A comprehensive review of nanostructured materials by ultrasonic nanocrystal surface modification technique

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Abstract: Nanostructured materials (NMs) possess outstanding properties than conventional coarse-grained (CG) materials. Hence designing potentially cost-efficient and environmentally products made of NMs with better are on high demand. This paper gives a comprehensive review of the most recent progress in production, characterisation and fundamental understanding of NMs produced by ultrasonic nanocrystal surface modification (UNSM) technique. In this review, we demonstrate a detailed description of the literature on the subject as well as highlight challenges for the production of NMs. Recently, this technique has also been applied to thermal spray ceramic coatings and the newly obtained experimental results are also discussed.

1 Introduction

It is well known that nanostructured materials (NMs) are structurally characterised by nano-grains (NGs) on the order of a few nanometers, which have higher strength and smaller grains than coarse-grained (CG) materials. Grain size refinement is the major microstructural parameter in dictating the surface properties of materials. Hence, control over grain size has long been recognised as a method to design microstructures and increase the strength of materials with desired and superior properties and performance. It has been reported earlier that most of the mechanical properties of materials benefit significantly from NGs [1]. As the competition and demand for stronger materials performance are consecutively going on, considerable attempts have been made to develop viable and eco-friendly techniques for strengthening a material by grain refinement. A number of previous studies have proved that surface modification techniques are able to substantially improve the mechanical and tribological properties of materials [2–4]. Also, a number of studies on these surface modification techniques have previously been investigated to give insight into the improvement in those properties of materials. However, it is important to note in this context that all mentioned surface modification techniques have own advantages and disadvantages since they involve several problematic steps or high-tech instruments. For this reason, the development of cost-effective and time-saving technique that is adaptable to various materials still remains in high demand.

From an industrial perspective, an ultrasonic nanocrystalline surface modification (UNSM) technique is a simple surface modification process for improving the strength and performance of materials by the application of severe plastic deformation (SPD). The UNSM technique has gained a new importance in the field of mechanical engineering, materials science, tribology etc. owing to the superlative improvements in numerous surface properties of materials such as mechanical, tribological, fatigue and resistance to corrosion through the formation of NGs. Hence, the main objective of this review is to present the state-of-the-art of UNSM technique, to bring together all the hitherto obtained experimental results and to discuss the beneficial effectiveness on material properties. Furthermore, this review provides a brief methodology and describes the major potential applications of UNSM technique.

2 Method of producing nanostructured materials by UNSM technique

Materials with a grain size less than of 1 μm may be generated in two different methods [1]. The approach in which bulk CG materials are processed by SPD to introduce a high dislocation density without any change in the dimensions of the specimens. In this section, the general principles of UNSM technique are described. The processing of metallic materials by UNSM was first developed Prof. Y.S. Pyun and his co-workers in the middle of 1990s at Sun Moon University, South Korea. Later on, this technology has been patented and commercialised by DesignMecha Co., Ltd. [5]. Initially, the objective was to develop a metal forming processing for industrial knives, but later the application of UNSM technique was extended from bearings to shafts.

The main principle and processing of UNSM technique are shown in Fig. 1. As can be seen from Fig. 1*a* that not only the static load (P_{st}), but also the dynamic load ($P_{dy} = P\sin 2\pi ft$) are exerted in this process. The processing is conducted striking a workpiece surface up to 20 K or more times per second with shots of an attached ball to the horn in the range of 1 K-100 K per square millimeter. In general, a silicon nitride ceramic (Si_3N_4) and/or a tungsten carbide (WC) ball/tip is used as the strike media. Typical size of balls/tips are in the range of 1.2–6 mm in diameter and these can be chosen for different purposes depending strongly upon materials and mechanical properties of workpiece. The strikes produce dimples on the treated surface with a depth is less than 100 nm. The number of micro-dimples, n in m^{-2} can be quantified using the following expression

$$n = \frac{f}{2\pi R\,(V \times S)} \tag{1}$$

where f is the frequency [s^{-1}], V is the machine spindle speed [Rev s^{-1}], S is the feed rate [m Rev^{-1}], so that ($V \times S$) is [m s^{-1}] and $f/(V \times S)$ is [m^{-1}] whereas n is [m^{-2}], r is the radius at which the ball/pin contacts the surface to be treated.

Moreover, the strikes, which can be described as cold-forging, introduce SPD to the surface layers with NGs to increase the strength of material. The strength generally follows the Hall-Petch relationship [6] so that

$$\sigma_y = \sigma_0 + k_y d^{-1/2} \tag{2}$$

where σ_y is the yield stress, σ_0 is the lattice friction stress, k_y is a constant of yielding and d is the grain size. Thus, the strength of the material increases when the grain size is reduced. Moreover, this UNSM technique modifies the surface morphology, reduces surface roughness and induces compressive residual stress in the surface layer.

The UNSM technique is characterised by its excellent performance and short cycle times, resulting in lower operating costs and reduced time requirements and thus, provides the users with

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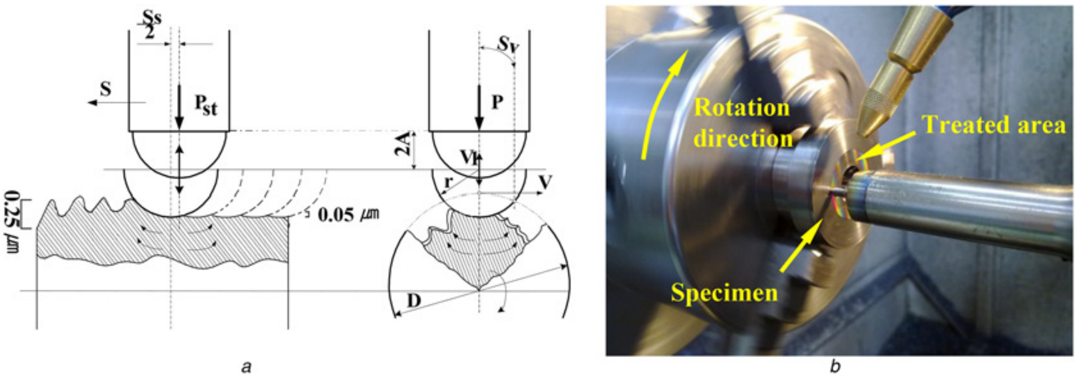

Fig. 1 *Principles of processing by UNSM technique*

Table 1 Basic UNSM treatment parameters.

Frequency, kHz	Amplitude, μm	Speed, rpm	Impact load, N	Interval, mm	Tip (ball) diameter, mm	Tip (ball) material
20	0~100	0~100	0~200 N	0.01~0.1	1.2~6.0	WC, Si_3N_4

significant competitive advantages. This simple surface modification technique is in full compliance with the today's modern requirements. The accuracy and repeatability are guaranteed by special, fully-automatic process control. In the processing, a workpiece can be installed into a magnetic board on a flexible manufacturing system carrier, which moves linearly in two axes, and also into a computer numerical control machine, which provides with a rotational movement. The range of UNSM treatment input parameters are shown in Table 1 that can control the overall surface properties including grain size. This technique has been successfully employed for a number of metallic materials. More details of UNSM technique can be found in our previous studies [7, 8].

3 Nature of the nanostructured materials produced by UNSM technique

Understanding of the formation of NGs during the UNSM process is very crucial for further development of UNSM technique. A gradient size distribution from a few nanometers (in the topmost surface layer) to several submicrometers is developed, which provides a unique opportunity to examine the microstructure characteristics at different levels of surface layer. Therefore, the underlying mechanism for deformation-induced grain refinement in the micro- and nano-meter regimes can be deduced. It is generally accepted that transmission electron microscopy (TEM), X-ray diffraction (XRD), atomic force microscopy (AFM) and electron backscatter diffraction (EBSD) are major techniques which may be successfully used for nanostructure characterisation.

The introduction of UNSM technique has led to a major interest in using this technique and producing NMs with NGs. Unlike from the inception, many results are currently available showing the wide range applications of this technique. It has been confirmed by EBSD technique in our previous study that the UNSM technique is capable of producing an NM in bearing steel with NGs as shown in Fig. 2*a* [8]. It was found that the effective depth of nanostructured surface layer with NGs was found to be about 50–60 μm at the top surface. Also, it can be seen that the NG size increased with increasing the depth at the top surface. Li *et al.* have pointed out the possibility of refining grain size of Cu-Sn alloy by UNSM technique obtained using a cross-sectional TEM images [9]. They have found that at a depth of about 300 μm from the surface, mechanical twins with dislocations are formed as shown in Fig. 2*b*.

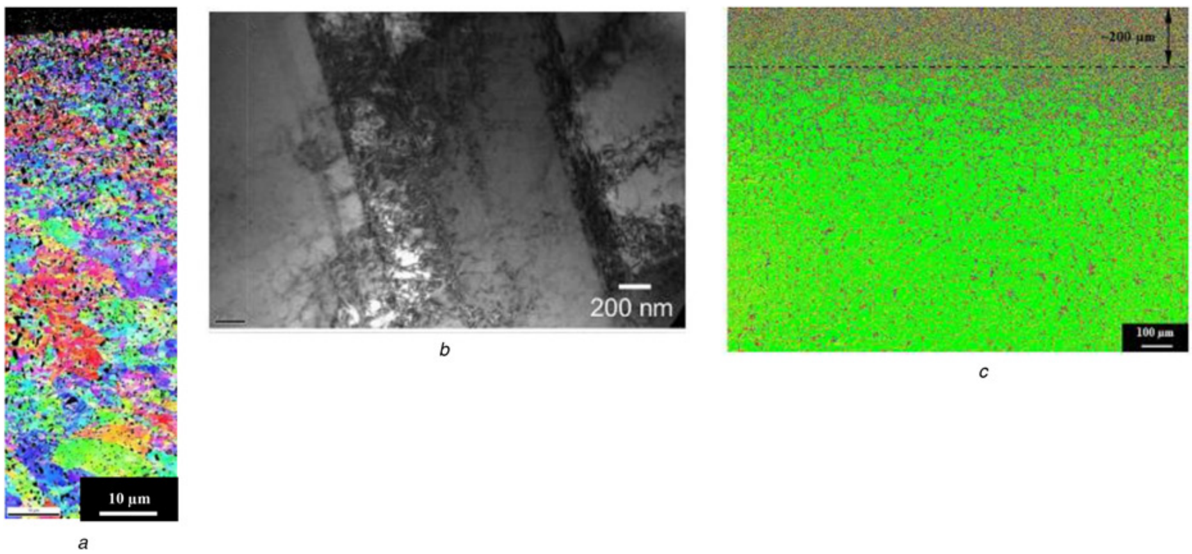

Fig. 2 *Microstructural evolution of UNSM-treated bearing steel (a), Cu-Sn alloy (b) and Cu-based alloy (c)*

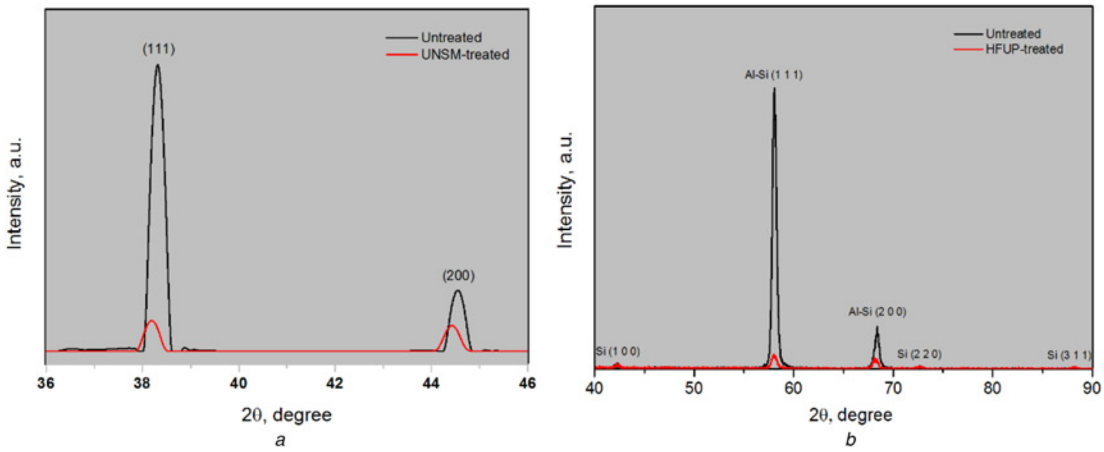

Fig. 3 *X-ray diffraction patterns obtained on the surface of the untreated and UNSM-treated* Al6061-T6 alloy (*a*) and Al-Si alloy (*b*) specimens

Moreover, Fig. 2*c* shows the cross-sectional laser microscope image of the UNSM-treated specimen [10]. Evidently, the strikes of a WC tip generated a NS surface layer with a thickness of about 200 µm, leading to grain refinement at the top surface. Overall surface characterisation revealed that the UNSM technique is capable of producing NMs by refining CGs into NGs. A material may be strenghtened by grain size refinement, alloying with impurity atoms and strain-hardening. During SPD process the basic mechanism of the grain size refinement is the formation of disclocation cell structures with high angle grain boundaries [11]. Moreover, NG structures are typical steady-state characteristics of bulk metals processed by means of SPD. As can be seen from Fig. 2*a* that the thickness of the nanostructured layer is not uniform, which may be attributed to the heterogeneous nature of plastic deformation within and between grains. There are two stages during UNSM treatment, one is the elastic-plastic deformation stage and the other one is the dynamic restoring stage. The strain and strain rate gradually decrease from the surface layer into the specimen, and this is correlated to the gradient that exhibits nano- to submicro- to micro-structure from the UNSM-treated surface to the strain-free matrix. A higher strain and strain rate are more effective in causing to the formation of NGs. However, there seems to be a limitation to the increase in the thickness of nanostructured layer due to the balance between the elastic-plastic deformation stage and the dynamic restoring stage.

Fig. 3 presents the XRD patterns obtained on the untreated and UNSM-treated Al6061-T6 and Al-Si alloy specimens. It is obvious from the XRD patterns of the UNSM-treated specimens that the full width at half maximum (FWHM) of diffraction peak broadened and the diffraction intensity peaks decreased compared to those of the untreated specimens, which means that the grains of the UNSM-treated specimens were refined and mean lattice mean microstrain was increased [12, 13]. These improvements may be ascribed to the increase in strain due to plastic deformation is responsible for the subdivision of the subgrains into NGs. The average grain size and mean microstrain can be calculated by broadening the diffraction peaks using the Scherrer and the Stokes-Wilson Eqs. [3] and [4], respectively

$$D = \frac{K\lambda}{\beta^C \cos\theta} \tag{3}$$

$$e = \frac{1}{4}\beta^G \cot\theta \tag{4}$$

where D is the average grain size, K is the shape factor, λ is the wavelength, e is the mean lattice strain, β^C is the integral breadth of the size broadened profile (Cauchy component), and the β^G is the integral breadth of the strain broadened profile (Gaussian component), which are calculated by an approach of Keijiser *et al.* [14] It is believed that more dislocations are generated and annihilated in the sub-boundaries with increasing lattice strain after UNSM process. The subdivision takes place on a finer scale with increasing lattice strain. An increase in lattice microstrain is not only responsible for the subdivision of the CGs into NGs, but also further formation of twins that will reduce the size of the CGs very fast. The effective grain size decreases due to the fact that twin boundaries are found to act as obstacles for slip and dislocations may be blocked by twin boundaries. The average grain size and mean microstrain of the UNSM-treated Al6061-T6 and Al-Si alloy specimens were found to be about 96 nm and 0.11, and 44 nm and 0.18, respectively [12, 13]. It is essential to note that the mechanism of deformation and some properties of NMs not only depend on the average grains size, but also strongly influenced by the grain size distribution and boundary structure.

4 Mechanical properties of materials by UNSM technique

It is well known that sliding contact often induce SPD in the near-surface region, which accordingly changes the corresponding microstructure and properties of surface and subsurface, generates local discontinuities and micro-cracks, and finally results in detachment of wear particles. In this regard, the investigation of mechanical properties of materials has always been an important issue to improve the tribological and fatigue properties of materials. The mechanical properties of UNSM-treated Cu-based alloy have been primarily obtained using a nanoindenation [10]. Typically, NMs with NGs exhibit significantly higher strength relative to the CG materials. Furthermore, it has been reported earlier that the mechanical properties were found to increase with decreasing grain size in the range from 100 nm to 15 nm [15]. However, some previous experimental results have indicated that below a grain size of about 10 nm, the mechanical properties decrease with further grain refinement, which so-called “inverse Hall-Petch relationship”.

In the last several decades much attention has been focused on understanding the phenomena obtained by the Oliver-Pharr nanoindentation analysis in order to estimate true contact area and materials mechanical properties [16]. This testing method provides accurate measurements of the continuous variation of indentation load as a function of the penetration depth at the nano-scale. Fig. 4 shows the typical load-displacement (*P-h*) curves obtained from the nanoindentation tests using the untreated and UNSM-treated Cu-based and Al6061-T6 alloy specimens [10,

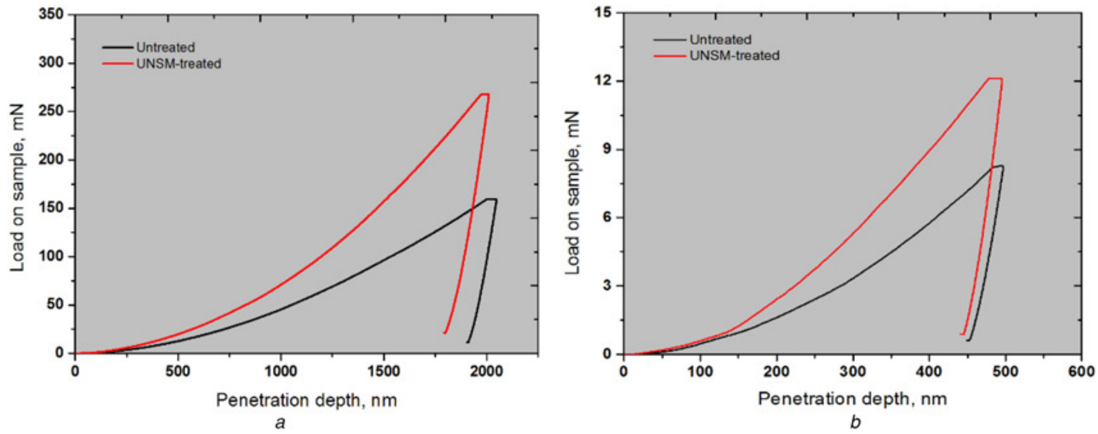

Fig. 4 *Typical nanoindentation load-displacement curves of the untreated and UNSM-treated* Cu-based alloy (*a*) and Al6061-T6 alloy (*b*) specimens

12]. It is evident from figure that the UNSM-treated specimens exhibited a higher hardness than the untreated specimens.

Fig. 5 shows the variation in nano-hardness and Young's modulus for those specimens as a function of displacement into the surface. It can be clearly seen that the nano-hardness and Young's modulus of the UNSM-treated specimens were evidently increased at the top surface by either strain-hardening and grain size refinement, respectively, and then gradually decreased with increasing displacements into the surface. The increase in nano-hardness and Young's modulus for the UNSM-treated specimens may be attributed to the NGs at the top surface, while for the untreated specimen it may be attributed to the mechanical polishing. It has also been reported earlier that the NG Cu had a higher hardness than the CG Cu [17]. As anticipated, the grain refinement introduced by SPD processing produces NGs having high strength.

5 Tribological properties of materials by UNSM technique

It has been proved that the friction coefficient and wear behavior of materials can be improved by UNSM technique using tribometers. Fig. 6 presents the friction coefficient behavior of the untreated and UNSM-treated specimens of Cu-based alloy [10]. It is evident that the UNSM-treated specimen led to a lower friction coefficient under dry and oil-lubricated conditions. Fig. 7*a* shows the friction coefficient of the untreated and UNSM-treated and Al6061-T6 specimens [12]. The friction coefficient of both specimens gradually increased

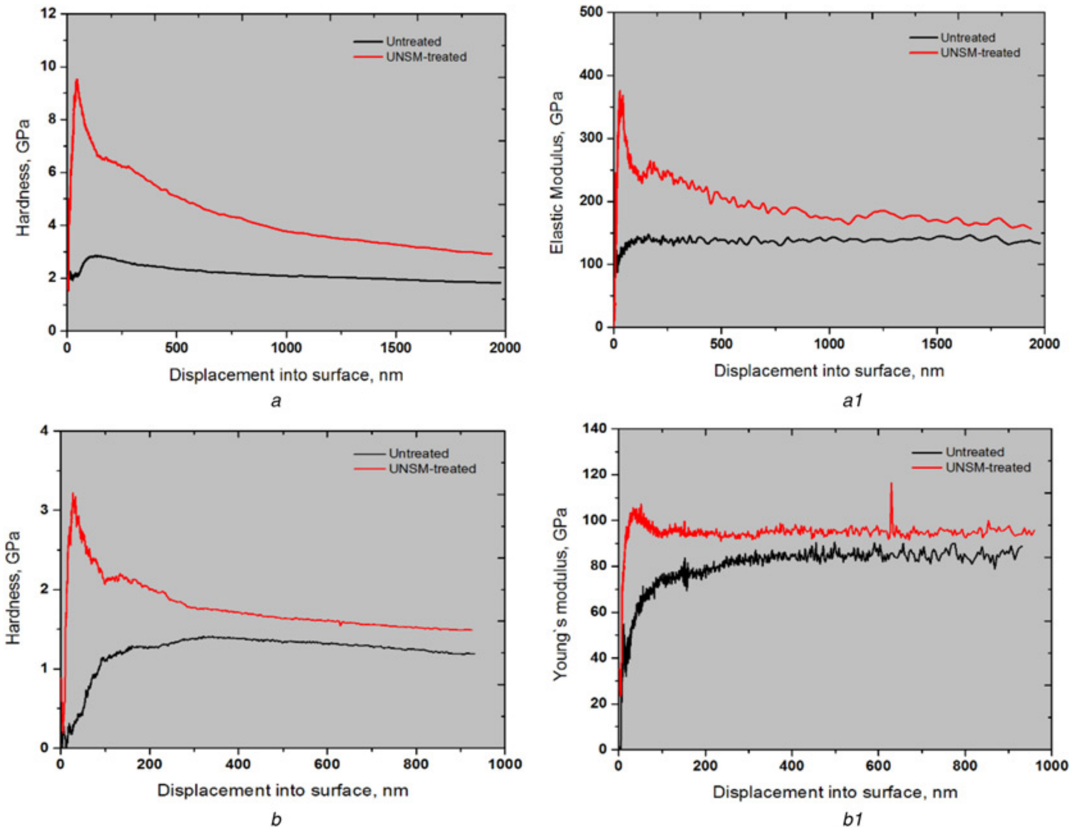

Fig. 5. *Variations in nano-hardness (a, b) and Young's modulus (a1, b1) of the untreated and UNSM-treated Cu-based alloy and Al6061-T6 alloy specimens, respectively*

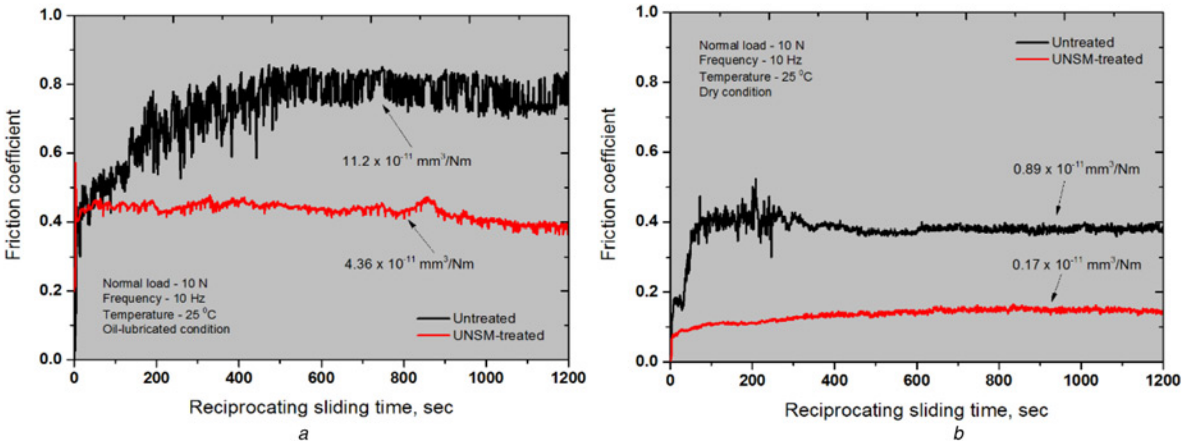

Fig. 6 *Variations in friction coefficient of the untreated and UNSM-treated Cu-based alloy specimens under dry (a) and oil-lubricated (b) reciprocating sliding conditions against bearing steel ball*

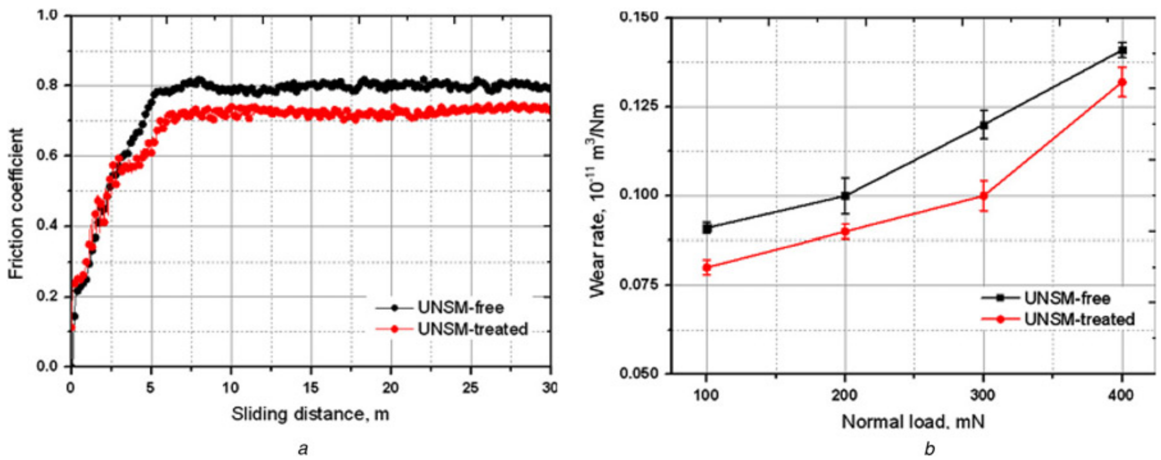

Fig. 7 *Variation in friction coefficient (a) and wear rate (b) as a function of sliding distance for the untreated and UNSM-treated Al6061–T6 alloy specimens at a normal load of 400 mN and a reciprocating speed of 4 mm/s*

in the initial period of about 5 m of sliding distance, which can be considered as a running-in period. Then it transitioned to a steady-state value of 0.81 and 0.73 for the UNSM-free and UNSM-treated specimens, respectively. Fig. 7*b* shows the wear rate of the untreated and UNSM-treated specimens as a function of normal load at a sliding distance of 28.88 m. In addition to the benefit in friction reduction, the UNSMtreated specimen showed nearly 15% higher wear resistance compared to that of the UNSM-free specimen for the entire range of normal load. The improvements may be attributed to the increased hardness, reduced contact area and corrugated structure which is able to remove and trapping some of the wear debris and particles from the tribocontact interface. The inset in Fig. 6 shows the wear rate results for the untreated and UNSM-treated specimens. It was found that the UNSM-treated specimens exhibited a significant lower wear rate than the untreated specimens. It has been reported in our previous study that the UNSM technique increased the wear resistance of AZ91D Mg alloy where the width of wear track was found to be 1.115 mm and 0.76 mm for the untreated and UNSM-treated specimens, respectively [7]. The enhancement in wear of the UNSM-treated specimens was associated with the high hardness and the low work-hardening rate of the NG structure, and easy oxidation of wear debris, which are all related to grain refinement. Bellemare et al. have reported earlier similar findings establishing a quantitative framework to assess frictional sliding properties [15]. Also, during wear, the UNSM-treated specimens with a lower friction coefficient led to a smaller lateral tearing force. To be more specific, a high hardness decreased the contact area and asperity penetration. Yao et al. have studied the wear properties of NG Cu of different purities in comparison with the CG Cu. They found that the NG Cu exhibited an enhanced wear resistance than the CG Cu [17].

6 Conclusions

In this review, the UNSM technique background and its effectiveness on the structural, mechanical and tribological properties of metallic materials were presented. We have highlighted some of the most recent experimental results that demonstrate the general feasibility of this surface modification approach. The obtained results confirmed the possibility of producing NG materials and its effectiveness on some properties of metallic materials. In perspective, these recent progresses have pointed to promising routes to the new developments and presented new challenges to the understanding of intrinsic NGs behaviours.

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8 References

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