Microstructure -Mechanical Property correlation of Cryo rolled Zircaloy-4

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Abstract

The evolution of microstructure and the mechanical properties of cryo-rolled Zircaloy-4 were both investigated to understand the origin of the alloy's strength processed at a cryogenic temperature. The correlation of dislocation density, grain size and yield stress of the rolled product indicated that an increase in dislocation density due to the suppression of dynamic recovery is the primary source of strengthening.

Keywords: Cryo rolling, Zircaloy-4, Tensile tests, X-ray diffraction, Dislocation density

1. Introduction

Zirconium (Zr) alloys are the backbone materials for thermal reactors [1, 2]. These alloys are used in thermal reactors because of their low neutron absorption cross section, in addition to suitable high temperature mechanical and corrosion properties. Different Zr based alloys are used for various structural applications. Zircaloy-4 (Zr4) is most commonly used as fuel cladding, for intermediate grid applications in pressurized water reactors (PWRs), and channel boxes in boiling water reactors (BWRs). Zircaloy cladding acts as a barrier between the radioactive fuel and exterior coolants. Therefore, the structural integrity of the cladding tube is extremely important in the safe operation of reactors. Efforts are being made to produce Zr4

products with better mechanical properties. Different processing routes involving: forging, extrusion, and pilgering have been developed over the years to fabricate components with improved in-reactor performance [3]. The aim of this work is to devise an alternate processing method and study its effect on the microstructure and mechanical properties of Zr4.

The development of severe plastic deformation (SPD) processes has received considerable attention over the past decades [4]. Metals and alloys processed by SPD are shown to have an ultra fine grain (UFG) structure with average grain size in the submicron range [4-6]. UFG materials produced via the SPD process exhibit superior properties of mechanical strength when compared to their coarse grain counterparts [7-9]. There are many methods to produce UFG alloys, including: cryo-rolling [10-14], accumulative roll bonding (ARB) [15], cryo-milling [16], equal channel angular pressing (ECAP) [10, 13, 17], multi-axial forging (MAF) [18, 19] etc. Extensive research has been carried out on various UFG materials produced by different methods over the last three decades [4-10, 13-23]. The primary distinction between UFG materials produced by cryo-rolling and other UFG materials produced by SPD methods is the nature of the grain refinement process and, by extension, the character of the grain boundary. The hindrance of dynamic recovery is central to the process of grain refinement via cryo-rolling which is accomplished by straining the material at cryogenic temperatures. In the other SPD methods a continuous dynamic recovery/recrystallization caused by applying very high strain at ambient temperatures, contributes to the process of grain refinement. Cryo-rolling has been carried out on Al [12, 24], Cu [25-27], and Ti [28, 29] alloys. Recently, Guo et al. studied the mechanical properties and microstructure of the cryo-rolled Zr [30-33]. Kamalnath et al. [34] and Goel et al. [35] reported their results on the investigation of cryo-rolling of Zircaloy-2. In this work, a nuclear grade Zr4 plate was rolled to different reductions using cryo-rolling. The microstructure

and mechanical properties of the rolled materials have been examined in detail with the aim to develop the understanding of the evolution of mechanical properties in a cryo-rolled sheet.

2. Experimental details

A 4.2 mm thick Zr4 plate with a nominal chemical composition of (Zr-1.5Sn-0.1Cr-0.2Fe) was used for this study. The plate was annealed at 760 °C for 2 hours before rolling. The annealed plate was then dipped in liquid nitrogen for 15 min and then rolled from 4.2 to : 3.35, 2.10 and 1.25 mm in different passes. These thicknesses corresponded to 20, 50 and 70 % reduction. To prevent cracking, each thickness reduction was achieved in about 10 passes. After each pass, the plate was immersed in liquid nitrogen for over 5 min before the next reduction. Transverse sections of the rolled plates were polished using conventional techniques for the electron back scattered diffraction (EBSD) scan. Polished samples were electro-polished using an electrolyte of 80:20 (by volume) methyl alcohol and perchloric acid under 21 V at –40 °C. The EBSD measurements were taken by a FEI Quanta-3D-FEG scanning electron microscope using a Tex. SEM Ltd. – Orientation Imaging Microscopy (TSL-OIM) EBSD package. In each sample, an approximate area of 100 µm × 100 µm was scanned by the EBSD. Beam and video conditions were kept identical between the scans and a step size of 0.2 µm was used. In EBSD analyses, grains were identified based on a 15° misorientation criterion. Specimens for transmission electron microscopy (TEM) were prepared by twinjet electropolishing using an electrolyte consisting of a solution of 80% methanol and 20% perchloric acid at a temperature of –50 °C, using a voltage of 25 V. TEM studies were carried out using a JEOL 2000 FX microscope. Specimens for X-ray diffraction (XRD) were prepared from the rolled surface by slow polishing. XRD scans were recorded by a Bruker D8 diffractometer using step scan mode.

A step size of 0.01 degree was used for these analyses. The time per step was 5 seconds. Tensile specimens with a gauge length of 10 mm were machined from the annealed and rolled plates along the rolling direction. Tensile tests were carried out using an Instron screw driven machine at a nominal strain rate of $1 \times 10^{-3} \text{ s}^{-1}$. Three samples were tested for each condition.

3. Results and discussions

Fig. 1 a-d shows the EBSD maps of the initially annealed and rolled samples. In these EBSD maps black portions indicate unindexed regions. Grains are represented by colored regions. It can be seen that the initially annealed sample has large grains with clearly visible grain boundaries. The average grain size in the annealed sample is 12 μm . With increasing strain there are signs of grain fragmentation. However, due to large amount of strain accumulation at higher reductions most of the points are unindexed. The higher dislocation density at higher strain deteriorates the quality of the diffraction pattern due to the higher lattice distortion [36, 37]. The average grain size decreased to 3 μm at 70% reduction. Fig. 1e shows the TEM image of the sample rolled to 70% reduction and regions of high dislocation population are evident in the microstructure. However, the estimation of microstructural parameters from the TEM images of heavily deformed samples is not straight forward [38]. XRD line profile analysis has emerged as a powerful tool to characterize the dislocation microstructure of deformed samples [39, 40]. XRD gives average information on the microstructure of the material from a relatively larger volume of the sample. Fig. 2a shows the XRD profiles of the annealed and 70% rolled samples. It can be seen that diffraction peaks are broadened for the rolled sample. Microstructural information of the material is primarily derived from the width and shape of the diffraction peaks. Different approaches have been developed in the past two decades for analyzing the XRD profiles of deformed samples. Microstructural parameters like: domain size, microstrain,

dislocation density etc. are evaluated using this analysis. The convolutional Whole Powder Pattern Fitting (CMWP) method developed by Ungar and coworkers has been successfully used to characterize the microstructure of different materials [41, 42]. XRD profiles of the initially annealed and the rolled samples have been analyzed using the CMWP method. In the CMWP approach, the profile functions are calculated as the convolution of the theoretical size and strain functions and the measured instrumental profiles. The observed whole powder pattern is then fitted using the sum of constructed profile functions and a background function using a non-linear least square method to work out the microstructure parameters [41-44]. The main advantage of this method with respect to profile fitting and whole powder profile fitting in general is that no profile shape function is used to model the size-strain broadening. Analytical functions frequently used in profile fitting like the Rietveld method such as: Gauss, Lorentz, modified Lorentz, Voigt, pseudo-Voigt, Pearson VII, and similar shape functions cannot adequately describe the effects of strain and size broadening on diffraction line profiles, especially where line broadening causes anisotropic strains. Fig. 2b shows a typical CMWP fit of the XRD profile of the sample rolled to 70% reduction. Microstructural parameters (domain size (D), microstrain (ϵ), and dislocation density (ρ)) obtained from the CMWP analysis are listed in Table 1, along with the mean grain size from the EBSD. Domain size obtained from XRD/LPA essentially represents the regions bounded by low angle boundaries. It is seen from Table 1 that domain size decreased due to rolling, while microstrain and dislocation density increased in consecutive rolling passes.

Fig. 3a shows the engineering stress-strain curves of the annealed and rolled samples. Initially annealed sample showed considerable work hardening and a higher ductility. With increasing rolling reduction there is an increase in yield stress (YS) and ultimate tensile stress

(UTS). However, ductility or percentage of total elongation (%EL) decreased due to rolling. Fig. 3b shows the variation of YS, UTS and %EL with rolling reduction. It is pertinent to note here that, pure Zr has been shown to exhibit increase in ductility after cryo rolling [45]. This is in contrary with the present observation in cryo rolled Zr 4. This may be attributed to the difference in microstructure (presence of precipitates in Zr 4) of two materials.

3.1 Estimation of strength: The yield stress σ_y of a material can be written as the sum of the hardening contributions from grain boundaries (Hall–Petch type) and that from dislocations within the subgrains/grains [46, 47]

$$\sigma_y = \sigma_0 + \alpha M G b \sqrt{\rho} + K_{HP} d^{-0.5} \quad (1)$$

where $\sigma_0 = 20$ MPa [48] is the frictional stress of the Hall–Petch equation, α is a constant around 0.3 [48], $M = 4$ is the Taylor factor [48], $G = 40$ GPa is the shear modulus [48], b is the magnitude of the Burgers vector, ρ is the total dislocation density contributing to dislocation forest strengthening, K_{HP} is the Hall–Petch slope used here as $0.25 \text{ MPa m}^{0.5}$ [49], and d is the average grain size.

The dislocation densities determined from the XRD line profile analysis and the average grain size values obtained from EBSD maps are used to estimate the 0.2% offset yield stress using eqn. (1). The experimental results and estimated stress are compared in Fig. 4a where the contribution of different components of strengthening – the term σ_0 , the grain boundary term and the dislocation density term – are plotted as stacks. The bottom stack is σ_0 and is taken as a constant for all conditions. The second stack represents the grain boundary strengthening term and is a significant fraction of the total strength for the annealed sample but becomes a relatively smaller

fraction of the total strength of the 20, 50 and 70% rolled conditions. The third stack is the dislocation density term. This becomes relatively a significant fraction of the total strength for the cryo-rolled conditions. The above observations clearly indicate that strengthening due to dislocations is significant in cryo-rolled materials.

3.2 Grain size and work hardening: The work hardening capability of the processed materials provides the resistance to tensile mechanical instabilities, thereby controlling ductility. Thus it is essential to assess the effect of grain size achieved via an SPD method on the work hardening behavior of the processed material. Dependence of work hardening on the grain size of polycrystalline materials has been subject of investigation for a considerable amount of time [50-52]. In the present case, the plastic region of true stress vs. true strain tensile curves for deformed samples has been fitted with the Crussard–Jaoul [53] equation:

$$\sigma = \sigma' + k\varepsilon^n \quad (2)$$

to determine the strain hardening exponent (n). Here σ' is the true stress at zero plastic strain. The value of n essentially represents the work hardening capability of a material. Fig. 4b shows the variation of n with the grain size of the rolled samples and it is clear n decreases with decreasing grain size; exhibiting a power law dependence ($n \propto \text{grain size}^{3.9}$). Rapid decrease in the value of n in deformed samples indicates that grain boundary deformation did not increase with decreasing grain size. Dislocations within the grains also play an important role in determining the work hardening behavior. Increase in dislocation density due to cryo rolling in Zr4 resulted in enhanced interaction among the dislocations. These two facts decreased the work hardening capability and lead to decreased ductility in the cryo rolled Zr4 samples. This paper has been focused on investigating the effect of cryo rolling on tensile properties of Zr4.

However, fracture toughness is another important mechanical property to be investigated in SPD materials. In the case of Zr, cryo rolling has been found to improve the fracture toughness [54].

Thermal annealing has been employed to optimize the mechanical properties of different ultrafine grain metals and alloys produced via SPD [55, 56]. In most of the cases, annealing resulted in improved ductility with little loss in strength of the alloys. In case of cryo rolled Zr, annealing at 450 °C yielded multimodal grain size distribution which lead to simultaneous increase of strength and toughness [31]. The effects of annealing on the microstructure and mechanical properties of Zr4 will be the subject of a future study.

4. Summary and Conclusions

To summarize, an annealed Zr4 plate has been rolled at cryogenic temperature to different reductions and the microstructures and mechanical properties of each of these reductions has been examined. This study indicates that the increased strength in the cryo-rolled sample is primarily due to a rise in dislocation density. However, decrease in grain size results in poor work hardening, leading to reduced ductility.

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References

- [1] K. Linga Murty, I. Charit, Progress in Nuclear Energy, 48 (2006) 325-359.
- [2] S. Banerjee, P. Mukhopadhyay, Phase transformations: examples from titanium and zirconium alloys, Elsevier Science, 2010.
- [3] D. Srivastava, G. Dey, S. Banerjee, Metallurgical and Materials Transactions A, 26 (1995) 2707-2718.
- [4] R.Z. Valiev, R. Islamgaliev, I. Alexandrov, Progress in materials science, 45 (2000) 103-189.
- [5] R. Valiev, Nature materials, 3 (2004) 511-516.
- [6] R.Z. Valiev, Y. Estrin, Z. Horita, T.G. Langdon, M.J. Zechetbauer, Y.T. Zhu, Jom, 58 (2006) 33-39.
- [7] R. Valiev, A. Korznikov, R. Mulyukov, Materials Science and Engineering: A, 168 (1993) 141-148.
- [8] R.Z. Valiev, Materials Science and Engineering: A, 234 (1997) 59-66.
- [9] Y. Zhao, X. Liao, Z. Jin, R. Valiev, Y. Zhu, Acta Materialia, 52 (2004) 4589-4599.
- [10] A. Chatterjee, G. Sharma, A. Sarkar, J. Singh, J. Chakravartty, Materials Science and Engineering: A, (2012).
- [11] T. Lee, C. Chang, P. Kao, Materials Science and Engineering: A, 408 (2005) 131-135.
- [12] N. Rangaraju, T. Raghuram, B.V. Krishna, K.P. Rao, P. Venugopal, Materials Science and Engineering: A, 398 (2005) 246-251.
- [13] J.B. Singh, A. Sarkar, G. Sharma, V. Basavaraj, J. Chakravartty, in: Materials Science Forum, Trans Tech Publ, 2012, pp. 89-92.
- [14] G. Sharma, A. Sarkar, I. Samajdar, J. Chakravartty, in: Materials Science Forum, Trans Tech Publ, 2012, pp. 93-96.

- [15] Y. Saito, H. Utsunomiya, N. Tsuji, T. Sakai, *Acta materialia*, 47 (1999) 579-583.
- [16] D. Witkin, E.J. Lavernia, *Progress in Materials Science*, 51 (2006) 1-60.
- [17] Y. Iwahashi, J. Wang, Z. Horita, M. Nemoto, T.G. Langdon, *Scripta Materialia*, 35 (1996) 143-146.
- [18] A. Bhowmik, S. Biswas, S.S. Dhinwal, A. Sarkar, R.K. Ray, D. Bhattacharjee, S. Suwas, in: *Materials Science Forum*, Trans Tech Publ, 2012, pp. 774-777.
- [19] R. Kapoor, A. Sarkar, R. Yogi, S. Shekhawat, I. Samajdar, J. Chakravartty, *Materials Science and Engineering: A*, (2012).
- [20] A. Yamashita, Z. Horita, T.G. Langdon, *Materials Science and Engineering: A*, 300 (2001) 142-147.
- [21] G. Sharma, A. Sarkar, I. Samajdar, J. Chakravartty, in: *Materials Science Forum*, 2011, pp. 93.
- [22] A. Sarkar, A. Bhowmik, S. Suwas, *Applied Physics A*, 94 (2009) 943-948.
- [23] T.C. Lowe, R.Z. Valiev, *Investigations and applications of severe plastic deformation*, Springer, 2000.
- [24] P. Das, R. Jayaganthan, I. Singh, *Materials & Design*, 32 (2011) 1298-1305.
- [25] Y. Wang, T. Jiao, E. Ma, *Materials Transactions*, 44 (2003) 1926-1934.
- [26] S. Nagarjuna, U. Chinta Babu, P. Ghosal, *Materials Science and Engineering: A*, 491 (2008) 331-337.
- [27] U.C. Babu, K. Prasad, S. Kamat, *Transactions of the Indian Institute of Metals*, 64 (2011) 321-324.
- [28] S. Zherebtsov, G. Dyakonov, A. Salem, V. Sokolenko, G. Salishchev, S. Semiatin, *Acta Materialia*, (2012).

- [29] D. Yang, P. Hodgson, C. Wen, Scripta materialia, 63 (2010) 941-944.
- [30] D. Guo, Z. Zhang, G. Zhang, M. Li, Y. Shi, T. Ma, X. Zhang, Materials Science and Engineering: A, 591 (2014) 167-172.
- [31] D. Guo, M. Li, Y. Shi, Z. Zhang, H. Zhang, X. Liu, X. Zhang, Materials Letters, 66 (2012) 305-307.
- [32] D. Guo, M. Li, Y. Shi, Z. Zhang, H. Zhang, X. Liu, B. Wei, X. Zhang, Materials & Design, 34 (2012) 275-278.
- [33] D. Guo, M. Li, Y. Shi, Z. Zhang, T. Ma, H. Zhang, X. Zhang, Materials Science and Engineering: A, (2012).
- [34] P.A.R. Kamalanath, A. Sarkar, American Journal of Materials Science, 2 (2012) 138-141.
- [35] S. Goel, N. Keskar, R. Jayaganthan, I.V. Singh, D. Srivastava, G.K. Dey, N. Saibaba, Materials Science and Engineering: A.
- [36] A.J. Schwartz, M. Kumar, B.L. Adams, D.P. Field, Electron backscatter diffraction in materials science, Springer, 2009.
- [37] A.J. Wilkinson, T.B. Britton, Materials Today, 15 (2012) 366-376.
- [38] V. Richard, R. Chiron, P. Gerber, M. Gaspérini, B. Bacroix, Advanced Engineering Materials, 5 (2003) 161-165.
- [39] P. Mukherjee, A. Sarkar, P. Barat, S. Bandyopadhyay, P. Sen, S. Chattopadhyay, P. Chatterjee, S. Chatterjee, M. Mitra, Acta materialia, 52 (2004) 5687-5696.
- [40] A. Sarkar, P. Mukherjee, P. Barat, Materials Science and Engineering: A, 485 (2008) 176-181.
- [41] G. Ribárik, Physics Doctorate School, PhD, Eotvos Lorand University, (2008).

- [42] T. Ungár, J. Gubicza, G. Ribárik, A. Borbély, *Journal of Applied Crystallography*, 34 (2001) 298-310.
- [43] A. Sarkar, A. Alsabbagh, K. Murty, *Annals of Nuclear Energy*, 65 (2014) 91-96.
- [44] J. Gubicza, *X-Ray Line Profile Analysis in Materials Science*, IGI Global, Hershey, PA, USA, 2014.
- [45] Y. Shi, M. Li, D. Guo, T. Ma, Z. Zhang, X. Li, G. Zhang, X. Zhang, *Advanced Engineering Materials*, 16 (2014) 167-170.
- [46] N. Kamikawa, X. Huang, N. Tsuji, N. Hansen, *Acta Materialia*, 57 (2009) 4198-4208.
- [47] N. Hansen, *Scripta Materialia*, 51 (2004) 801-806.
- [48] J. Dunlop, Y. Bréchet, L. Legras, Y. Estrin, *Materials Science and Engineering: A*, 443 (2007) 77-86.
- [49] B. Kad, J.-M. Gebert, M. Perez-Prado, M. Kassner, M. Meyers, *Acta materialia*, 54 (2006) 4111-4127.
- [50] A.W. Thompson, *Acta Metallurgica*, 25 (1977) 83-86.
- [51] A.W. Thompson, M.I. Baskes, *Philosophical Magazine*, 28 (1973) 301-308.
- [52] A.W. Thompson, M.I. Baskes, W.F. Flanagan, *Acta Metallurgica*, 21 (1973) 1017-1028.
- [53] C. Crussard, B. Jaoul, *Revue de Métallurgie*, (1950) 589-600.
- [54] M. Li, D. Guo, T. Ma, G. Zhang, Y. Shi, X. Zhang, *Materials Science and Engineering: A*, 606 (2014) 330-333.
- [55] D.G. Morris, M. Munoz-Morris, *Acta materialia*, 50 (2002) 4047-4060.
- [56] H. Mughrabi, H. Höppel, M. Kautz, R. Valiev, *Zeitschrift für Metallkunde*, 94 (2003) 1079-1083.

Table 1 Values of microstructural parameters obtained from CMWP analysis and grain size from EBSD

Sample	Grain size (μm)	Domain Size (nm)	Microstrian	Dislocation Density (m^{-2})
Starting annealed	11.90	108	1.2×10^{-4}	9.0×10^{13}
20% Cryo-rolled	6.74	35	8.2×10^{-4}	4.6×10^{14}
50% Cryo-rolled	6.19	23	1.7×10^{-3}	1.1×10^{15}
70% Cryo-rolled	4.20	11	2.4×10^{-3}	1.5×10^{15}

Fig. 1 EBSD maps of (a) the annealed, (b) 20% cryo-rolled (c) 50% cryo-rolled (d) 70% cryo-rolled and TEM image of 70% cryo-rolled Zr4 samples.

Fig. 2 (a) XRD profiles of starting annealed and 70% cryo-rolled sample and (b) CMWP fit of the XRD profile for 70% cryo-rolled Zr4sample.

Fig. 3 (a) Engineering stress-strain curves for annealed and cryo-rolled Zr4 samples and (b) variation of YS, UTS and %EL with rolling reduction.

Fig. 4 (a) Comparison of calculated and experimental stress and (b) variation of strain hardening exponent with grain size from cryo rolled Zr4 samples.