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Effect of water and mercury quenching on the microstructure and mechanical behavior of room temperature rolled Zircaloy-2

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The present study investigates the effect of water and mercury quenching on the microstructural and mechanical behavior of room temperature rolled Zircaloy-2. Solution treatment of Zircaloy-2 at 1073 K followed by quenching in mercury and water has been performed prior to rolling. Different reduction from 25% to 85% of the quenched alloy and further characterization has been performed by tensile testing, Electron back scattered diffraction (EBSD) and Transmission Electron Microscopy (TEM). Enhanced tensile strength (745 MPa) after 85% rolling reduction was obtained compared to 389 MPa after water quenching. Rolling reduction results an increase in the dislocation density, thereby enhancing the mechanical strength. Initial deformation has been observed by the activation of extension twinning from EBSD microstructure. Twinning results the inclination of 'c' axis towards the normal direction which makes near basal grains orientation along the deformation direction. Due to hard orientation i.e. 'c' axis aligned along the loading direction, the grain fragmentation is heterogeneous. Grain fragmentation leads to improvement in the ductility with minimal loss in strength owing to rearrangement of dislocations after annealing at 400^o C for 30 minutes. By optimizing the annealing temperature (400^o C for 30 minutes), bulk ultrafine grained Zircaloy-2 have been produced in 85% room temperature rolled Zircaloy-2.

Keywords: Ultrafine grains, Zircaloy-2, Transmission electron microscopy, Electron back scattered diffraction, Annealing, Quenching

1 Introduction

Due to better mechanical properties, corrosion resistance and low neutron absorption cross section, Zircaloy-2 has been used as in nuclear power reactors as pressure tubes and structural material[1-3]. The alloying elements of Zircaloy-2 are tin, iron, chromium and nickel with their concentration less than 2%. The 'α' phase which is hexagonal closed pack (HCP) structure is stable below 1080 K. While the 'β' phase, which is body centered cubic (BCC) is stable above 1250 K[4-7]. Rolling and optimized annealing of Zirconium effects the microstructure and texture evolution, which effects the corrosion, creep and mechanical behavior of Zirconium alloys.

Twinning activates at low deformation strain in the HCP crystals with mainly two types, extension twin in $\{10\bar{1}2\} < \bar{1}011 >$ and $\{11\bar{2}1\} < \bar{1}\bar{1}26 >$ and contraction twins in $\{11\bar{2}2\} < \bar{1}\bar{1}23 >$ and $\{10\bar{1}1\} < \bar{1}012 >$ (at high temperature)[8]. With c/a ratio less than 1.633, $\{10\bar{1}0\}$ prismatic slip is always dominants. Twin causes large lattice orientation of basal planes from the pole. $\{11\bar{2}2\}$ twinning is being activated, when basal pole orients 0-50^o from the normal direction. While $\{10\bar{1}2\}$ twinning activates at 50-90^o orientation of basal poles towards normal direction, and if basal pole tilt from 0-90^o, means $\{11\bar{2}1\}$ twinning has been activated. After rolling, the basal pole $\{0002\}$ aligns parallel to the normal direction and moves 20-40^o towards the transverse direction[9].

Grain size influences the physical and mechanical response of materials. Grain size can be controlled by optimizing mechanical and thermal processing of a material to get the desired properties. Ultrafine grain materials are produced mostly by severe plastic deformation techniques (SPD) such as ARB, ECAP, multiaxial forging, repeated corrugation and

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straightening[10-13]. Rolling and optimized annealing of Zirconium alloy affects the microstructure and texture evolution, which influences the corrosion, creep and mechanical behavior of alloys[14-15]. Many articles have been published showing the grain refinement of mercury quenched Zircaloy-2 by room temperature rolling and cryorolling[16-19]. The room temperature rolled, cryorolled, wire rolled at cryogenic temperature, cross rolled at room temperature showed 679 MPa, 891 MPa, 1015 MPa and 991 MPa tensile strength respectively. The enhanced dislocation density to 10^{15} m/m^3 and grain refinement was found to be the main cause of strengthening[16].

It is difficult to perform mercury quenching on industrial scale, as it is costly and its fumes are hazardous. Therefore, the present work has been focused to differentiate the effect of water quenching and mercury quenching on the grain size and mechanical behavior of room temperature rolled (RTR) ultrafine grained Zircaloy-2.

2 Materials and Methods

Zircaloy-2 procured from NFC Hyderabad has been rolled at 800^o C temperature having 4 mm plate thickness. Samples with 3 cm x 5 cm dimensions have been cut from the plate and grounded to remove the oxide layer which has been presented on the Zircaloy-2. After that, the samples have been heated in argon environment up to 800^o C for 2 hours followed by water quenching. Rolling has been performed on 2 high rolling mill having 110 mm roller diameter with 8 rpm rolling speed. A reduction of 0.4 mm has been given in every pass followed by water quenching to suppress the dynamic recovery during processing. Tensile samples were cut along the rolling direction with a gauge length of 16 mm and were tested with a strain rate of 5 x 10^{-4} s^{-1} at room temperature.

For EBSD microstructure, the samples were fine polished with alumina solution and electropolished by using 20:80 solutions of perchloric acid and methanol at a temperature of -20^o C with a voltage of 20 V. EBSD of the samples was performed using FEI Quanta 200 FEG SEM with a voltage of 200 KV. Analysis has been performed using TSL/OIM software package. TEM sample preparation has been done by thinning of the sample upto 0.1 mm and punching them to 3mm disc. The punched samples have been electropolished in twin jet polisher using the same etchant used in EBSD. TEM was performed using FEI Technai 20 with a voltage of 200KV.

3 Results and Discussion

3.1 Electron Back Scattered Diffraction

Initially sample contains homogeneous microstructure with an average grain size of 20 µm which can be seen from Fig. 1(a). The grains size of mercury quenched Zircaloy-2 was 10 µm. The difference in grain size was observed due to the variation in cooling rate of water and mercury. Moreover, mercury might have higher heat absorption capacity than water. Fig.1 (b-d) represents the deformed structure of water quenched Zircaloy-2 after rolling upto 25-75% thickness reduction. Minimum confidence index of 0.03 has been excluded from the image, so that the completely deformed area can be observed as dark. The 25% rolled image shows basal texture with some undeformed grains having near basal orientation, which are elastically harder[20]. Grains with orientation other than basal are formed due to activation of twinning at low strain. This orientation is considered to be soft orientation. However, the twin boundaries are responsible for initial hardening of strength due to formation of special boundaries.

On further reduction up to 50% reduction, larger fraction of deformed area can be seen with some undeformed near basal grains. Normally, the basal plane is perpendicular to the direction of resultant force[8-9]. Even after 75% reduction in thickness the

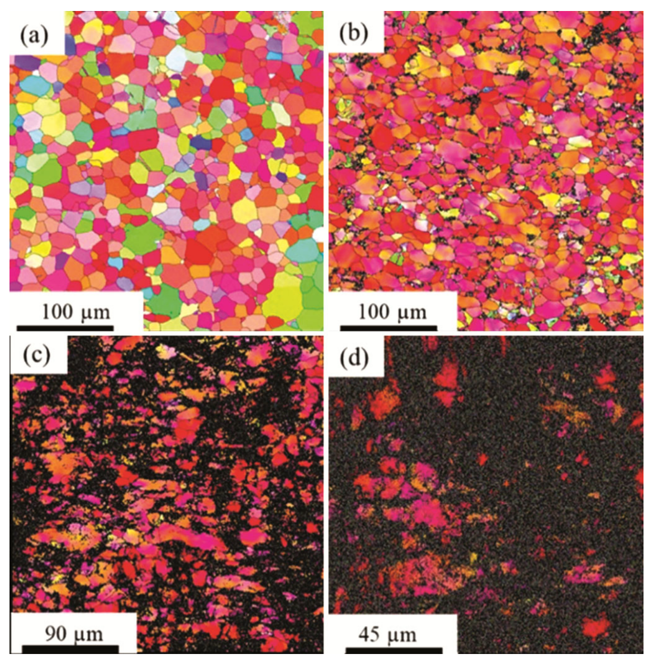

Fig. 1 — (a) EBSD image of water quenched Zircaloy-2, (b) 25%, (c) 50%, and (d) 75% RTR Zircaloy-2.

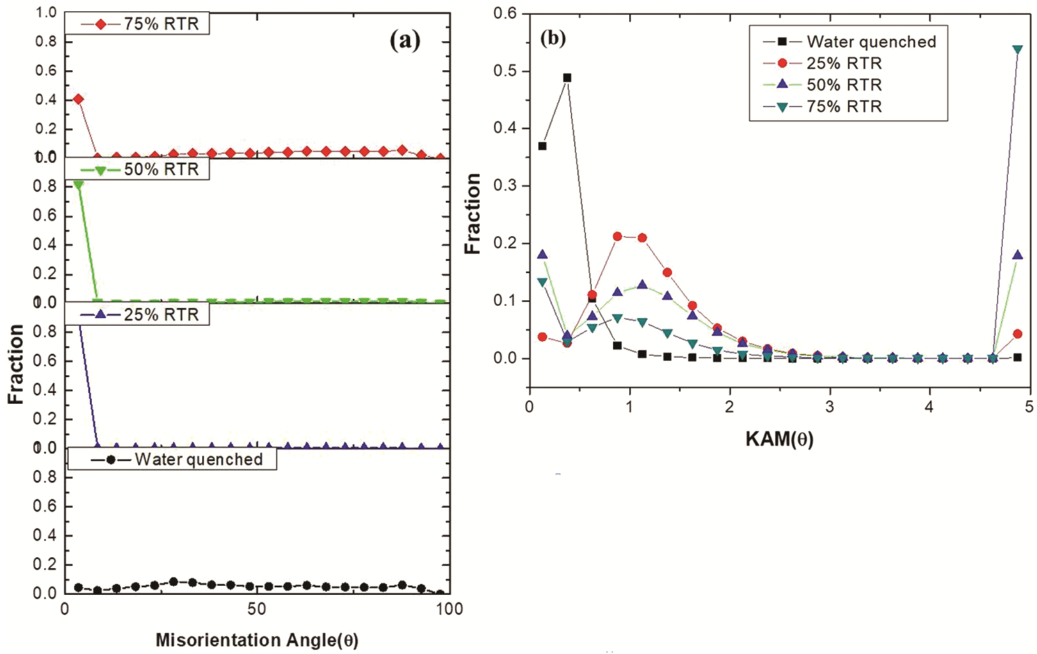

Fig. 2 — (a) Grain boundary misorientation, and (b) KAM of water quenched, 25%, 50% and 75% RTR Zircaloy-2.

undeformed and non-fragmented near basal grains have been observed. The alignment of 'c' axis towards the normal direction makes the grains elastically harder[20]. Deformation leads to the reorientation of grains along the hard orientation. This phenomenon is mostly accelerated by the formation of twins at low strain. In Zirconium, at higher strain value deformation is mostly governed by the slip activity and also responsible for basal orientation of grains. Some of these hard basal oriented grains do not disintegrate even at very high strain during deformation (Fig. 1(c-d))[16-19]. Misorientation curve shows large fraction of low angle grain boundary with no traces of twins in the graphs due to lesser fraction of twins as shown in Fig. 2(a). Even with more rolling strain, the fraction of low angle grain boundaries (LAGBs) are very high. On the contrary, mercury quenched sample does not show that much fraction of LAGBs after rolling. This difference might be due to the presence of small precipitates formed during water quenching.

Kernel Average Misorientation (KAM) image depicted in Fig. 2(b) shows that the average KAM value increases with rolling reduction. KAM explains that the stored Energy and dislocation density in water quenched deformed Zircaloy-2 is increasing with the increase in rolling percentage. The KAM values are increasing near 5^{o} misorientation after 85% rolling reduction might be due to the formation of more fraction of LAGB between 5^{o} and 15^{o}misorientation.

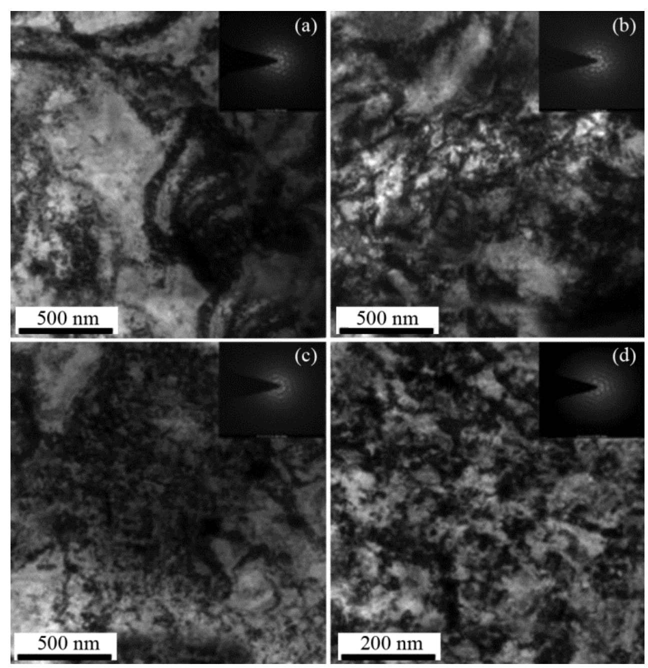

Fig. 3 — TEM image of (a) 25%, (b) 50%, (c) 75%, and (d) 85% RTR Zircaloy-2.

3.2 Transmission Electron Microscopy

The TEM microstructure image (Fig. 3(a-d)) of RTR water quenched Zircaloy-2 represented almost same feature as of RTR mercury quenched Zircaloy-2 as discussed[16-19], showing dislocation cells and tangles. Dislocation tangles has been vanished and converted to dislocation cells due to dynamic recovery at room temperature. Repeated plastic deformation orients the dislocation tangles to very small angles and resulting in the formation of dislocation cells, which is also known as low angle grain boundary[21-23]. These low angle grain boundaries have been formed in almost 90% area which has been observed in misorientation graph explained above. On repeated deformation, increase in fraction of heterogeneous microstructure can be observed. Heterogeneous structure contains both coarse and ultrafine grains, and the fraction of these grains increases with strain[23].

After 85% rolling reduction of Zircaloy-2, multimodal microstructures can be seen and can be compared with the EBSD and TEM images as shown (Fig. 1 and 3). These images clearly represent grains of various sizes ranging from 50nm to 10 µm. The grains with size greater than 5 µm contain dislocation tangles and cells. The same observations were also found from KAM maps (Fig. 2(b)). The structure observed after RTR Zircaloy-2 have high strength and ductility. The average grain size of the UFG regions is 167 nm which has been calculated using the TEM image.The grain size increases and dislocations get annihilated on further annealing of 85% RTR Zircaloy-2 at different temperatures of 400 °C and 500 °C for 30 minutes. Fig. 4 (a-c) depicts TEM micrographs, showing the effect of annealing temperature on 85% RTR Zircaloy-2. The average grain size increases to 220 nm after annealing at 400 °C while annealing at 450 °C increases the grain size to 320 nm. At 500 °C temperature the grains size increases to an average of 800 nm size.

3.3 Mechanical Properties

The effect of room temperature rolling on the mechanical behavior has been studied by performing tensile test in Table 1. The water quenched Zircaloy-2 shows lesser tensile strength (389 MPa) and ductility (17%) as compared to mercury quenched Zircaloy-2[19]. Repeated rolling reduction increases the dislocation density inside the crystal, and with higher reduction, ultrafine grains formation takes place. The reduction in grains size and stored dislocation density after RTR, increases the strength of water quenched Zircaloy-2. The tensile strength increases from 389 MPa to 745 MPa with 4% ductility in rolling direction after 85% RTR. The mechanical properties after 85% RTR mercury quenched sample showed 679 MPa with 5.5 percent ductility[16-19]. The difference may be due to the higher strain hardening capacity of water quenched Zircaloy-2, as it is having lesser ductility than mercury quenched as well.

Annealing releases the stored energy of deformed Zircaloy-2 by annihilating the dislocation density and formation of reoriented ultrafine grains of high angle grain boundary takes place. The temperature selected for annealing 85% RTR Zircaloy-2 is 400°C for 30 minutes. At annealing above 400 °C, a very sharp decrease in the tensile strength has been observed. The tensile strength after annealing reduces to 669 MPa from 745 MPa with increase in ductility from 4 to 5 %. On comparing it to our earlier work, 85% RTR mercury quenched sample shows almost same tensile strength of 664 MPa with 6% ductility[16-19].

Table 1 — Mechanical properties of alloy at different condition

Conditions	Tensile Strength (MPa)	Yield Strength (MPa)	Ductility (%)
Water quenched	389	304	17
25% RTR	598	577	7.1
50% RTR	650	628	7
75% RTR	686	634	5.9
85% RTR	745	717	4
25% RTR Annealed	580	559	10
50% RTR Annealed	606	588	9
75% RTR Annealed	621	595	7.1
85% RTR Annealed	669	633	5

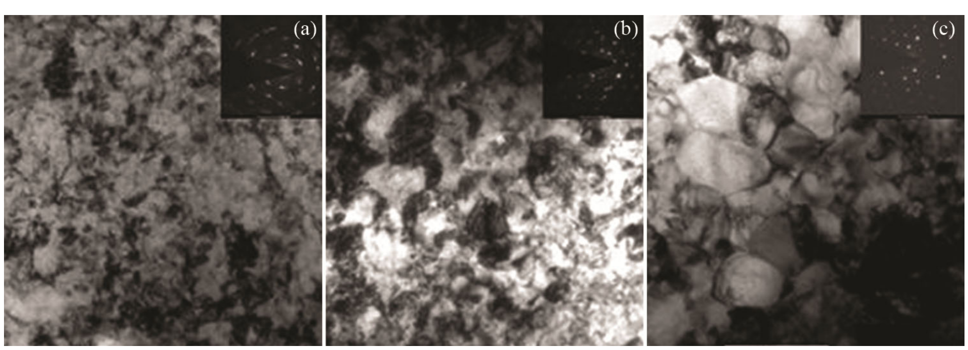

Fig. 4 — TEM microstructure of (a) 400°C, (b) 450°C, and (c) 500°C annealed Zircaloy-2 after 85% RTR.

The reason for lower ductility and higher strengthening response of water quenched compared to mercury quenched Zircaloy-2 might be due to the formation of incoherent secondary phase after water quenching. This can also be explained by the difference in grain size (20 µm), which is almost twice than the grain size (10 µm) obtained by mercury quenching. This clearly shows slow cooling occurred during water quenching, which allows the evolution of secondary phase inside the matrix. The phase must have been incoherent because incoherent phase is responsible for strengthening and less ductility during straining.

4 Conclusion

- Initial grain size after water quenching is 20 µm bigger than mercury quenched, because cooling rate during mercury quenching must be higher.
- Initial deformation up to 25% rolling reduction takes place by the activation of slip and extension twinning. After 25% reduction, non-fragmented and undeformed near basal grains are formed.
- With the increase in rolling reduction, stored energy and dislocation density inside the material is increasing as observed from KAM.
- Heterogeneous microstructure with grain size ranging from 50nm to 5µm having an average grain size of 167 nm was obtained after 85% room temperature rolling of water quenched Zircaloy-2. Annealing at 400^{o}C and 450 ^{o}C for 30 minutes increases the average grains size to 220 nm and 320 nm, respectively. The grains size increases to 800 nm after annealing at 500^o C for 30 minutes.
- 85% RTR water quenched Zircaloy-2 shows enhanced tensile strength (745 MPa) and 4% ductility while annealing at 400 ^{o}C for 30 minutes consequence the tensile strength to reduce upto 664 MPa with 5% ductility.

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