**Microstructural Evolution and Mechanical Properties of Ultrafine-Grained Ti Fabricated by Cryorolling and Subsequent Annealing**

*Hailiang Yu*[[1]](#footnote-1), *Lin Wang*, *Ming Yan\**, *Hou Gu*, *Xing Zhao*, *Charlie Kong*, *Yu Wang*, *Alexander Pesin*, *Alexander P. Zhilyaev\**, *Terence G. Langdon*

**Abstract**: Ultrafine-grained (UFG) commercial purity titanium (CP Ti) has a significant potential for use in medical implants and aerospace structural parts. In this study, UFG CP Ti sheets were processed by cryorolling and room temperature rolling (RTR), respectively, followed by annealing for 1 hour at temperatures from 250 to 350ºC. The grain size was reduced from ~75 µm to ~85 and ~220 nm after cryorolling and RTR, respectively. The results show that the curves of tensile stress vs engineering failure strain for samples subjected to cryorolling and subsequent annealing are above those for samples subjected to RTR and subsequent annealing. In addition, the curves of ultimate tensile stress × fracture elongation vs grain size after cryorolling and annealing are above those for RTR and annealing. It is demonstrated that a combination of cryorolling and annealing leads to improved toughness by comparison with processing by RTR and annealing.

**Keywords**: annealing; cryorolling; mechanical properties; microstructure, titanium.

**1. Introduction**

Ultrafine-grained/nanograined (UFG/NG) materials have attracted considerable attention due to their superior mechanical properties [1-5]. Furthermore, UFG commercial purity titanium (CP Ti) shows excellent mechanical properties [6] and corrosion resistance [7] which leads to a potential for use as medical implants and for structural parts in aerospace applications [8, 9]. Earlier research showed that the strength and microhardness of UFG Ti follow the conventional Hall-Petch relationship [10].

Several severe plastic deformation (SPD) techniques have been used to fabricate UFG samples, including Ti, such as high-pressure torsion (HPT) [11-13], multi-directional forging [14], friction stir welding [15], equal-channel angular pressing (ECAP) [5, 16, 17] and special rolling technology [18, 19]. It was reported that the strength of UFG Ti processed by HPT reached ~1200 MPa [11] and there was a strength of ~930 MPa in UFG Ti fabricated by multiforging and subsequent rolling [14]. There is a report that the mechanical properties and corrosion resistance of CP Ti after continuous ECAP plus short-duration annealing was comparable to the as-received sheets [20] and UFG Ti prepared by ECAP + rolling had a higher strength than Ti-6Al-4V alloys [21]. Recently, a shear drawing technique was developed to fabricate UFG Ti bars and the results showed that the strength was improved to ~590 MPa compared to ~470 MPa in conventional drawing [22].

Deformation at cryogenic temperature may further refine the grain size compared with deformation at room temperature (RT). Aluminum alloys [23-25] and copper alloys [26-28] showed high strength and high ductility after cryorolling and the ductility of UFG CP Ti from cryogenic deformation at 77 K was higher than the value obtained at RT [29, 30]. Cryorolling was also used to produce UFG Ti and alloys [31-37] and there is a report that both strength and the fatigue limit were increased after cryorolling compared to Ti processed by ECAP when all other processing parameters were similar [32].

Cryorolling in conjunction with surface mechanical attrition treatment may be applied to CP Ti as a strategy to engineer a multilayered hierarchical structure with a graded microstructural transition between successive layers showing simultaneous high strength and good ductility [33,34]. The micromechanical gradation across the layers and in the junctions between the layers gave a more gradual stress redistribution and thereby provided increased resistance to catastrophic failure [34]. It was reported also that a cryorolled Ti alloy had nano-sized grains with a grain size of the order of ~60 nm with edge dislocations and nanotwins lying within the grains [35]. There is a report that twinning activity in CP Ti was significantly higher when rolling at 77 K compared with 293 K [36]. Although there is a report of compression twins and extension twins in CP Ti during cryorolling [37], it appears that there have been no detailed investigations of the mechanical response of UFG Ti after fabrication by cryorolling and subsequent annealing.

Accordingly, the present investigation was initiated to fabricate UFG Ti sheets by cryorolling and room-temperature rolling (RTR), respectively, and then to anneal for 1 hour at various temperatures from 250 to 350 ºC and thereafter to examine the strength and thermal stability. The results show that the cryorolled CP Ti sheets have higher strength and improved thermal stability compared to the samples rolled at RT. In addition, it was found that the curves of tensile stress vs engineering failure strain and the ultimate tensile stress × fracture elongation vs grain size for samples subjected to cryorolling and annealing lay above the similar curves obtained from samples subjected to RTR and annealing.

**2. Experimental Material and Procedures**

CP Ti sheets having an initial thickness of 1.5 mm were used in this study. The rolling experiments were carried out at RT and liquid nitrogen temperature using a four-high rolling mill with work rolls of Cr12 steel having diameters of 50 mm. The work rolls were freshly polished before rolling and the rolling was carried out under dry friction. The final thickness of the rolled sheets was 0.4 mm. For cryorolling, the sheets were cooled by liquid nitrogen for more than 8 min before rolling. The rolled sheets were cut into six parts where five parts were annealed for 1 hour at temperatures of 250, 275, 300, 325 or 350 ºC, respectively. It was established earlier that for NG Ti the mechanical properties drop significantly when the annealing temperature is 200 ºC [38].

 Dog-bone-shaped tensile samples with gauge lengths of 18 mm, widths of 3 mm and thicknesses of 0.4 mm were machined from the rolled sheets and tensile tests were then conducted at RT using a strain rate of 1.0 × 10-3 s-1 on an Instron testing machine. To provide overall consistency in the experimental results, each test was repeated three times. The Vickers microhardness was measured using a load of 5 g and a dwell time of 12 s and each hardness test was repeated five times. A focused ion beam with in-situ lift-out was used to prepare samples for transmission electron microscopy (TEM) and the TEM observations were conducted using a Philips CM200 Field Emission Gun microscope (FEG-TEM) operating at 200 kV.

**3. Experimental results**

**Figure 1** summarizes the mechanical behavior of CP Ti processed by RTR, cryorolling and by subsequent annealing. Specifically, Figs 1a and 1b show the stress-strain curves for the RTR and cryorolled samples, respectively. In Fig. 1a as the annealing temperature increases from 250 to 350ºC the yield stress and ultimate tensile strength (UTS) of the CP Ti sheets rolled at RT gradually decrease but the engineering failure strain increases. In Fig. 1b the tensile stress decreases during annealing compared to the initial cryorolled CP Ti sheet, but the value of the reduction of tensile stress is smaller than in Fig. 1a for the RTR condition. In addition, the engineering failure strain changes slightly during annealing from 250 to 350ºC.

Figure 1c shows the UTS of CP Ti subjected to different processing routes and annealing treatments. After rolling, the UTS of the RTR-processed and cryorolled samples are ~1040 and ~1130 MPa respectively. The UTS of the RTR-processed CP Ti decreases reasonably linearly to ~910 MPa with increasing annealing temperature from 250 to 350 ºC and the UTS of the cryorolled CP Ti falls to ~990 MPa at the highest annealing temperature. In Fig. 1d, the UTS is plotted against the engineering fracture strain and the data for the cryorolled samples lie above the data for the RTR-processed samples. This demonstrates that cryorolling plus a reasonably low temperature annealing leads to improved mechanical properties compared to RTR samples also subjected to low temperature annealing.

The microhardness of CP Ti samples subjected to different processes is summarized schematically in **Figure 2**. The microhardness of the as-received CP Ti was ~170 HV but this increased to ~250 HV and ¬265 HV after RTR and cryorolling, respectively. During annealing, the microhardness of both the RTR-processed and the cryorolled CP Ti samples gradually decrease with increasing annealing temperature and this behavior is consistent with the decrease in UTS in Fig. 1c.

For the as-received Cp-Ti, TEM images are shown in **Figure 3** in (a) bright field and (b) dark field. Although only a few large grains are visible in the TEM images, inspection by optical microscopy revealed the presence of large equiaxed grains having an initial average size of ~75 µm. The selected area electron diffraction (SAED) pattern shown in Fig. 3(b) shows sharp points that are typical of annealed metals without any significant straining.

The TEM image of the RTR-processed samples without annealing, as shown in **Figure 4a**, is typical of a severely deformed structure with a large imposed strain and the weak spots visible in the SAED pattern shows that some ordered crystal structure remains in the sample after rolling at RT. **Figures 4b-d** show samples annealed for 1 hour at temperatures of 275, 325 and 350ºC, respectively. In these images, there is clear evidence for recrystallization and some small crystal domains are visible. The evidence from the SAED patterns is that the samples are in the initial stages of recovery. In **Figures 4c** and **4d**, the recovery level increases as the annealing temperature increases and this leads to a minor increase in grain size and a reduction in the tangled nature of the dislocation microstructure.

**Figure 5** shows TEM images of CP Ti samples subjected to cryorolling and subsequent annealing. The microstructure of the cryorolled sample without heat treatment exhibits a typical severely deformed structure with small domains and a high density of tangled dislocation cells. The corresponding SAED pattern shows scattered spots plus circular arcs for the deformed crystal structure exhibiting limited strain. Figures 5b to d show the microstructures after annealing for 1 hour at 275, 325 and 350ºC, respectively. There is no evidence in these TEM images for initial recrystallization but the scattering of spots in the SAED patterns suggests a layered ordered nanosheet structure which appear to exist in thin lamellae having thicknesses of ~100 nm. These nanosheets have probably transformed from the original grains so that the original crystals govern the overall structure. This type of microstructure may be formed during the cryorolling process because of the application of severe compression and a twisting force at the cryo-temperature. It is concluded that the hardened Ti crystal, having a very limited possibility for elastic deformation at such a low temperature, may form twisted nanosheets through sliding over limited distances with concurrent twisting as in a deck of cards. The uniformly distributed screw structure of such layered ordered nanosheets will form a strong pinning mechanism, thereby hindering the activation of normal crystal recovery and significantly strengthening the cryorolled material. In Figures 5c and 5d, the annealing temperature increases and no significant recovery is visible at higher annealing temperatures so that the domain structure remains visible even at 350ºC.

**4. Discussion**

In Figure 1, the UTS of the RTR-processed and cryorolled samples are ~1040 and ~1130 MPa respectively, and this is similar to an earlier report for CP Ti where the measured values of the UTS were ~900 and ~1100 MPa, respectively, after RTR and cryorolling to a true strain of 2.66 [39]. In addition, the tensile stresses of the samples drop during annealing for both the cryorolled and RTR-processed sheets and the rate of decrease is higher for the samples subjected to RTR. The engineering failure strains of the cryorolled sheets change slightly during annealing from 250 to 350ºC. This is similar to HPT-processed nanocrystalline CP Ti during annealing where the engineering strength is reduced significantly while the failure engineering strain changes only slightly with increasing annealing temperatures from 200 to 700ºC [40].

Generally, the grain size determines the mechanical properties of UFG CP Ti and it was shown earlier that the strength of UFG Ti directly follows the Hall-Petch relationship [10]. Inspection of Figure 4 and shows that the grain size of samples subjected to cryorolling and annealing is smaller than after RTR and annealing. The grain size distributions of the CP Ti samples subjected to cryorolling and RTR and subsequent annealing are summarized in detail in **Figures 6 and 7** for the cryorolled and RTR samples, respectively. Thus, the mean grain size of CP Ti sheets subjected to cryorolling is ~86 nm (Figure 6a) but this value increases to ~90 nm after annealing at 275ºC for 1 hour (Figure 6b) and finally increases to ~193 nm after annealing at 350ºC for 1 hour. Nevertheless, this is smaller than in CP Ti after RTR without annealing where the grain size is ~218 nm (Figure 7a). During annealing, the mean grain size for the RTR samples increases with temperature to ~539 nm after annealing at 350ºC for 1 hour (Figure 7d).

It is obvious that the smaller grain size contributes to the higher strength of the samples so that the sheets subjected to cryorolling and annealing have a higher strength. However, the RTR-processed Ti sheet has a higher strength compared to processing by cryorolling and annealing at 350ºC although the mean grain size in the Ti sheets subjected to RTR is coarser. In addition, the elongation to failure is much smaller than for the cryorolled + annealed samples, as shown by the region marked by a rectangle in **Figure 8**. Thus, the mechanical properties are determined not only by the grain size but also they are affected by the dislocation density within the grains after the annealing treatment. For the cryorolled + annealed samples, the grain size is smaller and the dislocation density is lower. There are some reports that the cryogenic deformation of CP Ti will lead to nano twins [41] although no twins are visible in Figure 5 due to the small grain size.

The combination of a high UTS and high elongation leads to materials having high toughness. **Figure 9** shows the UTS × fracture elongation plotted against grain size in the Ti sheets after cryorolling or RTR and annealing. It is readily apparent that the Ti sheets subjected to cryorolling and annealing have improved toughness compared with the Ti sheets subjected to RTR and annealing when they have the same mean grain size. This means that a combination of cryorolling and annealing can achieve much better toughness in the CP Ti sheets compared with the traditional processing of RTR and annealing.

**5. Summary and conclusions**

1. CP titanium was severely deformed by cryorolling or room temperature rolling (RTR) followed by annealing for 1 hour at temperatures from 250 to 350ºC. The initial grain size of ~75 µm was reduced to ~85 and ~220 nm after cryorolling and RTR, respectively.

2. The ultrafine-grained CP Ti sheets subjected to cryorolling have higher mechanical strength than those subjected to RTR due to their finer grain size. The values of the UTS were ~1130 and ~1040 MPa for these two processing conditions, respectively.

3. After annealing for 1 hour at temperatures from 250 to 350ºC, the plot of UTS vs. failure strain after cryorolling and annealing was above that for samples processed by RTR and annealing.

4. The cryorolled CP Ti sheets have finer grains compared with the RTR-processed sheets when the annealing temperature is the same. This demonstrates that better mechanical properties may be attained through cryorolling and annealing. For the annealed samples, the results show that both the grain size and the dislocation density contribute to the measured mechanical properties.

**Acknowledgements**

HY acknowledges financial support from the National Natural Science Foundation of China (Grant number: 51674303), National Youth Thousand Plan Program of China, Huxiang High-Level Talent Gathering Project of HUNAN Province (Grant number: 2018RS3015), Innovation Driven Program of Central South University (Grant number: 2019CX006), and the Research Fund of the Key Laboratory of High Performance Complex Manufacturing at Central South University. AMP and APZ received financial support from the Ministry of Science and Higher Education of the Russia Federation through grant 14.Z50.31.0043

**Conflict of Interest**

The authors declare no conflict of interest.

**References**

[1] Y. Cao, S. Ni, X. Liao, M. Song, Y. Zhu, *Mater. Sci. Eng. R*. **2018**, *133*, 1.

[2] I.A. Ovid’ko, R.Z. Valiev, Y.T Zhu, *Prog. Mater. Sci.*, **2018**, *94*, 462.

[3] M. Kawasaki, B. Ahn, P. Kumar, J.I. Jang, T.G. Langdon, *Adv. Eng. Mater.*, **2017**, *19*, 673.

[4] L. Mishnaevsky, E. Levashov, R.Z. Valiev, J. Segurado, I. Sabirov, N. Enikeev, S. Prokoshkin, A.V. Solov’yov, A. Korotitskiy, E. Gutmanas, I. Gotman, E. Rabkin, S. Psakh’e, L. Dluhoš, M. Seefeldt, A. Smolin, *Mater. Sci. Eng. R* **2014**, *81*, 1.

[5] R.Z. Valiev, T.G. Langdon, *Prog. Mater. Sci.* **2006**, *51*, 881.

[6] X. Liu, Q. Zhang, X. Zhao, X. Yang, L. Luo, *Mater. Sci. Eng. A* **2016**, *676*, 73.

[7] A. Balyanov, J. Kutnyakova, N.A. Amirkhanova, V.V. Stolyarov, R.Z. Valiev, X.Z. Liao, Y.H. Zhao, Y.B. Jiang, H.F. Xu, T.C. Lowe, Y.T. Zhu, *Scr. Mater.* **2004**, *51,* 225.

[8] R. Mahmoodian, N.S.M. Annuar, G. Faraji, N.D. Bahar, B.A. Razak, M. Sparham, *JOM* **2019**, *71*, 256.

[9] M.D. Morehead, Y. Huang, Y.T. Zhu, T.C. Lowe, R.Z. Valiev, *Trans. North Am. Manuf. Res. Ins. SME* **2006**, *34*, 539.

[10] N. Balasubramanian, T.G. Langdon, *Metal. Mater. Trans. A*, **2016**, *47*, 5827.

[11] A.V. Sergueeva, V.V. Stolyarov, R.Z. Valiev, A.K. Mukherjee, *Scr. Mater.* **2001**, *45*, 745.

[12] K. Edalati, T. Daio, M. Arita, S. Lee, Z. Horita, A. Togo, I. Tanaka, *Acta Mater.* **2014**, *68*, 207.

[13] A.P. Zhilyaev, T.G. Langdon, *Prog. Mater. Sci.* **2008**, 53, 893.

[14] H. Miura, M. Kobayashi, T. Aoba, H. Aoyama, T. Benjanarasuth, *Mater. Sci. Eng. A* **2018**, *731*, 603.

[15] L.H. Wu, X.B. Hu, X.X. Zhang, Y.Z. Li, Z.Y. Ma, X.L. Ma, B.L. Xiao, *Acta Mater.* **2019**, *166*, 371.

[16] S. Fintova, M. Arzaghi, I. Kubena, L. Kunz, C. Sarrazin-Baudoux, *Int. J. Fatigue*, **2017**, *98*, 187.

[17] R. Naseri, M. Kadkhodayan, M. Shariati, *Trans. Nonfer. Met. Soc. China*, **2017**, *27*, 1964.

[18] X. Wu, M. Yang, F. Yuan, G. Wu, Y. Wei, X. Huang, Y. Zhu, *P. Natl Acad. Sci. USA* **2015**, *112*, 14501.

[19] H.L. Yu, C. Lu, K. Tieu, H.J. Li, A. Godbole, S.H. Zhang, *Adv. Eng. Mater.* **2016**, *18*, 754.

[20] Y. Gu, A. Ma, J. Jiang, H. Li, D. Song, H. Wu, Y. Yuan, *Mater. Charact.* **2018**, *138*, 38.

[21] V.V. Stolyarov, Y.T. Zhu, I.V. Alexandrov, T.C. Lowe, R.Z. Valiev, *Mater. Sci. Eng. A* **2003**, *343*, 43.

[22] A.G. Raab, E.V. Bobruk, G.I. Raab, *J. Mater. Eng. Peform.* **2018**, *27*, 2414.

[23] H.L. Yu, L.H. Su, C. Lu, K. Tieu, H.J. Li, J.T. Li, A. Godbole, C. Kong, *Mater. Sci. Eng. A* **2016**,*674*, 256.

[24] H.L. Yu, H. Wang, C. Lu, K. Tieu, H.J. Li, A. Godbole, X. Liu, C. Kong, X. Zhao, *J. Mater. Res.* **2016**, *31*, 797.

[25] D.C.C. Magalhaes, A.M. Kliauga, M. Ferrante, V.L. Sordi, *Mater. Sci. Eng. A* **2018**, *736*, 53.

[26] H.L. Yu, Q.L. Du, A. Godbole, C. Lu, C. Kong, *Metal. Mater. Trans. A* **2018**, *49*, 4398.

[27] H.L. Yu, C. Lu, K. Tieu, H.J. Li, A. Godbole, C. Kong, X. Zhao, *Metal. Mater. Trans. A* **2016**, 47, 3785.

[28] R. Li, E. Guo, Z. Chen, H. Kang, W. Wang, C. Zou, T. Li, T. Wang, *J. Alloy. Compd* **2019**, *771*, 1044.

[29] X. Sun, Y. Guo, Q. Wei, Y. Li, S. Zhang, *Mater. Sci. Eng. A* **2016**, *669*, 226.

[30] Y. Wang, E. Ma, R.Z. Valiev, Y. Zhu, *Adv. Mater.* **2004**, *16*, 328.

[31] H.L. Yu, M. Yan, J.T. Li, A. Godbole, C. Lu, K. Tieu, H.J. Li, C. Kong, *Mater. Sci. Eng. A* **2018**, *710*, 10.

[32] A. Mendes, A.M. Kliauga, M. Ferrante, V.L. Sordi, *IOP Conf. Series: Mater. Sci. Eng.* **2014**, 63, 012161.

[33] D.K. Yang, P.D. Hodgson, C.E. Wen, *Scr. Mater.* **2010**, *63*, 941.

[34] D.K. Yang, P. Cizek, D. Fabijanic, J.T. Wang, P.D. Hodgson, *Acta Mater.* **2013**, *61*, 2840.

[35] A. Dasgupta, S. Murugesan, S. Saroja, M. Vijayalakshmi, M. Luysberg, M. Veron, E. Rauch, T. Jayakumar, *J. Mater. Sci.* **2013**, *48*, 4592.

[36] S.W. Choi, J.W. Won, S.W. Lee, J.K. Hong, Y.S. Choi, *Mater. Sci. Eng. A* **2018**, *738*, 75.

[37] Z.W. Huang, S.B. Jin, H. Zhou, Y.S. Li, Y. Cao, Y.T. Zhu, *Int. J. Plast.* **2019**, *112*, 52.

[38] S. Zhang, Y.C. Wang, A.P. Zhilyaev, E. Korznikova, S. Li, G.I. Raab, T.G. Langdon, *Mater. Sci. Eng. A* **2015**, *641*, 29.

[39] S.V. Zherebtsov, G.S. Dyakonov, A.A. Salem, V.I. Sokolenko, G.A. Salishchev, S.L. Semiatin, *Acta Mater.* **2013**, *61*, 1167.

[40] H.K. Lin, G.Y. Li, S. Mortier, P. Bazarnik, Y. Huang, M. Lewandowska, T.G. Langdon, *J. Alloy. Compd* **2019**, *784*, 653.

[41] S. Choi, J. Won, S. Lee, J.K. Hong, Y.S. Choi, *Mater. Sci. Eng. A* **2018**, 738, 75.

1. Prof. Dr. H.L. Yu, L. Wang, H. Gu, Dr. X. Zhao,

Light Alloy Research Institute, Central South University, Changsha, 410083, China;

State Key Laboratory of High Performance Complex Manufacturing, Central South University, Changsha 410083, China;

College of Mechanical and Electrical Engineering, Central South University, Changsha 410083, China;

Email: yuhailiang1980@tom.com, yuhailiang@csu.edu.cn

A/Prof. Dr. Ming Yan

Department of Materials Science and Engineering, South University of Science and Technology of China, Shenzhen 518055, China

Email: yanm@sustc.edu.cn

Dr. Charlie Kong, Dr. Yu Wang

Electron Microscope Unit, University of New South Wales, Sydney, NSW 2052, Australia

Prof. Dr. Alexander Pesin and Prof. Dr. Alexander P. Zhilyaev

Laboratory of Mechanics of Gradient Nanomaterials, Nosov Magnitogorsk State Technical University, Magnitogorsk 455000, Russia

Email: alex.zhilyaev@hotmail.com

Prof. Terence G. Langdon, Materials Research Group, Department of Mechanical Engineering, University of Southampton, Southampton SO17 1BJ, UK

Email: langdon@soton.ac.uk [↑](#footnote-ref-1)