High Strength and Wear Resistance of Tantalum by Ultrasonic Nanocrystalline Surface Modification Technique at High Temperatures

A Amanov[1]*, Y S Pyun[1] and V K Vasudevan[2]
[1]Mechanical Engineering Department, Sun Moon University, Asan 31460, Korea
[2]Department of Mechanical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221, USA
E-mail: amanovtribo@gmail.com

Abstract. Enhancing the strength of materials is of great concern in that the failures such as wear, corrosion and fatigue occur on the surface. A tantalum (Ta), which is a refractory metal, was subjected to severe plastic deformation induced by ultrasonic nanocrystalline surface modification (UNSM) technique at room- and high-temperatures of 200^0C and 800^0C. The mechanical properties and wear resistance of Ta before and after UNSM treatment were characterized by X-ray diffraction (XRD), hardness tester, and ball-on-disk tribometer, respectively. The UNSM treatment at 800^0C led to the intensity reduction and broadening, and the diffraction peaks were shifted to lower angles, which means the presence of compressive residual stress and grain size refinement. The hardness of the UNSM-treated sample at room temperature was higher than that of the untreated one, and it was further increased with increasing the UNSM treatment temperature. In addition, the effect of UNSM treatment at high-temperature on wear resistance was significant than that of the UNSM treatment at room-temperature. We demonstrate the possibility of further increasing the mechanical properties and wear resistance of Ta by UNSM treatment at high-temperatures in comparison with the untreated and UNSM-treatment at room temperature, which would be beneficial for applications of Ta.

1. Introduction

In the past few decades, a new era of severe plastic deformation (SPD) technologies have attracted considerable both scientific and technological interests in order to increase the strength of materials by producing a nanocrystalline surface layer with a thickness of several hundreds of microns [1]. A number of newly developed SPD techniques such as surface mechanical attrition treatment (SMAT), equal channel angular pressing (ECAP), etc. have been developed [2, 3]. These technologies are based on imposing high deformation and refining the grain size of coarse-grained (CG) structure of bulk materials into refined nano-grained (NG) structure [4]. In general, an NG structure has a plenty of advantages over the CG one, and besides improving the mechanical properties, while no change in chemical composition after SPD processes, it gives a possibility of applying superplastic deep drawing process to material [5].

Tantalum (Ta) is a refractory metal, which has a wide range of applications in several industries such as electrical devices, aircraft engines, surgical implants, heat exchangers in boilers, nuclear power plants and missiles due to its strength, ductility, toughness, wear resistance, corrosion resistance, thermal conductivity, etc. [6]. In particular, Ta has excellent resistance to corrosive attack by acids and liquid metals, where it displays an oxide film on its surface [7]. Despite the fact that excellent corrosion resistance makes Ta ideal for use in the manufacture and repair of chemical process equipment, heat exchangers in boilers and nuclear power plants, but the wear resistance and fatigue strength are still on

demand to be improved. In this regard, there is a need to increase the mechanical properties of Ta by producing a nanocrystalline surface layer with an NG structure. Limited studies can be found in the literature involving the nanostructured Ta by surface modification techniques though it has drawn great attention from industries, which may be due to its high plastic resistance. Zhang et al. have studied the formation of nanocrystalline structure in Ta by sliding friction treatment (SFT) [8]. A nanocrystalline structure was produced successfully with an average longitudinal grain size of about 20 nm. Moreover, Ta sample was subjected to equal channel angular extrusion (ECAE), where an ultrafine grain size was obtained [9].

Ultrasonic nanocrystalline surface modification (UNSM) technology is also an SPD technology, which induces a plastic deformation at the surface and sub-surface regions in order to produce a nanocrystalline surface layer a thickness of several hundreds of microns [10]. The process utilizes an ultrasonic vibration superimposed on a combination impact of static and dynamic loads, which is a core advantage of the UNSM technology over other SPD technologies, to induce high-strain-rate plastic deformation on a material near-surface region. It is also an effective and economical method to produce a nanocrystalline surface layer with NG structure. The UNSM treatment has been used to improve the friction behavior, wear resistance, corrosion resistance, and fatigue strength of various materials through the presence of NG structure having a high hardness and compressive residual stress in the near-surface region [11, 12].

In the present study, we propose a newly developed high-temperature UNSM technique, by means of which a further high strength and smaller grain size were obtained compared to the existing room temperature UNSM technique. It is believed that this high temperature UNSM technique, which is a simple and more efficient holds great potential for various industries, and plays an important role in further improving the overall properties of materials. Hence, so far, the main objective of this present study is to make a comparison between the effects of room- and high-temperature UNSM technique on mechanical properties and wear resistance. Detail microstructural evolution as a function of depth from the top surface by electron backscattered diffraction (EBSD) and transmission electron microscopy (TEM) is still in progress.

2. Experimental procedures

2.1. Sample preparation

Refractory Ta with a body-centred cubic (bcc) crystal structure is a high-density, ductile metal that exhibits exceptional corrosion resistance and good high-temperature strength. Cold worked Ta has a purity of 99.95% (metal base) with a surface of about 194 HV was employed in this study. The round bar Ta was cut into disk samples with a diameter of 20 mm and a thickness of 5 mm. The samples were ground and then were polished with silicon carbide (SiC) abrasive papers down to 2000 grit. Some physical and mechanical properties of Ta are listed in Table 1.

Table 1. Some physical and mechanical properties of Ta employed in this study.

Density (g/cm^3)	UTS (MPa)	Elastic modulus (GPa)	Elongation (%)	Hardness (HV)	Poisson`s ratio
16.6	900	186	5	200	0.35

2.2. Ultrasonic nanocrystal surface modification (UNSM) technique

A UNSM is an ultrasonic-based technology, where a ball (tip) made of tungsten carbide (WC) or silicon nitride (Si_3N_4) attached to a horn strikes the surface of a workpiece at a frequency of 20 and 40 kHz, at an amplitude of up to 100 µm with 1000 to 10000 shots per square millimetre. A static load is exerted on the tip against the surface to control the pressure with which the tip contacts the workpiece surface. In comparison with other SPD technologies, such as shot peening (SP), SMAT, etc. the UNSM technology offers a higher repeatability and reliability because of its capability for precise control of the strike intensity and density. Ta samples were subjected to UNSM technique at room- (25^0C) and high-

(200^0C and 800^0C) temperatures under the parameters listed in Table 2. A high temperature of 800^0C can be reached within 90 s and cooling up to 25^0C reaches in 15 min. The distance between the sample and the halogen lamp was about 15 cm. Details of the UNSM technique can be found in our previous publication [10, 11].

Table 2. UNSM technique treatment parameters of Ta employed in this study.

Frequency (kHz)	Amplitude (μm)	Static load (N)	Speed (mm/min)	Tip material	Tip diameter (mm)	Interval (μm)
20	40	30	2000	WC	2.38	70

2.3. Friction and wear test performance
The friction coefficient and wear resistance of the untreated and UNSM-treated at both room and high temperatures were investigated using a ball-on-disk tribometer (CSM Instruments, Switzerland) against a bearing steel with a diameter of 6 mm in dry test conditions listed in Table 3. The counterface ball was fixed to the sample holder, while the lower sample was fixed to the main stage, which reciprocated backward and forward.

Table 3. Ball-on-disk wear test conditions.

Normal load (N)	Reciprocating speed (cm/s)	Sliding distance (m)	Temperature (^{0}C)	Relative humidity (%)
10	2.51	30	25	52

2.4. Surface and sub-surface characterizations
The surface hardness was measured with the Vickers hardness tester (Mitutoyo, MVK E3, Japan) at a load of 300 gf and a dwell time of 10 s, while the *P-h* curves were obtained by nano-indentation tester (CSM Instruments, Switzerland) with a Berkovich indenter at a maximum load or 100 mN and a holding time of 10 s. The average six measurements are reported for each data point. The residual stress was measured with Cu-Kα radiation (λ=1.5418Å) using a laboratory based X-ray diffraction (XRD) residual stress analyser (LXRD, Proto, Canada) at an accelerating voltage of 20 kV and a current of 10 mA. The stress was determined using the $\sin^2\psi$ method along two orthogonal directions ($\varphi0^0$ and $\varphi90^0$). Full XRD patterns in the range of 30 to 90 degree were obtained using a Rigaku RU-300 with Cu-Kα radiation. The cross-sectional profiles of the wear tracks were measured using a two-dimensional (2D) surface profilometer (Surfcom 1500 SD3, Accretech, Japan). The specific wear rate and the corresponding standard deviation were quantified as the ratio of wear volume loss over the normal load multiplied by total reciprocating sliding distance.

3. Results and discussions

3.1. Surface hardness by the Vickers hardness tester and P-h curve by nanoindentation
The variation in surface hardness of Ta samples before and after UNSM treatment is shown in Figure 1. It can be seen that the surface hardness of Ta was increased by about 19% after UNSM treatment at 25^0C as shown in Figure 1(a). However, no significant increase in surface hardness was found after heat treatment at 200^0C, while the surface hardness was increased by about 26% using the combination of heat treatment with UNSM treatment at 200^0C. Furthermore, the surface hardness was increased significantly up to 489 HV when the heat treatment performed at 800^0C, which was more increased by about 11% by combination of heat treatment with UNSM treatment at 800^0C. In addition, the *P-h* curves of the samples was obtained by nanoindentation as shown in Figure 1(b). It was found that the sample subjected to the combination of heat treatment and UNSM treatment at 800^0C performed the shallowest penetration depth of about 786 nm, which is nearly less than two times than the corresponding

penetration depth of the untreated sample. In case of the UNSM-treated samples, the high hardness values may be attributed to a significant grain size refinement and a relatively high dislocation density and the mechanism of increase in hardness can be explained by the Hall-Petch relationship [13].
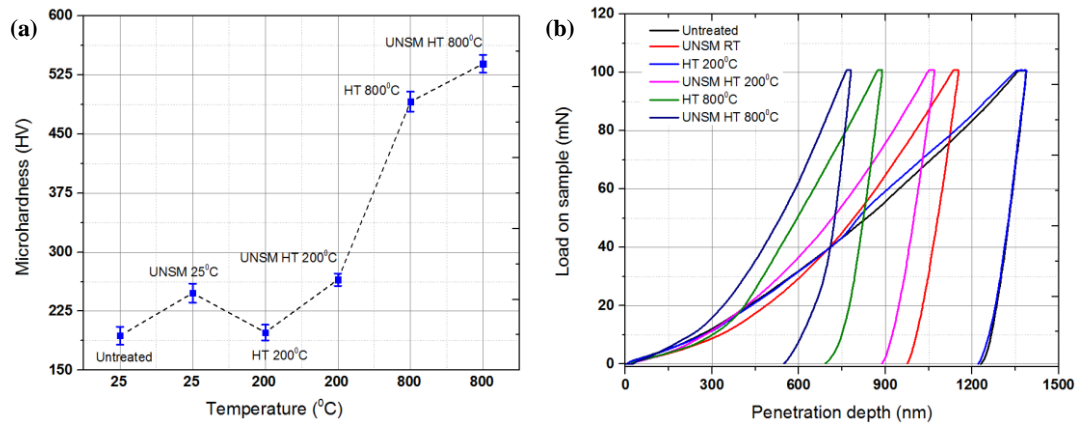

Figure 1. Variation in surface hardness (a) and *P-h* curves (b) of the untreated and UNSM-treated Ta samples, respectively.

3.2. Surface compressive residual stress and XRD patterns

The variation in surface residual stress and XRD patterns of Ta samples before and after UNSM treatment is shown in Figure 2. Residual stresses perpendicular and along to the UNSM treatment direction are represented as $\varphi 0^0$ and $\varphi 90^0$, respectively. The untreated and heat treatment samples at both 200^0C and 800^0C with no UNSM treatment exhibit a tensile residual stress at the surface as shown in Figure 2(a). The UNSM treatment induced a deep compressive residual stress of about -600 MPa, which is quite higher than the corresponding residual stress value of the untreated sample. The residual stress value of the UNSM-treated sample decreased with increasing the temperature to 200^0C perpendicular orthogonal direction of $\varphi 0^0$ and it increased along orthogonal direction of $\varphi 90^0$. It further increased up to -976 MPa and -1057 MPa by the combination of heat treatment and UNSM treatment at 800^0C perpendicular and along orthogonal directions, respectively. Notably, the compressive residual stress of the samples along orthogonal direction of $\varphi 90^0$ was found to be higher than that of the along orthogonal direction of $\varphi 0^0$ UNSM treatment at both high temperatures, which may be attributed to the number of strikes along the two different UNSM treatment directions as determined by the treatment speed and interval.

Summarized XRD patterns obtained from the surface of the samples are plotted in Figure 2(b). Obviously, the intensities of diffraction peaks reduced and broadened after UNSM treatment at 25^0C and 800^0C. However, no significant difference in intensities of diffraction peaks was found for the sample heat treatment and UNSM treatment at 200^0C in comparison with the untreated sample. Increasing the temperature from 200^0C to 800^0C resulted in again reduction and broadening in intensity of diffraction peaks. Moreover, a new diffraction peak was detected at a diffraction angle of 36.7 degree, which is believed due to oxidation during high-temperature treatment. A qualitative estimation of the plastic strain, work hardening and grain size refinement by the UNSM treatment can be made by analysing the intensity and full-width at half maximum (FWHM) of the diffraction peaks [14]. The diffraction peaks of the samples treated at both 200^0C and 800^0C shifted to a slightly lower angle, which indicates the presence of compressive residual stress induced by micro-strain [15,] while no shift for the UNSM-treated sample at 25^0C. It is also known that a reduction in intensity and broadening in FWHM after UNSM treatment may also be attributed to the internal stresses, especially stacking faults or twinning [12]. Moreover, when the grains are subjected to a uniform compressive strain, diffraction peaks shift to the lower angles [15]. The grain size quantified according to the Scherrer equation of the UNSM-treated sample at 25^0C was found to be 84 nm, which was further refined by high-temperature UNSM treatment at 800^0C up to 36 nm.
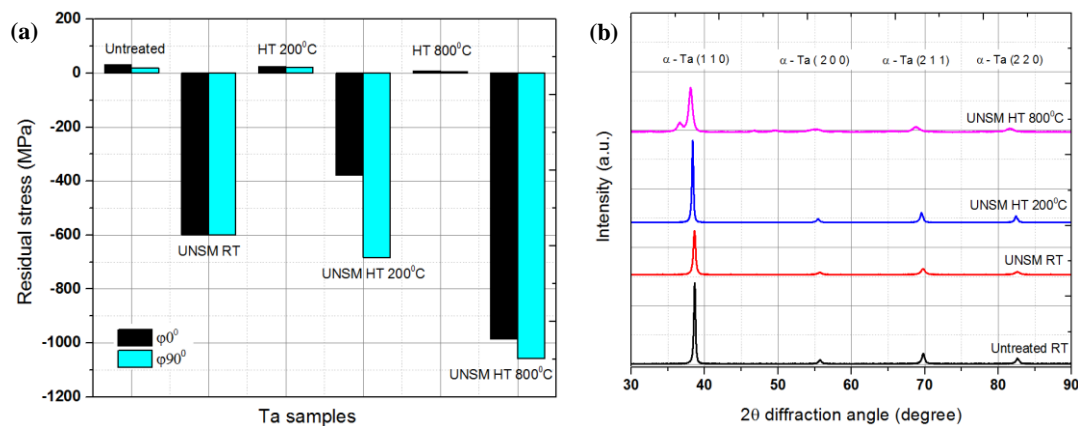
Figure 2. Variation in surface residual stress (a) and XRD patterns (b) of the untreated and UNSM-treated Ta samples.

3.3. Friction coefficient and wear resistance

The variation in friction coefficient of the Ta samples before and after UNSM treatment is shown in Figure 3(a). Clearly, it can be seen that the friction coefficient of the UNSM-treated samples at both room and high temperatures exhibited a lower friction coefficient compared to that of the untreated ones as shown in Figure 3(a). First, in case of the untreated sample, the friction coefficient was found to be about ~0.67 for the first 8 m of sliding, and with continuing the testing time the friction coefficient started reducing to a value of about ~0.58 up to a sliding time of about 17 m, and finally got stabilized to a value of about ~0.47 in the last stage of testing. In case of the UNSM-treated sample at room temperature, the friction coefficient abruptly increased to a value of about ~0.60 at the initial stage of the testing, and then with continuing the testing time the friction coefficient started reducing to a value of about ~0.52 up to a sliding time of about 17 m, which is a similar friction behaviour (trend) occurred for the untreated sample, and finally, it also got stabilized to a value of about ~0.42 in the last stage of testing. Second, in case of the heat treated and UNSM-treated samples at 200^0C, the friction behaviour was found to be similar to the friction behaviour (trend) untreated and UNSM-treated samples at 25^0C, but the UNSM treated sample at 200^0C exhibited a bit lower friction coefficient than that of the UNSM-treated sample treated at 25^0C, while no difference in friction coefficient for the untreated sample at 25^0C and 200^0C. Finally, in case of the heat treated and UNSM-treated samples at 800^0C, the heat treated sample exhibited a similar friction behaviour, which is increased first and then reduced for a while and again reduced and finally got stabilized to a value of about ~0.37 by the end of test. However, the UNSM-treated sample had a different friction behaviour unlike other samples, where the friction coefficient gradually increased up to a sliding time of about 17 m, where friction coefficient increased sharply and got stabilized to a value of about ~0.51 by the end of test. Interestingly, even though the heat treated sample at 800^0C had a higher hardness than other untreated, UNSM-treated at 25^0C, heat treated and UNSM-treated at 200^0C samples could not improve the friction behaviour of Ta at the initial stage of the test, but it exhibited the lowest friction coefficient value of about ~0.37, which is about 19% lower than that of the friction coefficient of the UNSM-treated sample at 800^0C. Ta exhibited a higher friction coefficient with increasing the temperature [16]. The reduced friction coefficient after UNSM treatment is mainly due to the surface morphology modification and reduced surface roughness.

Figure 3(b) shows the comparison in wear rate of the of Ta samples before and after UNSM treatment. It was found that the variation in wear resistance of the UNSM treated at 800 ^{0}C is significant in comparison with the untreated one, but no remarkable change in between the untreated and UNSM treated at 200 ^{0}C. The UNSM treatment at 25^0C increased the wear resistance by about 29%, while the UNSM treatment at 800^0C increased by about 94%. The increase in wear resistance of the UNSM-treated samples is directly related to the increased surface hardness and induced compressive residual stress. Moreover, a modified microstructure having a reduced surface roughness of Ta subjected to UNSM treatment at both room and high temperatures is also responsible for the increase in wear

resistance. It has been reported earlier that the wear resistance of NG materials is related to the subsurface deformation behaviour and surface morphology [17].
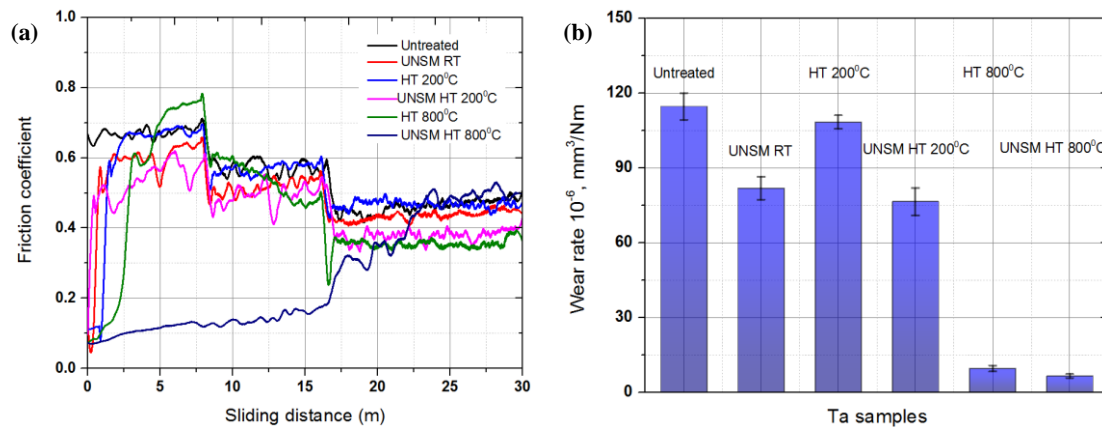

Figure 3. Variation in friction coefficient (a) and comparison in wear rate (b) of the untreated and UNSM-treated Ta samples.

4. Conclusions

In this study, the effect of UNSM treatment at room and high temperatures on the mechanical and tribological properties of Ta was studied. The surface hardness value for the UNSM-treated samples at 25^0C and 800^0C temperatures increased by about 19% and 65% compared to that of the untreated one. The presence of induced compressive residual stress at the surface after UNSM treatment was reached to less and more -1000 MPa for the UNSM-treated at 800^0C sample, which was significantly higher than that of the untreated sample. The grain size refinement after UNSM treatment at both 25^0C and 800^0C was confirmed by diffraction patterns, where the intensity reduced and broadening occurred. The friction and wear performance of the UNSM-treated sample at 800^0C improved considerably in comparison with those of the untreated and UNSM-treated samples at 25^0C. These findings would be beneficial for high-temperature applications of Ta in various industries.

5. References

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