Characterization of the near-surface nanocrystalline microstructure of ultrasonically treated Ti-6Al-4V using ASTAR™/precession electron diffraction technique

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ABSTRACT

The surface of Ti-6Al-4V was treated mechanically by applying ultrasonic nanocrystal surface modification. The effect of this treatment on the hardness, compressive residual stresses and fatigue performance were investigated. It is shown that in terms of the measured nanoindentation hardness values and the presence of compressive residual stresses, the treated sample only differed from the as-received sample in the first 200 μm to 300 μm area far from the surface. Also, the microstructure very close to the treated surface ($<5 \mu\text{m}$) was characterized using a relatively new transmission orientation microscopy technique named ASTAR™/precession electron diffraction. Based on different types of results (e.g., index map and virtual bright field image) acquired by this technique, it is concluded that titanium grains smaller than 10 nm exist within the distance of less than 1 μm from the treated surface. Difficulties associated with ASTAR™/precession electron diffraction technique to characterize this challenging near-surface area are discussed.

Keywords

UNSM, titanium alloys, nanostructured materials, residual stresses, fatigue, nanoindentation

1. Introduction

The presence of a thin nanocrystalline layer at the surface of metallic materials can improve their mechanical properties considerably [1]. Conventionally, sand blasting and shot peening have been used for inducing grain refinement and compressive residual stresses at the treated surface in metallic alloys [2]. However, sand blasting and shot peening may non-uniformly treat the surface due to the random flow of the peening media [3]. Surface damage may lead to metal failure as a result of fatigue fracture, corrosion induced surface rupture, etc. Therefore, surface treatment techniques which lead to the formation of nanocrystalline grain structure at the surface are of significant importance for structural materials. This refined microstructure in the near-surface region after a surface treatment has been demonstrated to improve significantly the surface strength [4, 5], abrasion as well as corrosion resistance [6, 7], and compressive residual stresses [8, 9] that subsequently enhance fatigue properties [10, 11].

The formation of a nanocrystalline surface layer on a material can be achieved by using coating and deposition technologies such as chemical vapor deposition, electroplating, physical vapor deposition and electrodeposition. However, in comparison to other surface treatment techniques (e.g., surface mechanical attrition treatment) used for the formation of nanostructured surfaces, the aforementioned conventional methods cannot be implemented easily in industrial applications [12].

It is possible to induce nanometer-size grains on the surface of materials by applying high strain rate deformations at relatively low temperatures. In this case, a considerably large number of dislocations are generated on the surface which results in the local rotations of crystals and formation of new, large misorientation angles at the surface [13]. Similarly, mechanical surface treatments result in the formation of large dislocation densities and macroscopic compressive

residual stresses close to the surface [14]. Grain refinement at the surface of metallic materials has been achieved by various methods. For instance, ultrasonic shot peening [15], ultrasonic surface rolling processing [8], ultrasonic cold forging [16], mechanical attrition treatment [17, 18] and laser shock peening [19] have been used to improve properties such as fatigue resistance of a nickel-base alloy [20], and wear resistance of steels [21]. Notably, while these techniques improve corrosion resistance, mechanical properties, etc., of the surface-treated materials, they do not change the chemical composition of the surface. Also, due to the formation of a hierarchical microstructure along the depth of the sample from the treated surface, the sample has typically contradicting properties such as high strength and ductility. Remarkably, depending upon the desired application, the selection of the surface treatment technique can be made based on the analyses of the effect of each treatment on the microstructural changes, magnitude and depth of the compressive residual stresses, the extent of plastic deformation, etc.

Ultrasonic nanocrystal surface modification (UNSM) is a surface treatment technique which induces surface grain refinement by applying severe plastic deformation. It is a simple, safe and cost-effective surface treatment technique which provides a relatively uniform treated surface. Notably, the uniformity of the surface treatment process can be achieved by applying an appropriate static load [22]. The driving force for this metal dimpling process is ultrasonic vibrations. In this technique, the surface of a material is treated with a constant pressure (static load) and a cyclic low amplitude ultrasonic striking at the rate of 10-30 kHz (dynamic load) [23]. The total energy which is transferred to the surface of the treated material is the summation of the energies of the static and dynamic loads. Generally, the static energy is 20% to 40% of the dynamic energy. The ultrasonic vibration is applied by a piezoelectric transducer and is transmitted to the material via a tungsten carbide ball. Through control over the processing

conditions and set up (e.g., the number of strikes per unit area and intensity of the strikes) makes UNSM technique highly attractive for industrial manufacturers.

UNSM treatment has been used extensively for a wide range of materials [10, 16, 24, 25]. Due to the formation of compressive residual stresses close to the surface and increase of surface hardness, UNSM technique improves the wear [24, 25] and fatigue [10, 16] performance of materials. It has been shown that increasing the number of UNSM strikes leads to a better fatigue performance [10]. Also, the formation of compressive residual stresses by UNSM reduces the possibility of fatigue crack nucleation. The fatigue performance of SUS304 stainless steel as a function of UNSM static loading was studied by Yasuoka et al. [26]. It has been claimed that applying a 90 N static loading resulted in ~80% improvement in the fatigue performance while larger static loadings (i.e., 100 N and 110 N) lead to a broken surface layer. Also, it has been reported that high impact loadings may refine the grains and reduces friction [25]. It can be said that processing parameters such as static load and number of strikes play a key role in the performance of UNSM technique.

In spite of the considerable research done on UNSM, there are few works related to the direct observation of the microstructures specifically very close to the treated surface (~15 nm to ~500 nm) in the literature [27, 28]. Most of the results presented in the literature are related to the effect of UNSM treatment on the properties such as fatigue, corrosion and wear resistance while limited studies focused on the direct observation of the microstructural variations with respect to distance from the treated surface by one of the aforementioned surface treatment techniques. For instance, transmission electron microscopy (TEM) technique was used to study grain refinement induced by mechanical surface treatments in iron [29], aluminum [30], copper [31], stainless steel [18], cobalt [32], magnesium [33] and titanium [34]. Generally, the information provided in

these studies are very similar and limited to (1) showing the fact that the grain size increases by exploring areas having a larger distance to the treated surface, (2) indicating the formation of twins and dislocations due to a severe plastic deformation and (3) calculating the grain boundary misorientation between selected adjacent grains for very few grain boundaries which cannot provide a general data-rich interpretation of the orientation variations between a statistically meaningful number of grains. However, these studies have not provided a comprehensive and detailed perspective of the microstructure (specifically very close to the treated surface) with a high spatial resolution due to the fact that techniques (i.e., selected area diffraction pattern and dark field imaging) used in all of these studies to investigate microstructural variations (e.g., grain size distributions) provide information from a relatively broad area. For instance, the closest area to the treated surface of the alpha phase titanium studied by Zhu et al. [34], was about 15-30 μm far from the surface and no information is provided for the microstructure variations within the first 20-100 nm from the treated surface.

A relatively new TEM-based orientation microscopy technique has emerged which makes the characterization of extremely fine features possible due to the spatial resolution of ~ 2 nm [35] in severely deformed metallic materials. This orientation microscopy technique is named ASTARTM/precession electron diffraction (ASTARTM/PED). ASTARTM represents the hardware and software packages which control the scanning of the electron beam across the electron transparent TEM specimens with a predetermined step size (e.g., 2 nm). In this technique, the electron beam (also called direct beam) is precessed for a small angle ($\sim 1^\circ$) from the optic axis. Precessing the direct beam results in a considerable improvement in the quality¹/reliability² of

¹ The quality of a recorded diffraction pattern can be attributed to the reduction (or removal) of Kikuchi lines from the diffraction pattern and significant reduction in the background (or noise) of each diffraction pattern image in comparison to the intensity of the spot diffraction patterns in that image.

the recorded diffraction patterns due to the removal (or reduction) of any dynamical diffraction effects [36] and formation of diffraction patterns with quasi-kinematical diffraction condition [37, 38]. ASTAR™/PED technique has been used to study dislocation density evolutions in severely deformed metallic materials [39], characterization of nanotwins [40], determination of grain boundary character distributions of nanocrystalline copper [41], investigation of the early stages of Zircaloy-4 oxidation behavior [42], etc.

In this study, the effect of UNSM surface treatment on the microstructures very close to the treated surface (i.e., <5 μm) of Ti-6Al-4V was studied by ASTAR™/PED orientation microscopy technique. Also, the effect of UNSM surface treatment on the hardness, residual stresses and fatigue performance of the studied material was investigated.

2. Experimental methods

The studied material was Ti-6Al-4V (all compositions in weight percent) which is a α/β titanium alloy. Notably, the crystal structures of the α and β phases are hexagonal close packed (*hcp*) and body centered cubic (*bcc*), respectively.

In the UNSM surface treatment technique, a tungsten carbide ball (with a diameter of 2.38 mm) attached to an ultrasonic transducer strikes the material at a high frequency (10–30 kHz) [27]. The penetration depth of the ball into the target material during a strike is called amplitude (usually, varies from 10 μm to 40 μm). Simultaneously, a static load (usually, varies from 10 N to 100 N) is applied to the ball against the material surface. In the current study, the surface treatment was conducted by an LM-520 UNSM system. The static load, dynamic amplitude and

² The reliability of a recorded diffraction pattern can be attributed to avoiding double diffraction events and preventing 180° ambiguity problem of indexing diffraction patterns by recording higher order Laue zone reflections as well as zero order Laue zone reflections.

scan speed were set to 60 N, 20 μm and 2000 mm/min, respectively. Also, the distance between the adjacent paths was 70 μm and the ultrasonic peening frequency was 20 kHz.

Residual stresses were measured on the UNSM treated Ti-6Al-4V coupons with a PROTO Laboratory X-Ray Diffraction system along two orthogonal directions (i.e., $\phi 0^\circ$ and $\phi 90^\circ$) using the $\sin^2\psi$ method. Lattice strain measurements were performed using Cu $K\alpha_1$ radiation ($\lambda = 1.5412 \text{ \AA}$) for the $\{21\bar{3}3\}$ peak (Bragg angle of 142°) of the α phase titanium with a 2 mm aperture. To calculate residual stresses, the $\sin^2\psi$ method was applied with the plane specific X-ray constant S_1 equals to $2.83 \times 10^{-6} \text{ MPa}^{-1}$. UNSM treated Ti-6Al-4V coupons were electropolished to remove layers of predetermined thickness using an 87.5:12.5 vol.% methanol to the sulfuric acid solution. In addition, full width at half maximum (FWHM) values were recorded for the same peak to compare the extent and depth of plastic deformation after applying the UNSM surface treatment [28].

Three-point bending fatigue experiment was conducted using an MTS Bionix servo-hydraulic fatigue test machine. The loading pattern, stress ratio, frequency and span were set to a sine function, 0.1, 5 Hz and 30 mm, respectively. Samples (50 mm in length, 10 mm in width and 1.6 mm thick) were cut using a wire electric discharge machining system. These samples were UNSM surface treated and then tested at various stress amplitudes for two million cycles or until failure.

Hardness values were measured using the CSM nanoindentation system with a load of 100 mN and a loading/unloading rate of 200 mN/min. At least five measurements were recorded at each depth to obtain hardness values through depth profile after applying the UNSM surface treatment.

Scanning electron microscope-based orientation microscopy was conducted using an FEI Nova 230 NanoSEM field emission gun microscope (FEI Instruments, USA) equipped with an electron backscatter diffraction (EBSD) detector operating at 20 keV. An EBSD scan was collected using a step size of 400 nm. A foil for TEM analyses was prepared using a Dual-BeamTM Focused Ion Beam Scanning Electron Microscope (FIB/SEM). Transmission electron microscopy analyses were conducted on an FEI Tecnai G2 F20 S-Twin FEG scanning/transmission electron microscope (S/TEM) operating at 200 keV. Compositional analyses were done using energy-dispersive spectroscopy (EDS). TEM-based orientation microscopy was performed using ASTARTM/PED (NanoMEGAS, Belgium) hardware and software packages installed on the TEM instrument. The electron beam was precessed at the angle of 1.3° from the optic axis for the orientation microscopy analyses. The scanning step size was 3 nm. The recorded diffraction patterns were indexed automatically by cross-correlating the acquired diffraction patterns with the simulated diffraction patterns (templates) for α titanium ($a=0.295$ nm and $c=0.468$ nm, $P6_3/mmc$) and β titanium ($a=0.33$ nm, $Im\bar{3}m$) phases at the operating accelerating voltage of 200 keV. Notably, to improve the accuracy of indexing by distinguishing areas containing titanium alloys from the other areas (e.g., deposited platinum area which is used to protect the thin foil during sample preparation by Dual-BeamTM focused ion beam system, holes on the foil and damaged areas of the foil from which diffraction patterns cannot be captured), templates were made in which the distance between the direct beam and the first diffraction spot(s) in the reciprocal space is considerably large. In this work, these templates are called amorphous templates. These templates were also used for indexing the acquired diffraction pattern images.

3. Results and discussion

To investigate the effect of UNSM surface treatment on the hardening of the studied samples, nanoindentation hardness values on the cross-section of the as-received and UNSM surface treated samples were measured. The variation of the hardness values through the depth is presented in Fig. 1 for the as-received and UNSM surface treated samples. The hardness value of the UNSM treated sample at the surface is ~5700 MPa which is more than two times larger than the corresponding hardness value of the as-received sample. The hardness values of the UNSM treated sample decreases with increasing distance from the treated surface and at the depth of ~280 μm , the measured hardness value of the treated sample is very close to the as-received sample. Notably, the depth of the UNSM treated layer as determined by the nanoindentation hardness for a 304 austenitic stainless steel was not larger than 400 μm [27] which is close to the value reported in this study for Ti-6Al-4V. The large hardness values close to the surface may be attributed to a significant grain refinement and a relatively high dislocation density. As expected, the hardness values of the as-received sample did not change considerably with respect to distance from the surface.

The through-the-depth profile of residual stresses plays a key role in improving the fatigue performance of materials after applying UNSM surface treatments. As stated previously, consecutive layer removal by electrochemical polishing and subsequent XRD residual stress measurements were conducted up to a depth of 200 μm . Residual stresses after gradient and depth correction in both orthogonal directions (i.e., $\phi 0^\circ$ and $\phi 90^\circ$) are plotted in Fig. 2. Stresses along and perpendicular to the scan direction are represented as $\phi 90^\circ$ and $\phi 0^\circ$, respectively. As expected, the profile of the residual stresses for the treated sample follows the trend observed previously in other surface treated materials [27]. The magnitudes of the compressive residual

stresses at the surface were maximum along both $\phi 0^\circ$ and $\phi 90^\circ$ directions and they reduced gradually with increasing distance from the UNSM treated surface. Compressive residual stresses were induced to a depth of $\sim 200 \mu\text{m}$ along both directions. Interestingly, the magnitude of the compressive residual stresses for the $\phi 90^\circ$ direction (which is $\sim 415 \text{ MPa}$) is almost two times larger than the $\phi 0^\circ$ direction (which is $\sim 225 \text{ MPa}$). This difference in the compressive residual stresses is related to the number of strikes along the two directions as determined by the scan speed and scan interval.

A qualitative assessment of the plastic strain induced by the UNSM surface treatment can be made by studying the FWHM of the diffraction peaks as a function of distance from the treated surface [28]. The FWHM values with respect to the distance from the treated surface are plotted in Fig. 2. This plot can be divided into three distinct areas. The first area is associated with the region close to the treated surface in which a considerable gradient of plastic strain is observed. The width of this area is less than $25 \mu\text{m}$ and the FWHM values vary from $\sim 3^\circ$ to $\sim 2.47^\circ$. The large values of FWHM close to the surface can be assigned to the remarkable grain refinement and plastic deformation in this area. The second area covers the region in which the plastic strain did not change considerably. The width of this area is $\sim 80 \mu\text{m}$ and the average FWHM value is $\sim 2.4^\circ$. It is expected that the grain size values do not vary astonishingly in this area and the average grain size must be far larger than the first region [28]. Finally, the third region has a moderate gradient of FWHM with respect to distance from the UNSM treated surface. The width of this region is $\sim 100 \mu\text{m}$ and FWHM values decrease from $\sim 2.4^\circ$ to $\sim 2.1^\circ$. From the sharp gradient in the first area of the FWHM profile as well as the corresponding hardness values, it can be concluded that UNSM technique forms large stresses very close to the surface and the magnitude of the stresses attenuates extensively by increasing the distance from the treated

surface. These facts highlight the importance of meticulous investigation of microstructural variations very close to the surface (e.g., less than 5 μm far from the UNSM treated surface).

The long-term performance of structural materials is affected significantly by their fatigue performance. As presented in Fig. 3, the UNSM surface treatment substantially improved the fatigue properties of the treated sample with respect to the as-received material. For instance, the fatigue life for a maximum bend stress of 650 MPa in the case of the UNSM surface-treated sample was 466377 cycles while the as-received sample failed in 174355 cycles. Similarly, significant improvements in the fatigue life at different stress levels were observed. Further, the fatigue strength of the UNSM surface-treated sample was about 50 MPa higher as compared with the as-received material. This type of enhancement can be attributed to the presence of compressive residual stresses at the surface, grain refinement [43] as well as surface hardening [26]. Clearly, the presence of compressive residual stresses at the surface reduces the magnitude of the effective tensile stresses and results in an improved fatigue performance. Also, severe plastic deformation at the surface which results in a surface hardening hinders crack nucleation at the surface.

Generally, large static loading, the moderate linear velocity of processing as well as feed rate result in finer nanocrystalline grains at the surface, a larger work hardening zone and a larger compressive residual stress area which improve the fatigue property of a UNSM surface-treated sample [22].

EBSD was used to determine the grain size distribution of the α phase titanium for the as-received sample along the cross section. The associated inverse pole figure (IPF) plot for the α phase titanium is presented in Fig. 4. The arrow located on the right side of the plot shows that the top part of the scan represents the surface of the sample. Since the β phase features were too

fine, EBSD technique could not characterize the β phase features properly and generally, the confidence index (which represents the reliability of indexing an acquired Kikuchi diffraction pattern) of the β phase features was less than 0.1 which is common for Ti-6Al-4V alloy. Thus, the IPF plot for the β phase is not presented. Based on the IPF plot, the grain size values for the α phase titanium vary from few microns to $\sim 30\text{ }\mu\text{m}$. Also, there was no considerable difference between the surface and bulk of the sample in terms of the grain size distribution. It is imperative to note that since Kikuchi diffraction patterns degrade in areas with large plastic deformation [44], the EBSD technique cannot be used to accurately characterize the area very close to the surface ($<10\text{ }\mu\text{m}$) for the UNSM treated sample. However, IPF maps similar to Fig. 4 were captured from areas being more than $150\text{ }\mu\text{m}$ far from the UNSM treated surface. It can be concluded that UNSM treatment refined the grains within a small area (e.g., $150\text{ }\mu\text{m}$) from the treated surface. Also, the grain refinement at the UNSM treated surface was significant when comparing with the areas far from the surface. This fact is consistent with the results presented in Fig. 1 and Fig. 2.

The many-beam bright field TEM micrograph of the cross section of the UNSM treated surface is presented in Fig. 5. Three distinct areas can be observed in this image which are indicated by yellow, blue and purple arrows. During foil preparation by Dual-BeamTM (FIB/SEM), a layer of platinum with the approximate thickness of $2.5\text{ }\mu\text{m}$ was deposited on the top part of the UNSM treated sample to protect the surface from gallium ions used for trenching. Therefore, the top section of the bright field image (which is indicated by the yellow arrow) represents this deposited platinum. The second area shown in Fig. 5 is presented by the blue arrow. It is difficult to determine whether this area is associated with the surface of the UNSM treated sample (i.e., a severely deformed area) or it is the bottom part of the platinum layer which

was deposited with a very low deposition current (~0.5 nA) at the accelerating voltage of 30 keV. In this study, this blue-arrow layer is called an unknown area. The third layer which is indicated by the purple arrow in Fig. 5 contains distinguishable grains. Therefore, the composition of this area is expected to be dominated by titanium. Notably, the two holes (which are presented by the brightest pixels in this image) exist in this area of the thin foil are artifacts formed during the final milling of the thin foil by the Dual-BeamTM (FIB/SEM) instrument.

An area including all the three layers represented by yellow, blue and purple arrows in Fig. 5 was studied using the ASTARTM/PED technique. The virtual bright field (VBF) image of the scanned area by ASTARTM/PED technique is presented in Fig. 6(a)³. Each pixel of the VBF image is made by integrating the intensity of the pixels associated with the direct beam of the diffraction pattern acquired from the same location on the thin foil. Generally, in each horizontal scan line of the VBF image, three types of recorded diffraction patterns were observed which can be assigned to three distinct areas on the VBF image presented by yellow, blue and purple arrows in Fig. 6(a). To illustrate these differences, some of the recorded diffraction patterns located on a horizontal line are presented in Fig. 6(b-p). The location of each presented diffraction pattern is indicated by a colorful spot on the VBF image. For the sake of convenience, to find the diffraction pattern associated with each spot on the VBF image, the border of each diffraction pattern has the same color as the spot on the VBF image. The five diffraction spots belong to the yellow-arrow area in Fig. 6(a) are presented in Fig. 6(b-f). All of these diffraction

³ Regarding the horizontal line in the middle of the VBF image which leads to the general change of the contrast of the top and bottom of the VBP image, it should be mentioned that this general change of the contrast was the artifact of the experiment.

patterns have ring (or diffused ring) diffraction patterns around the direct beam. This type of diffraction patterns is attributed to the amorphous nature of the deposited platinum layer. In some locations, the platinum layer may be locally nanocrystalline. As an example in Fig. 6(e), some faint diffraction spots are visible in addition to the diffraction rings. The second type of diffraction patterns which are associated with the blue-arrow area are presented in Fig. 6(g-l). Although the recorded diffraction pattern images of this area have distinct diffraction spots, the recorded images have a large background (i.e., the signal to noise ratio is considerably low). In general, two reasons can be pointed out for the low quality of the recorded diffraction patterns in this area.

The first one is combined (i.e., overlapping, multiple scattering) diffraction patterns. In a case in which more than one grain exist along the thickness of the studied foil, a recorded diffraction pattern can be convoluted to more than one grain/orientation. Therefore, a combined diffraction pattern condition happens in a case in which the grain size values are much smaller than the foil thickness (which is generally less than 150 nm). This problem can be resolved partially by conducting the orientation microscopy using transmission EBSD. This technique is based on the formation of Kikuchi diffraction patterns. Interestingly, the formation of Kikuchi patterns is primarily based on the interaction of the electron beam with the last grain/orientation which exists along the foil thickness [45]. Therefore, higher quality Kikuchi diffraction patterns with less information about the variation of orientation with respect to the foil thickness can be achieved by using transmission EBSD technique.

The second (and probably less possible) reason for a lower quality of the recorded spot diffraction patterns can be assigned to the degradation of the diffraction patterns due to applying a severe plastic deformation to the material and formation of a considerable number of defects

(e.g., dislocations) which leads to lattice distortions. While spot diffraction patterns are less sensitive to lattice distortions [35, 46], lattice distortions create a significant challenge in the characterization of severely deformed materials using EBSD technique [44].

The diffraction patterns associated with the third region of Fig. 6(a) which is depicted by the purple arrow are presented in Fig. 6(m-p). The signal to noise ratio is high in these recorded diffraction pattern images. Also, the number of distinguishable diffracted spots in each image is high enough to determine the crystal orientation based on cross correlation of the recorded diffraction pattern with the simulated diffraction patterns. While significant variations in the acquired diffraction patterns in this area reveal that a remarkable grain refinement occurred (in comparison to the original microstructure presented in Fig. 4), considering the quality of the diffraction images associated with the blue-arrow area (Fig. 6(g-l)), it can be said that the purple-arrow area experienced far less deformation with respect to the blue-arrow area.

Each recorded diffraction pattern associated with the blue-arrow area in Fig. 6(a) contains multiple spots which reveals that the blue-arrow area is crystalline and it probably contains extremely fine titanium grains. The validity of this hypothesis can be assessed by studying the composition of this area. To determine whether the composition of the unknown area (i.e., blue-arrow area in Fig. 5 and Fig. 6) contains mostly platinum or titanium, an EDS line scan was conducted along the green-arrow direction presented in Fig. 6(a). As shown in Fig. 7(a), this line scan (represented by a green arrow) covers all the three regions presented in Fig. 5 and Fig. 6 (i.e., yellow, blue and purple-arrow areas). The concentration of platinum and titanium (in weight percent) with respect to distance from the beginning of the green arrow is presented in Fig. 7(b). From Fig. 7(a) and Fig. 7(b), it can be said that as expected the majority content of the yellow and purple-arrow regions is platinum and titanium, respectively. Also, based on the large

titanium concentration (~90 wt%), it can be concluded that the unknown region (i.e., the blue-arrow area) contains nanocrystalline titanium grains.

Interestingly, based on the virtual bright field image (Fig. 6(a)) and the composition analyses (Fig. 7(b)), it is feasible to get an estimate of the surface roughness value for the UNSM treated sample. According to the results presented in these figures, it can be concluded that the contrast of the VBF image changes sharply at the interface of platinum/titanium phases (yellow/blue arrows). This fact can be used to determine the surface roughness of the treated titanium. By looking carefully at the area surrounded by the red color square in Fig. 6(a), it is possible to draw a semicircle by connecting *A*, *B* and *C* letters which are located on the surface of the sample. Notably, the darker area in the square is a part of the deposited platinum layer. The radius of the hypothetical semicircle which can be drawn by *A*, *B* and *C* letters has an approximate radius of 500 nm. This value is close to the 320 nm roughness value reported for the UNSM surface treatment of a nickel-based superalloy [28] and ~160 nm for the UNSM surface treatment of plasma-nitrided S45C steel [47]. The relatively small roughness values associated with UNSM surface treatments can be assigned to inducing a severe plastic deformation very close to the treated surface in addition to small distances between successive treatment paths [28].

The capability of UNSM technique to induce severe plastic deformation to the treated surface with the minimum risk of crack nucleation leads to a considerable improvement of the fatigue performance as presented in Fig. 3. For titanium alloys, crack nucleation is accelerated by increasing the surface roughness while it is retarded by cold work. Residual compressive stresses have no considerable effect on crack nucleation. Also, crack propagation is accelerated by cold work while it is hindered by residual compressive stresses. Surface roughness has no major impact on crack propagation [48].

Although the EDS result revealed that the blue-arrow area is mainly titanium, it is not possible to get any quantitative estimation of the distribution of the titanium grain size in the blue and purple-arrow areas based on the EDS result (Fig. 7(b)), the bright field image (Fig. 5), or the virtual bright field image (Fig. 6(a)).

The index map associated with the ASTARTM/PED scanned area is presented in Fig. 8(a). This map is made based on the matching value between the recorded diffraction patterns and the most correlated simulated diffraction patterns (templates). A higher index value is assigned to a better match between a recorded diffraction pattern and the most correlated template. The higher index values are presented by a brighter color in this type of plot. The index plot shown in Fig. 8(a) represents the variation of grain size with respect to distance from the treated surface clearly. Distinguishing grains within the first 1 μm from the UNSM treated surface (i.e., blue-arrow area in Fig. 8(a)) is very difficult due to the severe grain refinement. However, while grains further than 1 μm from the surface are finer in comparison to the original grain size values (Fig. 4), they are distinguishable in Fig. 8(a). In addition to a better visualization of grains, index map (Fig. 8(a)) reveals holes exist on the foil more accurately in comparison to the virtual bright field image, Fig. 6(a). For instance, the hole exists in the purple-arrow area of the foil is visible readily in the index map while it is not distinguishable in the VBF map. This fact can be justified easily based on the mentioned methods used to make these maps. The capability of index map to reveal holes can be used to detect any possible crack nucleated at the surface by the UNSM surface treatment. In this study, crack nucleation due to UNSM surface treatment was not observed in the ASTARTM/PED scanned area according to the corresponding index map, Fig. 8(a).

The IPF map associated with α titanium and amorphous phases overlaid with the index map of the scanned area is present in Fig. 8(b). As stated previously, three types of templates (i.e., α titanium, β titanium and amorphous) were used to index the recorded diffraction patterns. Since the volume fraction of the β titanium phase was small, the recorded patterns indexed as the β titanium phase had a very low-reliability index (which is analogous to the confidence index in EBSD technique [35]). Therefore, the orientations of the β phase titanium were not included in Fig. 8(b). Holes are represented as dark red areas in Fig. 8(b). Except these holes, there are two distinguishable areas. The first area which is located on the right half side of Fig. 8(b) contains grains which could be resolved by applying grain dilation clean up algorithm with a minimum grain size of ten pixels in multiple rows as well as neighbor orientation correlation (level 4) clean up procedure in TSL OIMTM software. The possibility of resolving these grains can be assigned to recording a relatively large number of high-quality diffraction patterns in this area. By contrast, the left-hand side of the IPF map contains the amorphous region and titanium grains with the average grain size of less than ~ 10 nm. As expected, the deposited platinum layer (i.e., the yellow-arrow area in Fig. 8(a)) is amorphous and in some limited areas, it is crystallized partially. Therefore, the orientation of the platinum area varies almost randomly. Due to the way that the amorphous diffraction pattern templates were simulated and the general form of the recorded diffraction patterns in the yellow-arrow area (as presented in Figs. 6(b-f)), the reliability index values for the amorphous phase were considerably low. Therefore, the color legend for the amorphous phase is not presented for the platinum phase to avoid any misinterpretations. For the case of the titanium region, due to the reasons mentioned for the quality of the recorded diffraction patterns for Figs. 6(g-l) (e.g., the existence of more than one grain along the thickness of the foil), it is impossible to determine the correct orientation of titanium grains located in this

area. Therefore, the orientation of the grains looks to vary randomly with respect to the planar coordinate in Fig. 8(b). Differentiating the recorded diffraction patterns belong to titanium and platinum phases were done fairly well due to the substantial differences between the recorded diffraction pattern images associated with these two phases as shown in Figs. 6(b-f) and Figs. 6(g-p).

Since no twins were observed in the IPF map, it can be concluded that the severe plastic deformation was only accommodated by the formation of new dislocations. Therefore, the dislocation density in the severely deformed area increased considerably which resulted in higher strength/hardness in the plastically deformed area. Notably, it is expected that the dislocation density to be inversely proportional to the distance from the UNSM treated surface considering the fact that the magnitude of the plastic strain and strain rate decrease by going into the depth of the treated material.

The presence of grain sizes less than 10 nm can be attributed to the formation of subgrain boundaries (i.e., low angle grain boundaries) due to the generation of new dislocations. Different mechanisms for grain refinement have been proposed [26, 29-31, 49] which are based on the formation of new dislocations [50], twins [51, 52] and phase transformations [53]. In the current study, the grain refinement can be justified by the formation of new dislocations. Gradually, the accumulation of dislocations at low angle grain boundaries increases which results in grain refinement and formation of new grains with considerably different orientations from an originally single grain. Notably, it has been shown that for the case of UNSM treatment of iron, grain refinement follows the division of high-energy areas (induced by severely plastic deformation) in addition to dislocation walls and tangles [29]. Also, the formation of different dislocation structures is affected considerably by the magnitude of strain and strain rate. These

two parameters are a function of distance from the UNSM treated surface. Therefore, as shown in Fig. 8(b), grain refinement which is a function of dislocation formation varies with respect to depth [19].

Assigning a part of the UNSM treatment hardening to the Hall-Petch strengthening is common in the literature [25, 27]. While this type of interpretation is made based on the assumption that the idealized Hall-Petch relationship is valid, the results of the current study show that this relationship may not be valid very close to the UNSM treated surface. Notably, for grain sizes below a critical value [54], deviation from the commonly used Hall-Petch relationship may happen due to the presence of flaws [55] and rapid diffusional creep [54]. Various deformation mechanisms (e.g., failure of dislocation accumulations at grain boundaries [56-58]) have been suggested to justify the reduction in hardening with grain size reduction.

The surface-treated area can be studied more quantitatively by determining the dislocation density distributions of geometrically necessary dislocations [39, 40] and disclinations [59], developing phenomenological equations to correlate microstructure and composition with the mechanical response (e.g., yield strength) [60, 61] as well as investigating the microstructure and texture evolutions as a function of surface deformation (e.g., indentation) [62].

4. Conclusions

The effect of UNSM surface treatment on the mechanical properties and microstructural evolutions of a α/β titanium alloy was studied. The surface hardness value for the UNSM treated sample increased more than two times in comparison with the as-received sample. The presence of compressive residual stresses along and perpendicular to the UNSM scan direction were observed in areas being less than 200 μm far from the treated surface. FWHM results showed

that the area which was not more than a few microns far from the treated surface experienced a very large plastic deformation. The fatigue performance of the UNSM treated sample improved considerably in comparison with the as-received sample. Three distinct areas were observed in the recorded bright field image for a thin foil made from the cross section of the UNSM treated surface. Characterization of one of these areas with the bright field image was difficult. This area was characterized by EDS and ASTARTM/PED techniques to prove that it contains extremely fine titanium grains. Different maps (e.g., index map and virtual bright field image) which can be made from an ASTARTM/PED scan were presented and some of the essential information (e.g., grain size distributions and surface roughness) which can be derived were presented. The difficulty of the characterization of the extremely fine grain area by ASTARTM/PED technique was attributed to the combined diffraction pattern condition. Also, the importance of considering the deviation from the ideal Hall-Petch relationship for areas very close to the UNSM treated surface was mentioned.

Acknowledgments

The authors gratefully acknowledge the Iowa State University; the Center for Advanced Non-Ferrous Structural Alloys, which is a joint industry–university center between the Colorado School of Mines and the Iowa State University (NSF award no. 1134873) and the Center for Advanced Research and Testing at the University of North Texas. The authors are also grateful for financial support of this research by the National Science Foundation (Grant no CMMI-1334538), as well as the contribution of the State of Ohio, Department of Development and Third Frontier Commission (Grant no. TECH 10-014), which provided funding in support of

“Ohio Center for Laser Shock Processing for Advanced Materials and Devices” and the equipment in the center that was used in this work.

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Figure 1. In-depth nanoindentation hardness values for the as-received and UNSM surface treated samples are presented.

Figure 2. In-depth residual stresses along $\phi 0^\circ$ and $\phi 90^\circ$ directions as well as FWHM values versus depth for the UNSM surface-treated sample are depicted.

Figure 3. Stress versus number of cycles to failure (S-N) curves for the UNSM surface treated and as-received samples are shown.

Figure 4. Inverse pole figure plot of α phase titanium for the as-received sample is shown.

Figure 5. The bright field image associated with the cross section area of the surface which was treated by UNSM is shown.

Figure 6. (a) Virtual bright field image and (b-p) recorded diffraction patterns of the surface-treated sample are presented. The areas depicted by yellow, blue and purple colors are consistent with the areas shown in Fig. 5 with the same color.

Figure 7. (a) Yellow, blue and purple arrows represent the same areas introduced in Fig. 6 while the green arrow shows the EDS line scan interval. (b) Composition profile along the green arrow in part (a) is presented.

Figure 8. (a) Index map and (b) inverse pole figure map of the ASTAR™/PED scanned area are presented. The yellow, blue and purple arrows in part (a) represent the same areas mentioned in Fig. 5 and Fig. 6.