).

8. The study of the specific features of the fatigue crack propagation mechanism in the materials under consideration showed the intergranular fracture and the fracture by the mechanism of quasi-ductile grooved relief and secondary cracking along the grooves in the SMC materials, by contrast to the coarse-grained metallic materials, in which the stable fatigue crack propagation results in the ductile grooved relief of the fracture surface.

9. In spite of significant strengthening of the Zr-2.5 Nb alloy after ECAP, material retains a sufficiently high reserve of ductility and toughness upon both static and fatigue loading.

10. The Zr-2.5% Nb alloy with UFG structure is less susceptible to corrosion damage in comparison with the coarse-grained structure (annealed or cold rolling).

4. Literature