

**Cite this article as:** Chen Daoming, Liu Jingyuan, Chen Dehua, et al. Gradient Nanostructured Materials Induced by Ultrasonic Surface Rolling Process[J]. Rare Metal Materials and Engineering, 2021, 50(10): 3562-3576.

REVIEW

# Gradient Nanostructured Materials Induced by Ultrasonic Surface Rolling Process

Chen Daoming<sup>1,2</sup>, Liu Jingyuan<sup>2</sup>, Chen Dehua<sup>2</sup>, Su Bin<sup>2</sup>, Liu Kezhao<sup>2</sup>

<sup>1</sup> Science and Technology on Surface Physics and Chemistry Laboratory, Mianyang 621908, China; <sup>2</sup> Institute of Materials, China Academy of Engineering Physics, Mianyang 621907, China

**Abstract:** The application of ultrasonic surface rolling process (USRP) to obtain gradient nanostructured materials is presented with comprehensive researches. Concept and description of USRP treatment which has been proved to be able to create gradient nanostructured layers and induce residual compressive stress were depicted. Meanwhile, the microstructural evolutions and surface characteristics which critically depend on processing regimes were discussed. On this basis, it is found that the improvement of mechanical properties, i.e. hardness, strength, wear and fatigue performances, is obtained by USRP treatment while the corrosion/oxidation behavior depends on the composition and structure, surface integrity and stress, solution and service environment. In addition, some possible addresses for future research in this field were drawn and underlined.

**Key words:** ultrasonic surface rolling process; gradient nanostructure; surface characteristics; mechanical properties; corrosion behavior

In engineering applications, the components suffer from wear, corrosion, cracking and fatigue damage, leading to severe accidents and economic disasters. In most cases, mechanical failures occur in the exterior layers of the components and are sensitive to the corresponding surface microstructures<sup>[1,2]</sup>. Therefore, various advanced surface technologies have been developed especially in the activated metals, such as electron beam induced deposition<sup>[3]</sup>, pulsed laser treatment<sup>[4]</sup>, surface nitridation technique<sup>[5]</sup>, surface severe plastic deformation<sup>[6]</sup>, and the service properties of the materials can be improved by changing the surface structure and composition. In view of the fact that grain refinement can obtain higher strength and greatly improve the mechanical properties, such as wear resistance, hardness, and fretting fatigue, it is considerably effective to apply nanostructured approaches. In recent years, nanostructured materials processed by severe plastic deformation have attracted more and more interest of specialists in materials science. Undoubtedly, it is worth mentioning that nanostructures in metals induced by severe plastic deformation provide a strengthening mechanism that is different from the

conventional alloying and heat treatment. By playing with defects and grain boundaries in simpler alloys or pure metals, i.e. nanocrystals or plainification induced by severe plastic deformation, metals can achieve advanced properties and reduce material cost while increase their resource-independence and recyclability<sup>[7,8]</sup>. The basis of severe plastic deformation methods is to increase the free energy of the polycrystalline and generation of more defects and interfaces as well as grain refinement in various non-equilibrium processes<sup>[9]</sup>. The materials treated by various severe plastic deformation processes often have a mean grain size less than 100 nm and the grain usually possesses some substructure inside due to a highly distorted crystal lattice, indicating that severe plastic deformation has become one of the main techniques to obtain nanostructured materials<sup>[10]</sup>. Therefore, nanocrystals induced by severe plastic deformation show a new opportunity to obtain unprecedented improved properties for traditional or new materials by tailoring interfaces and microstructures. However, the formation of nanostructures in bulk materials induced by severe plastic deformation is impossible without application of special mechanical schemes

Received date: October 12, 2020

Foundation item: National Natural Science Foundation of China (U1630250); China Academy of Engineering Physics Research Fund (TA030202)

Corresponding author: Liu Kezhao, Ph. D., Professor, Institute of Materials, China Academy of Engineering Physics, Mianyang 621907, P. R. China, Tel: 0086-816-3626728, E-mail: liukezhaonsaf@163.com

Copyright © 2021, Northwest Institute for Nonferrous Metal Research. Published by Science Press. All rights reserved.

to provide severe deformation and surface integrity at relatively low temperatures. At the same time, the bulk nanostructured materials are difficult to enhance toughness and prevent crack damage during processing, according to their high strength in compliance with Hall-Petch relationship.

Based on the surface severe plastic deformation (SSPD) method, Lu<sup>[11]</sup> proposed surface nanocrystallization (SNC) technology, which can effectively improve the comprehensive service performance of various metals without change of the surface chemical constitution and component size by synthesizing a gradient nanocrystalline structure. Under the repeated action of external load, the metal surface is subjected to severe plastic deformation in different directions, and the coarse-grain structure in the core is gradually refined to the nanometer scale at the topmost surface. The essence of this structure is that the grain boundary density changes spatially in a gradient, which involves nanocrystals, ultrafine-grains, deformation and coarse-grain microstructures, corresponding to the spatial gradient change of residual compressive stress, work hardening and texture<sup>[12]</sup>. Since its inception, the gradient nanocrystal structure with a nanostructured surface layer and coarse-grained interior has attracted considerable research interest due to its excellent performance, which plays an important role in reducing crack initiation and prolonging service life. In recent years, SSPD based surface nanocrystallization has been recognized as one of the most prosperous ways for generating fine grains as well as introducing residual compressive stress and work hardening in the surface layers<sup>[13]</sup>. To obtain gradient nanocrystalline materials (grain size smaller than 100 nm), the SNC technology can be carried out in different ways, including surface mechanical attrition treatment (SMAT)<sup>[14]</sup>, surface mechanical grinding treatment (SMGT)<sup>[15]</sup>, high pressure surface rolling (HPSR)<sup>[16]</sup>, fine particle bombarding (FPB)<sup>[17]</sup>, fast multiple rotation rolling (FMRR)<sup>[18]</sup>, ultrasonic shot peening (USSP)<sup>[19]</sup>, and ultrasonic surface rolling process (USRP)<sup>[20]</sup>. However, the surface topography of component treated by different SNC technologies has different effects on the surface state, which may introduce surface defects and affect the global behavior<sup>[1,21]</sup>. Among all the proposed SSPD techniques, ultrasonic surface rolling process (USRP) seems to be very promising due to its advantages of relative simplicity and wide applicability, which offers a combination of ultrasonic frequency vibrations and static force<sup>[20]</sup>.

USRP is most commonly used for surface integrity manufacturing to produce severe elastic-plastic deformation and enhance the surface quality by decreasing surface roughness, refining grains, inducing residual compressive stress and improving surface properties. Additionally, there is no clear dividing line between plastic deformation layer and matrix because the strain and strain rate induced by USRP gradually change from the top surface to the interior of material. Finally, a gradient nanostructure consisting of nanocrystalline layer, refined structure layer, deformed coarse-grained layer and strain-free coarse-grained matrix is formed with a certain thickness beneath the treated surface. However,

several review papers have focused broadly on the deformation behavior of ultrafine-grained or nanostructured metals induced by severe plastic deformation, with very limited attention to SSPD techniques. Moreover, there are few studies available on USRP treatment, and the microstructure evolutions and service properties of materials induced by USRP treatment are still unclear. Also a proper relation between the processes, their parameters and the properties of the surface and subsurface layers obtained by USRP is to be found. In the present review, the focus on the microstructure evolution and surface properties to produce gradient nanostructures by USRP is discussed.

## 1 Concept and Description of USRP

Recently, it is relatively common to use ultrasonic equipment to provide desired kinetic energy required for the treatment. Ultrasonic technology has been integrated into conventional surface enhancement techniques to further increase the treatment capabilities<sup>[22]</sup>. USRP is a mechanical surface treatment that obtains homogeneous microstructure and changes in surface topography. It combines traditional rolling technology with ultrasonic technology and induces plastic deformation in near-surface area of the components, resulting in formation of residual compressive stresses, work hardening and excellent surface quality. In contrast to the traditional rolling technology, the static pressure is required only for maintaining the continuous contact of the tool with the surface during the treatment. The plastic deformation is mainly achieved by the dynamic forces caused by ultrasonic vibrations. Therefore, the use of ultrasonic vibrations reduces the amount of pressure applied on the part surface for achieving the required plastic deformation. Due to the difference in the degree of plastic deformation, the surface has a gradient nanostructure with different degrees of grain refinement.

The main concept and mechanism of USRP is as follows<sup>[1,20,22-27]</sup>: an ultrasonic apparatus which converts electric energy to mechanical energy of high-frequency and high-energy ultrasonic waves via amplification and generation of the amplitude transformer can be mounted onto the spindle of any vertical CNC machining centre. An ultra-hard scrollable rolling tip attached to the ultrasonic apparatus is applied to achieve impact on the surface with an ultrasonic vibration of certain amplitudes at high frequency in the normal direction. An air compressor is used for pushing ultrasonic apparatus unit with constant pressure on the surface of components. Therefore, the total energy acting on the surface of components is the sum of the dynamic energy generated through the ultrasonic vibration and the static energy pushing ultrasonic apparatus with constant pressure. Under the static load combined with the dynamic impact, the rolling tip transmits the ultrasonic vibration and constant pressure to the surface of components to be processed in a rotating state. The ball on the rolling tip then rotates freely as the tool is moved relative to the surface to be treated while a constant pressure is maintained. After processing, some recovery of elasticity will

take place on the processed surface. So the plastic flow will change the asperity of components, reduce the surface roughness and enhance the combination property of the finished surface.

As shown in Fig. 1, the cemented carbide ball on the rolling tip is used to crush the surface of samples. When the processed surface is hit by the ball on the rolling tip, the contact area between the surface and the ball can be regarded as two contact types, including the circular contact area and elliptical contact area. Under these different contact types, the ball on the rolling tip is used to process a flat surface (the contact area is a circle) and cylindrical surface (the contact area is an ellipse), thereby flattening materials and causing residual compressive stresses after the full coverage<sup>[28]</sup>. For the cylindrical sample in Fig. 1, it rotates at a certain speed  $v_1$ , and the velocity  $v_2$  slides axially along the surface. The ball with radius  $r$  is in physical contact with the surface of cylindrical sample. Due to the grinding and pressing action of the rolling ball, the surface at the front end of the ball is “stacked”. The plastic rheological part may be removed by the rolling ball or pressed into the material to form a plastic deformation layer. In this way, a single rolling forms a plastic deformation layer with a certain depth, and each treatment will produce local plastic deformation near the contact point between the sample and the ball. In the end, the strain and strain rate can be increased by the repeated plastic deformation, which can refine the grains of the surface layer to the nanometer scale. During USRP, the cutting oil is used in the process for cooling and lubricating. The surface temperature is always controlled far away from the melting point during processing under a controlled atmosphere. Therefore, this technology has certain industrial practical application value in the special component processing.

## 2 Surface Structural Characterization of Materials Induced by USRP

### 2.1 Structural evolution

SSPD based surface nanocrystallization is the process of formation, accumulation and evolution of surface defects and interfaces. Extensive research on the plastic deformation

induced surface structural evolution mechanisms has been carried out worldwide. As for USRP treatment, the dislocations generated from the repeated impacts initially accumulate and subdivide the original near-surface grains into sub-grains and deformed twin lamellae in different orientations. Further strain induced by the mechanical impacts creates more and more refined sub-grains with greater misorientations and these sub-grains presumably undergo rotation. Under the external force, the crystallographic orientations of grains must rotate with respect to defects moving in certain directions within certain planes. The smaller grains rotate more under stress due to the motion of grain boundary dislocations, and textures also evolve during plastic deformation, where polycrystals change their shape, finally leaving nano-grains or crystallites<sup>[29-31]</sup>. As we know, the stacking fault energy ( $\gamma_{\text{SFE}}$ ), crystal structure, grain size, temperature and other deformation conditions are the most important factors affecting the deformation mechanisms. It is found that deformation induced grain refinement is mainly caused by dislocation activities which are prone to multi-slip and cross-slip for materials with medium to high  $\gamma_{\text{SFE}}$  under low strain rates. The deformation are mainly generated through the movement and evolution of dislocations. There are several dislocation structures including clustered-small-cell wall (CSCW), uncondensed dislocation wall (UDW), isolated dislocation cell (IDC), dense-dislocation wall (DDW), and dislocation tangle zone (DTZ)<sup>[32,33]</sup>. Most screw dislocations of high  $\gamma_{\text{SFE}}$  materials form small-angle interface structures with various shapes through cross-slip interactions in early stage. As strain increases, the small-angle grain boundaries gradually evolve into equiaxed grains to complete grain refinement. Zhang et al<sup>[34]</sup> investigated 17Cr2Ni2MoVNB steel subjected to the USRP treatment, and found that several dislocation bands greatly increase and exist near the phase interface on the cementite interface of the top surface after the action of USRP. It is proposed that the grain refinement is associated with the increase in dislocation density, which leads to the dislocation walls or dislocation tangles and then turns into sub-boundaries or new grain boundaries. Ye et al<sup>[35]</sup> proposed that some bulk grains of commercial pure titanium processed by USRP are divided into small fragments and form

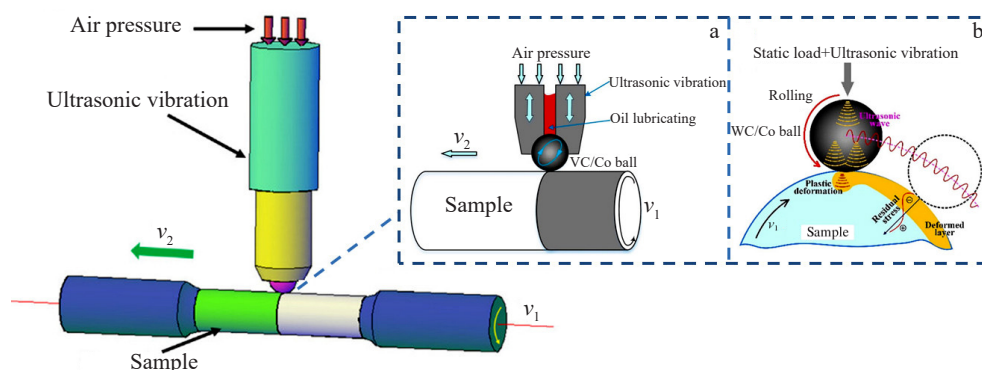


Fig.1 Schematics of USRP setup<sup>[20]</sup> (inset adopted from Liu et al<sup>[26,27]</sup>)

many sub-boundaries near the top surface, which indicates obvious grain refinement and dynamic recrystallization. Meanwhile, these grains which exist between the bulk grains are gradually refined with the increase in the depth because of the stress concentration and high dislocation density. Ao et al.<sup>[36,37]</sup> introduced USRP treatment to improve the microstructure of Ti6Al4V alloy, resulting in a phase transition of hcp-fcc lattice. The  $\beta$  grain size in thickness of USRP-induced Ti6Al4V alloy gradually changes from 0.76  $\mu\text{m}$  in core to 36.5 nm on the topmost surface via longitudinal splitting and transverse breakdown, which is formed primarily via dislocation activities (dislocation glide, entanglement, accumulation and rearrangement) without the occurrence of deformation twinning. However, it is noteworthy that dislocation slip and deformation twinning are two competing processes during plastic deformation. For the formation of twins, a critical twinning stress ( $\sigma_T$ ) must be reached and it can be described by<sup>[29, 38]</sup>:

$$\sigma_T = 6.13\gamma_{\text{SFE}}/b_p \quad (1)$$

where  $\gamma_{\text{SFE}}$  is the stacking fault energy and  $b_p$  is the Burgers vector of a Shockley partial dislocation. The lower the  $\gamma_{\text{SFE}}$ , the easier the dislocations are decomposed into stacking faults. This means that twin deformation is easy to occur under certain circumstances such as low  $\gamma_{\text{SFE}}$ , high strain rate and/or low temperature<sup>[39, 40]</sup>. The grain refinement of low  $\gamma_{\text{SFE}}$  materials is mainly achieved by sliding dislocation network and twin segmentation formed by dislocation transfer on the moving surface. As the  $\gamma_{\text{SFE}}$  reduces, the dominated plastic deformation mechanisms change from dislocation slipping to mechanical twinning. Twins are generated up to the depth where the critical resolved shear stress no longer exceeds  $\sigma_T$ . Evidently, it is well known that the strain rate significantly affects the deformation mechanisms of materials. This means that a deformation twin nucleates after a stacking fault ribbon spreads across the grain and the stress for deformation twin growth is low enough to be easily attained during a normal deformation. Simultaneously, the most common twins observed experimentally are those nucleated heterogeneously at grain boundaries via the emission of partial dislocations at the grain boundaries<sup>[41]</sup>. Liu et al.<sup>[42]</sup> prepared nano-grained AZ31B alloy by ultrasonic impacting and rolling process and believed that the deformation twins which are distorted and even broken to small size ones greatly emerge in early stage to coordinate with deformation. As strain increases, the interactions between twins and dislocations along with dislocation tangles in these twins become obvious, which turns grains into substructure. In addition, the USRP treatment also induces reorientation of grains and texture development in the surface layer. The marked change of grain orientation, grain-boundary rotation and the formation of strong (110) texture and (211) texture clearly occur in 17-4PH stainless steel after USRP<sup>[43]</sup>. Moreover, there is a decrease in the intensity of the texture from the matrix to the surface of a selective laser melted Ti6Al4V alloy using an USRP treatment<sup>[44]</sup>. The pole figure of coarse-grained structure in core shows that the lamellar  $\alpha$  structure has a strong basal

texture, and the intensity of the texture is significantly decreased in the ultrafine deformed layer. Furthermore, the nanograined layer near the surface shows that the structure is substantially refined and the preferred orientations of the texture shift towards the rolling direction. These results suggest that the mechanical deformation induced by USRP is the major cause for the texture changes, and a USRP treated surface can usually become nanostructured, accompanied by strong basal texture and potentially recrystallized process.

After the USRP treatment, the grain size is often governed by a balance between the hardening rate introduced by dislocation generation and the recovery rate arising from dislocation annihilation and recombination. However, it is well-documented that there is a saturation or minimum value in the grain size obtained by SSPD techniques, because the dislocation multiplication from strain is balanced by the dislocation annihilation due to grain boundary migration, strain-induced structural evolution ceases, and dislocation density reaches its limit<sup>[45]</sup>. This predicts that further refinement of surface microstructure is limited because of the enhanced mobility of grain boundaries and the value of minimum grain size acts as a function of material parameter<sup>[46]</sup>. Wang et al.<sup>[47]</sup> investigated evolution of a depth-dependent gradient ultrafine-grained layer of 40Cr treated by USRP and found that nanostructured layer, with minimum grain size of 3~7 nm in the top surface layer whose direction is consistent with the feed direction of the rolling ball, is formed after the USRP treatment. Meanwhile, increasing strain rate and reducing deformation temperature may be helpful to suppress dynamic recovery and enhance more flow stress, which leads to grains with smaller sizes.

## 2.2 Surface integrity

According to different material characteristics, original surface conditions and process parameters, the USRP treatment can produce a high frequency impact on the surface of material and reduce the surface roughness to less than 0.1  $\mu\text{m}$  under certain loading conditions based on surface rolling<sup>[24]</sup>. Ismail et al.<sup>[48]</sup> reported a three-dimensional finite element model of rigid hemisphere repeatedly rolling over a rough flat surface under constant normal load. It is found that the rough surface is predicted to be smooth due to repeated rolling contact between a rigid ball and a surface, which is relatively rough on micro-scale. As a result of ultrasonic rolling by orthogonal design and prediction model, the interactions between spindle speed and feed rate, static pressure and feed rate on surface roughness are obvious, but the interactions between static pressure and spindle speed on surface roughness are not significant<sup>[49]</sup>. Lu et al.<sup>[50]</sup> studied the 7050-T7451 aluminum alloy by USRP treatment and observed that surface roughness is reduced from 0.389  $\mu\text{m}$  of initial turning to 0.059  $\mu\text{m}$  at a feed rate of 0.10 mm/r after USRP treatment. For the untreated surface, visible tool marks or turning traces are observed along the cutting direction, which turn into crack source after alternating load is applied. However, turning traces are almost eliminated and an extremely flat surface is obtained after USRP treatment. The



same research on surface roughness of the 17-4PH stainless steel treated by USRP was carried out by Zhang et al.<sup>[43]</sup>. The results indicate that the surface roughness is decreased significantly, similar to other ultrasonically processed metals. These results should be attributed to the large plastic deformation in surface layer, which is the result of high dynamic force induced by the ultrasonic vibration.

Surface plastic deformation is capable of smoothing out majority of original micro cracks left by turning. Micro-dimple pattern produced by ultrasonic impacts on the surface has lower profile than original micro cracks<sup>[51]</sup>. So the roughened surface with many uniform grooves caused by turning is greatly smoothed after USRP treatment, which is correlated with process parameters. This also means that surface oxidation or adhesion behavior due to rolling contacts between a ball and a surface is often associated with the accumulation of plastic strain near the surface. Furthermore, the properties of materials induced by USRP are closely related to the surface integrity. The improvement of surface roughness and tooth marks reduction can greatly inhibit the fatigue crack nucleation and increase the surface electron work function, which is indeed helpful for achieving high fatigue resistance and corrosion resistance<sup>[52,53]</sup>. But the downside is that USRP treatment can also cause surface damage (e.g. micro cracks and defects) under the appropriate parameters, notwithstanding its smoother surface than turning ones. The processed surface by USRP may be deteriorated to a certain extent because of severe shear deformation and local fatigue damage, which favors the decrease of deformation resistance. Consequently, some micro cracks and fluctuations at certain positions can be noticed on the surface after USRP treatment, which may restrict the further improvement in surface roughness. Undoubtedly, these micro cracks will seriously restrict the performance, since the surface damage may potentially become crack sources and result in serious negative impact on service properties<sup>[54,55]</sup>.

### 2.3 Residual compressive stress

After the USRP treatment, there is a typical residual stress distribution with significant magnitude of compressive stress in surface layer, and the maximum residual compressive stress appears at a certain depth from the treated surface. The value and depth of residual compressive stress field induced by USRP are higher than those induced by conventional surface treatment. Lee et al.<sup>[56]</sup> found that the residual compressive stress of SAE52100 bearing material becomes -700~-900 MPa and the depth of residual compressive stress remains until 600  $\mu\text{m}$  when the slope is considered. It is also observed that the residual tensile stress changes to residual compressive stress, which only remains just at the top surface before treatment. The previous results<sup>[13,47,57-60]</sup> verified the relationship between ultrasonic rolling parameters and surface layer characteristics by finite element model simulation and experimental evaluation. The maximum residual compressive stress reaches -846~-1356 MPa for different parameters and the corresponding effective depth of USRP from treated surface is 1.0~1.4 mm. With the increase of static pressure and ultrasonic vibration

amplitude, the surface plastic deformation, superficial yield stress and residual compressive stress are enhanced greatly. Nevertheless, the increase of spindle speed and feed rate presents a striking contrast to static pressure and vibration amplitude, which decreases the residual compressive stress. The results also show that the magnitude of residual stress is determined at the first few repeated processing times, while further repeated processing times only cause a little rising tendency on residual stress in terms of maximum value and hardly affect the thickness of strengthened layer. Finally, the parameter optimization of the residual stress control is very important, and the better surface strengthening layer can be obtained by combining the optimal processing parameters under the premise of ensuring the surface roughness.

However, Liu et al.<sup>[27]</sup> reported that the surface residual compressive stress decreases gradually with increasing the repeated processing times, but the depth increases gradually. With increasing the repeated processing times, the residual compressive stress values are partly relaxed compared with that at the 1st processing. It is analyzed that the number of micro impact craters and the fold defects increase gradually with increasing the repeated processing times, and the sample of 1st processing has a smoother surface and lower surface roughness. This shows that the USRP parameters can achieve good processing effects within a certain range, but adverse effects are generated if this range is exceeded<sup>[61]</sup>. Hence, the residual compressive stress values and the corresponding effective depth of USRP are affected by the surface integrity associated with the interactions of different ultrasonic rolling parameters. In addition, the residual compressive stresses on surface and sub-surface of USRP-induced Ti6Al4V alloy, which is -870 MPa at a depth of ~530  $\mu\text{m}$  to the surface, still retain -200~-300 MPa in the ~400  $\mu\text{m}$  deep layer and the surface nanostructures still maintains a good thermal stability after annealing at 500  $^{\circ}\text{C}$  for 1 h<sup>[26]</sup>.

## 3 Properties of Gradient Nanostructured Materials Induced by USRP

### 3.1 Hardness and strength-ductility relationship

Hardness, strength and ductility, are primary grain-size-dependent characteristics of materials, which determine virtually all facets of the mechanical response. It is well known that hardness of materials induced by USRP can be improved through grain refinement, residual compressive stress and work hardening. Like many other surface deformation strengthening techniques, the surface hardness and strength distribution obtained by plastic deformation and strain in the USRP show a gradient characteristic, with the maximum value on the topmost surface, followed by a gradual decrease until the first layer of the original material is reached. Therefore, by selecting specific USRP parameters and processing routes, the surface hardness of Ti6Al4V alloy increases by about 30% and decreases gradually with increasing the distance from the surface, which attributes to a gradient distribution of the ultrafine-grained structure as the

depth of the surface increases<sup>[62]</sup>. In addition, the interactions of strength and hardness of nanostructured layer can be calculated as a 3-times empirical relationship in terms of the Taylor hardening mechanism<sup>[45,63]</sup>. It is pointed out that this 3-times relationship is based on analyzing the five triangular portions of materials tested and slip-line field of indentation, which makes hardness approximately 3 times of strength in work-hardened metals. However, high strength and good ductility are often mutually exclusive, and improving both of them at the same time is a very challenging task<sup>[64]</sup>. It is widely known that nanostructured materials show a high tensile strength, but this is accompanied by low ductility. The metal strengthening effect is closely related to the grain size based on dislocation interactions, from which mobile and/or sessile dislocations can be generated by severe plastic deformation. The increased grain boundaries introduced by grain nanocrystallization hinder the migration of dislocations, so that the dislocation motion is blocked by grain boundaries because of its incoherent structure and a dislocation pile-up is formed. In other words, a higher stress is needed to deform a metal with a smaller grain size, so a high strength is obtained. In addition, gliding of dislocations along nano-grain boundaries is unfeasible and ductility of nanostructured metals is found to decrease with smaller grain sizes<sup>[65]</sup>. For nanostructured metals, their strength and hardness increase with a reduction of grain size to nanometer regime, following the classical Hall-Petch relationship, which is a power law<sup>[66, 67]</sup>:

$$\sigma_s = \sigma_0 + kd^{-1/2} \quad (2)$$

where  $\sigma_s$  is the strength,  $\sigma_0$  is the friction stress to overcome when moving a single dislocation,  $d$  is the average grain size and  $k$  is a material constant which characterizes the degree of strengthening effect caused by grain boundary. In addition, materials strength can also be predicted by adding contributions from the reduction in grain size (grain boundary strengthening) and increase in dislocation density (work hardening) with plastic deformation<sup>[38]</sup>. Hence, according to the concept of USRP, grain refinement caused by ultrasonic impact strengthening is one of the important reasons for improving the strength and hardness of samples. However, it has been also found that the Hall-Petch relationship is not valid for very small grain sizes<sup>[68]</sup>. Zheng et al<sup>[69]</sup> performed USRP treatment on 7075 aluminum alloy to establish the relationship between the surface grain size and micro-hardness, and they found that the inverse Hall-Petch phenomenon occurs in the nanostructured surface layer, and the surface micro-hardness increases with the increment of the grain size. The smaller grain size will hinder the grain slip deformation, produce the grain boundary coordination and grain rotation, which result in the lower hardness of the material.

Lu<sup>[70]</sup> announced that the strength of a metal is increased at an expense of ductility in homogeneous plastic deformation of coarse-grained metals or homogeneous refinement of nanosized grains, which is similar to the random mixtures of coarse grains (CG) with nano-grains (NG). However, it is

figured out that the strength-ductility synergy is achieved with gradient nano-grained structures (GNG). The gradient nanostructured surface layer can improve the strength of material according to the Hall-Petch relationship, while maintaining its good ductility with the coarse-grained structures in core. Ye et al<sup>[71]</sup> obtained ultrafine-grained surface layer whose average grain size is 50 times smaller than that of the interior grains of AZ31B Mg alloy by USRP and considered the mechanical properties as the result of SSPD-induced gradient structures. For the properties of untreated and USRP-induced samples, the surface microhardness and elastic modulus are increased by 83.81% and 10.93% compared with the inner part, respectively. Meanwhile, the yield strength (YS) and ultimate tensile strength (UTS) of USRP-induced samples are increased by 24.08% and 19.33% compared with the untreated samples, respectively, as shown in Fig. 2. The research conducted by Wang et al<sup>[72]</sup> shows that the hardness, yield stress and tensile strength of AISI 304 stainless steel increase greatly after treatment for USRP. Meanwhile, the uniform elongation decreases from 49.8% before treatment to 45.2% after USRP, which means that the strength of USRP-induced sample increases significantly without excessive loss in ductility. Similarly, the tensile strength of Ti6Al4V alloy increases from 1018 MPa before USRP to 1046 MPa after USRP while the elongation and the percentage of area reduction have no obvious changes. Finally, the improvement of material strength is achieved and the ductility of original Ti6Al4V alloy is maintained, indicating that the USRP-induced sample has a good ductility<sup>[73]</sup>.

However, the improper USRP parameters and processing routes can weaken mechanical properties and cause severe surface damage. Panin et al<sup>[74]</sup> indicated that the zone of plastic deformation around the ultrasonic impact area becomes more and more confined and drives the deformation to the free surface, resulting in stacked pile-ups. Under the ultrasonic impact effects, continuous increase of the density of low- and high-angle grain boundaries due to dislocation glide and twinning as well as the development of compressive stresses in the surface layer retards dislocation motion into the core. After the surface plastic deformation reaching a certain level, a large number of dislocations and grain boundaries are accumulated, which restrict further grain refinement and increase surface strength, while reducing surface ductility partly. As a result, reports have shown that the ductility of cold-rolled Ti6Al4V alloy is noticeably improved while sacrificing the strength slightly under ultrasonic impact accompanied by electropulsing treatment<sup>[75]</sup>. The introduction of electropulsing may promote immobile dislocation migration and atomic diffusion, resulting in enhanced depth of ultrasonic treatment, thereby weakening the grain refining effect and releasing residual stress. In this report, the surface microhardness is dramatically enhanced from 2600 MPa to 4260 MPa by ultrasonic surface strengthening effect. With the help of electro-pulse treatment, electro-pulses decrease the dislocation pile-up and entangling, which weakens the

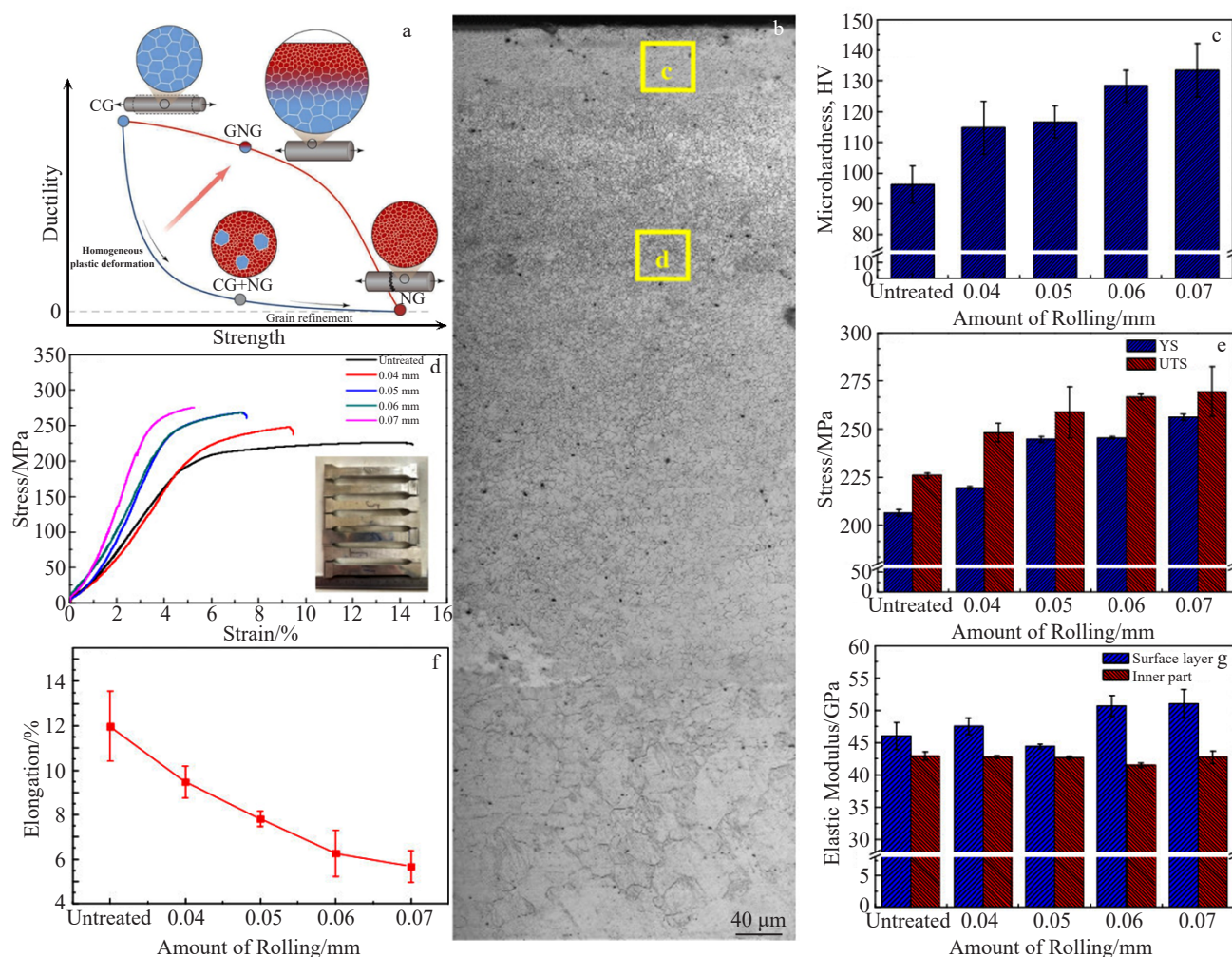


Fig.2 Strength-ductility synergy (a)<sup>[70]</sup>; structural image (b), microhardness (c), room temperature tensile stress-strain curves (d), yield strength (YS) and ultimate tensile strength (UTS) (e), elongation (f), and elastic modulus (g) of AZ31B samples after USRP<sup>[71]</sup>

strength slightly by 16.2%. Therefore, the ductility of treated sample is greatly improved and reaches a favorable value of 32.5%. In summary, the strengthening effect of gradient nanostructures by USRP can achieve high strength and hardness while still preserving high ductility, so that the comprehensive mechanical properties of materials are effectively improved.

### 3.2 Wear performance

The surface of materials can be damaged by repetitive localized stresses which can cause surface micro-crack initiation and propagation. Once the removal of discrete pieces of material which appear as micro-pits incubated, the micro-pits will expand, coalesce and evolve to a much larger area, leading to the formation of surface spalling and debris generation<sup>[76]</sup>. As a result, the tribological properties and wear behavior are important factors for industrial applications which act as functional parameters of mechanical components. It is well known that USRP treatment markedly enhances the surface hardness and strength of materials due to the formation of gradient nanostructures following the Hall-Petch relationship. The much enhanced surface hardness and

strength of USRP-induced sample relative to those of untreated sample may result from its superior microstructure, i.e., a smoother surface with smaller grain size and increased residual compressive stress. Then according to the relationship between hardness and wear, it can be derived as the empirical equation<sup>[35,77]</sup>:

$$W = K \frac{P}{H} \quad (3)$$

where  $W$  is volume worn per unit sliding distance,  $K$  is the wear coefficient,  $P$  is the applied load and  $H$  is the hardness of the worn surface. Evident improvements of friction and wear properties were achieved in HIP Ti6Al4V alloy with a hardened surface layer due to surface nanocrystallization by USRP at different temperatures<sup>[78]</sup>. The measured results of maximum residual compressive stress and the highest microhardness at the surface introduced by USRP are -491 and 4250 MPa, respectively, which increase greatly compared to those of untreated sample. The surface roughness of USRP-induced sample at low temperatures is obviously decreased, and the micro cracks are healed in top surface layer, and finally material surface quality is improved. Meanwhile, the



steady-state friction coefficient and wear volume loss of USRP-induced samples are significantly lower than those of untreated sample. The worn surfaces of USRP-induced samples at different temperatures are mainly composed of some obvious craters and grooves produced by adhesion, delamination and abrasive wear, as well as some slip regions caused by sliding wear. Similarly, the wear performance of the USRP-induced AZ31B Mg alloy in terms of wear mass loss and friction coefficient are only 9.07 mg and 0.279, respectively, which of untreated sample are 32.44 mg and 0.337, respectively<sup>[71]</sup>. The USRP-induced sample exhibits smaller wear width and depth, which has better wear resistance than coarse grain materials, while the untreated sample has a severe wear circumstance. Wang et al<sup>[79]</sup> found that hardness, strength, plastic toughness and defects of material are important factors in measuring wear resistance of Ti6Al4V alloy. Compared with untreated samples, the friction coefficient and wear volume are reduced from 0.74 to 0.64 and from 0.206 mm<sup>3</sup> to 0.195 mm<sup>3</sup>, respectively. Meanwhile, there are little debris, and no micro-crack and no delamination are observed around the wear tracks during the stable wear stage, so the width of grooves is narrow and the interior surface is smooth under the circumstance by USRP. Under cyclic loading for untreated sample, the crack initiations act as stress concentration sites and coalesce to form larger cracks, leading to wear damage.

However, the gradient microstructure inhibits stress concentration and crack nucleation after USRP treatment, causing the surface being insensitive to the delamination formation. Moreover, it has been established that the microstructure of USRP-induced layer is different from that of the pristine and the hardness is a gradient distribution perpendicular to the surface. Therefore, wear performance with increasing the thickness in the layer may be different, and the changes in the wear performance can be divided into three stages<sup>[35, 80]</sup>. The surface morphology plays an important role at the initial stage, called a rapid running-in period corresponding to the matching between the surface and contacted ball, and thus the smoother surface can decrease the matching time and achieve a lower friction coefficient. The second stable wear stage is the transition zone that depends on the thickness and mechanical properties of the modified layer. Higher surface hardness and deeper thickness of hardening layer will result in a perfect wear resistance due to repeated sliding action, and the introduction of residual compressive stresses also results in the lower value of wear mass loss. Once the modified layer is removed completely, the wear track in the substrate is typical of metallic wear dominated by severe abrasion, adhesion and delamination at the last stage, which is similar to the untreated sample. Wang et al<sup>[81]</sup> compared the wear behavior of a selective laser melted Ti6Al4V alloy with that of the USRP treated one, and they revealed that the untreated samples show severe abrasive wear and delamination, while the USRP treated samples display only mild abrasive wear. Moreover, the wear resistance of the USRP treated samples decreases with increasing the depth

from the surface due to the effect of gradient work hardening. Similarly, this observation is in accordance with other results in increasing the wear resistance<sup>[43, 82]</sup>. After USRP treatment, surface hardness and residual compressive stress are enhanced greatly, thereby showing an enhanced wear resistance at higher loading rates. Thus, it can be summarized from these researches that USRP treatment is effective to mitigate wear. The improvements in wear performance may be attributed to increased surface hardness, and induced residual compressive stress as well as a smoother surface owing to the gradient nano-grained structure and the thick hardening layer induced by USRP and other SSPD techniques.

### 3.3 Fatigue behavior

Modeling and experimental observations are used to evaluate the nanocrystalline metals in terms of fatigue resistance<sup>[83]</sup>. The research shows that fatigue behavior of bulk nanocrystalline metals exhibits improved fatigue resistance compared to that of traditional microcrystalline metals. In reporting and explaining the properties of nanocrystalline metals, a common perspective is that the unique mechanical properties of this class of metals are mostly thought within the framework of grain size and residual stress dependent behavior. According to the understanding of underlying mechanisms, the fatigue fracture consists of three typical regimes, including the crack initiation process, steady propagation process, and collapse fracture process<sup>[83, 84]</sup>. The crack initiation process in nanocrystalline metals is associated with both subsurface internal defects and surface extrusions, which show improved properties over coarse-grained metals. However, it is found that bulk nanocrystalline metals have very little resistance to crack propagation and collapse due to limited ductility and the lack of crack path tortuosity under stress controlled fatigue. With more understanding of fatigue behavior of bulk nanocrystalline metals, it is worthwhile to explain some of the improvements in fatigue behavior associated with USRP treatment and other SSPD techniques.

Although the strength of conventional bulk nanomaterials is higher than that of ordinary coarse-grained materials, deformation or crack propagation to a certain extent also causes the risk of sudden failure. However, for the gradient microstructures, the surface nanostructure can effectively prevent the initiation of fatigue cracks due to its high strength, and the coarse-grained structure in core can hinder the crack propagation due to its high ductility. Finally, the synergistic effects of the gradient nanostructure and the gradient residual compressive stress, etc, in the vicinity of surface can suppress the fatigue crack initiation and propagation<sup>[85]</sup>. For example, high-strength materials treated by USRP achieve the longest fatigue lives, which confirms that synthesized surface strengthening nanostructured layer with grain size ranging from 15 nm to 20 nm greatly improves fatigue performance<sup>[86]</sup>. Meanwhile, a gradient crystalline structure in surface layer of titanium alloy is obtained through USRP and surface characteristics including gradient microstructure, residual stress distribution, and surface roughness in modified layer were measured<sup>[87]</sup>. The results show that the crack initiation



sources of untreated samples are found in surface or near-surface areas, while crack initiation sources of USRP treated ones are distinctly located at subsurface or near central positions, so that a considerable improvement of almost 19.3% compared to untreated samples under the cycles of  $5 \times 10^6$  is obtained owing to the enhancement of surface characteristics.

For the untreated sample, visible surface tool marks/turning traces and irregular subsurface pores with random shapes and sizes are found along the cutting direction, which turn into fatigue crack nucleation and initiation source sites at some stress concentration zones after alternating load is applied, and the fatigue cracks expand immediately inward along a fan-shaped path until early fatigue fracture. Once the fatigue crack propagation process starts, some subsurface cracks or pores are connected to each other, and the materials close to the cracks or pores are bonded weakly to the substrate. Furthermore, the broken material is detached and the crack propagation is further deteriorated, thereby resulting in collapse<sup>[34]</sup>. Hence, according to Murakami's model, the relationship between the fatigue strength ( $\sigma_w$ ) and the square root of the area with pores ( $\sqrt{\text{area}}$ ) is<sup>[88,89]</sup>:

$$(\sigma_w)^n \sqrt{\text{area}} = C \quad (4)$$

where  $n$  is a positive number that can be determined through experimental data and  $C$  is a constant. It is obvious that the fatigue stress increases when the  $\sqrt{\text{area}}$  value decreases. Typically, it can be observed that the number of pores is significantly reduced and pores become smaller or even disappear due to the compression effect induced by USRP treatment, and the material flows from high peaks to low valleys. It is found that the USRP treatment results in much better surface finish, lower subsurface porosity and beneficial residual compressive stresses, leading to significant improvement in rotation bending fatigue performance of 3D-printed Ti64 samples<sup>[89]</sup>. The average pore area decreases from  $7948.48 \mu\text{m}^2$  of untreated sample to  $4963.80 \mu\text{m}^2$  in the treated sample, which resulted in improved fatigue strength. Additionally, the fatigue strength of S45C steel after USRP treatment increases as much as 33% compared with that of untreated sample. The results show that cracks usually initiate from intergranular microcracks on the surface and then extend along the tip traces, and USRP treatment can help to retard crack initiation by induced nanostructured layer and improved surface finish<sup>[90]</sup>. After USRP treatment, the fatigue behavior of Ti alloy is considerably enhanced owing to the fatigue strength ( $10^7$  cycles) of 695 MPa, which is 39% higher than that of the untreated sample<sup>[27]</sup>. On the other hand, a turned surface by a turning tool generates a high tensile stress in the area of the white layer, which is caused by plastic deformation or phase transformation, and the high tensile residual stress at the surface can lead to a much shorter fatigue life<sup>[91]</sup>. However, the residual stress of white layer induced by USRP is translated into compression stress and ultimately attains larger magnitude and affected depth than that generated by turning or polishing tools. Therefore, the fatigue strength can also be

related to material hardness and residual stress<sup>[88,89]</sup>:

$$\sigma_w = \frac{C_1 (HV + C_2)}{(\sqrt{\text{area}})^{1/n}} - \frac{1}{2} \sigma_m \quad (5)$$

where  $C_1$  and  $C_2$  are constants that can be determined through experimental data,  $HV$  is the material hardness,  $\sigma_m$  is the residual stress. Yasuoka et al<sup>[92]</sup> reported that the hardness and the residual compressive stress at the surface of typical SUS304 austenite stainless steel increase significantly after USRP treatment, so that the fatigue strength is improved by 80% from 280 MPa to 510 MPa. Similarly, a gradient nanostructured layer is synthesized on the surface of Ti6Al4V alloy by USRP<sup>[93]</sup>. It is figured out that the mean grain size on the topmost surface and residual compressive stress are approximately 45.8 nm and -867.7 MPa after USRP, respectively, and the surface hardness shows a 45.1% increment compared with that of the untreated sample. In the end, the fatigue strength is considerably enhanced, which shows a 113.6% improvement after USRP as compared with the untreated sample. As a result, the surface gradient nanostructures obtained by USRP treatment can effectively weaken the risk of sudden failure and improve the fatigue resistance of the material. The USRP-induced enhancement mechanism of the fatigue performance can be ascribed to the synergistic effect of gradient nanostructure, residual compressive stress, work hardening, and improved surface quality, and it is concluded that the compressive residual stress is the leading factor that controls the improvement of fretting fatigue resistance of metal materials<sup>[94,95]</sup>, as shown in Fig.3.

As for the synergistic effects of these factors introduced by USRP, integrated surface and gradient nanostructured layer of excellent mechanical properties are in positive relation with fatigue life improvement due to inhibited crack initiation and propagation process<sup>[26]</sup>. After USRP treatment, the fatigue crack initiation sites which are suppressed by surface integrality and gradient nanostructures are shifted toward subsurface with a deeper depth from the surface<sup>[96,97]</sup>. It is widely recognized that a decrease in grain size generally results in an enhancement in the fatigue endurance limit. Here, under the condition that all other structural factors remain roughly the same, the endurance limit of smooth-surface USRP samples generally scales with the strength of the material, which increases with decreasing the grain size. The high-density grain boundaries of the surface nanostructures and high hardness obtained also help delay the early growth of the fatigue cracks<sup>[38]</sup>. Once the fatigue cracks are formed, the stress concentration at the crack tip is very high, and increased local stress promotes the occurrence of crack propagation and collapse. Therefore, the residual compressive stress and work hardening are also helpful in preventing fatigue fracture, which can weaken the surface stress concentration<sup>[112,20,93]</sup>. In addition, the coarse-grained structure of gradient nanostructures in core can also lead to an increase in tangential force threshold level required for crack initiation and a decrease in the rate of crack propagation owing to mechanisms of periodic deflections in the path of the fatigue crack at grain boundaries

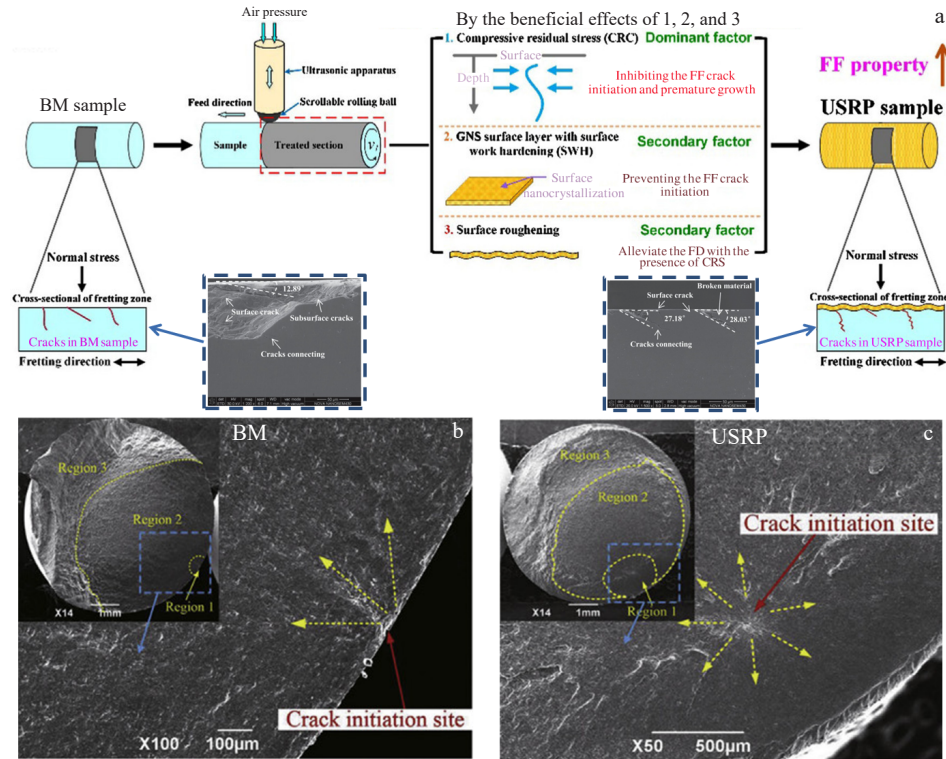


Fig.3 Fatigue fracture mechanisms of multiple factors induced by BM (untreated base material) and USRP<sup>[93]</sup> (the insets of cross-sectional subsurface damage of 17Cr2Ni2MoVNB steel adopted from Zhang et al<sup>[34]</sup>) (a); (b, c) fatigue fracture morphologies of Ti6Al4V alloy<sup>[94]</sup>

during crystallographic fracture<sup>[98]</sup>. Consequently, a larger tangential force is required to promote crack initiation and propagation, so that the synergistic effects make the fatigue fracture become more difficult.

### 3.4 Corrosion resistance

In general, the surface nano-grained structures of high-density grain boundaries are more prone to corrosion than coarse-grained structures, which can increase the surface free energy and chemical activity. However, it seems likely that grain refinement by severe plastic deformation, while enhancing mechanical properties without exceptions, shows complex characteristics in corrosion and has some contradictory results in the same materials and same environment, depending on the composition and structural factors, surface integrity and stress, environments and preparation processes, etc. Indeed, any processing or grain refinement that alters the reactivity of different material surface will impact the corrosion response. Miyamoto<sup>[99]</sup> conducted a comprehensive investigation on the corrosion resistance of ultrafine-grained materials by severe plastic deformation in light of the existing literatures, and found that the degree of impact of ultrafine-grained structure formation on corrosion is the highest in stainless steels followed by aluminum and magnesium alloys whereas it is relatively marginal in pure copper and titanium. Additionally, ultrafine grains of FeCr alloys exhibit the corrosion resistance superior to that of coarse grains, while ultrafine-grained copper and titanium are relatively comparable with coarse-grained

materials. However, aluminum and magnesium alloys are more sensitive to microstructural changes and show contradictory results. According to Ralston's research<sup>[100,101]</sup>, attention is paid specifically to how grain size affects the corrosion rate and the ability of surfaces with high grain boundary density to be passivated more readily, and this fundamental relationship is concluded as the following equation:

$$i_{\text{corr}} = A + Bg_s^{-0.5} \quad (6)$$

where  $i_{\text{corr}}$  represents the corrosion rate,  $A$  is a constant that depends on the environment,  $B$  is a material constant that differs according to composition or impurity level, and  $g_s$  represents the grain size. For the inner componential and structural factors, it is assumed that the grain boundaries can conduct particles and react, so that the corrosion rate is also related to the total length of grain boundaries which is associated with grain size, area term, and scale term. The rationalization of -0.5 dependence in Eq.(6) can be explained by a dispersed relationship that depends on the formation of perfectly equiaxed grains or random grains in more realistic case of the metals. Simultaneously, after USRP treatment, the texture with the most close-packed plane and the grain refinement contribute to a higher fraction of grain boundaries, which can promote oxidation and formation of passivation film and enhance the corrosion resistance significantly<sup>[43]</sup>. Xia et al<sup>[102]</sup> synthesized a gradient nano-structured layer on the surface of Cu-10Ni alloy by USRP. The results showed that the topmost surface possesses an average grain size of 70 nm,

and the corresponding corrosion resistance is enhanced in a 3.5wt% NaCl solution after USRP treatment. The higher corrosion resistance of the nano-grained Cu-10Ni alloy is attributed to the nano-grained surface promoting the formation of a passive film on the surface during the corrosion process, which can effectively prevent further corrosion. Furthermore, second-phase, impurity segregation, crystallographic texture and surface stress may also affect corrosion resistance and oxide formation. Nanocrystallization decreases the unstable points, i. e. surface defects and pores, on the surface of the materials, which decreases the possibility of local corrosion. Another important factor that needs to be mentioned is that the environment plays an important role in corrosion behavior, which seems to cause increase or decrease in corrosion susceptibility. In other words, grain refinement can increase the surface activity of a metal, and then enhance or suppress corrosion rate according to the environment within the same materials and the same processing routes. In active dissolution, if the corrosion products are dissoluble, the nano-grained structure will loosen the passive film and induce many defects, which lead to easy dissolution of the film in aqueous solution containing chlorides, thereby accelerating the corrosion reactions. On the contrary, if the corrosion products are insoluble or in a passively dissolved state, the passive film that forms quickly, firmly and stably due to the high reactivity of nanostructure acts as a block layer to delay the dissolution/corrosion depending on element diffusion and special adsorbed ability<sup>[103, 104]</sup>. Ultimately, with different ultrafine-grained systems reviewed, the effect is not consistent. The exact combination of environment, processing, and material will dictate whether the increased surface reactivity will lead to enhanced dissolution or passivation.

In addition, the corrosion behavior of gradient nanostructure induced by SSPD is affected not only by grain refinement but also by other microstructural changes occurring commonly, i. e. surface integrality, residual stress. SSPD treatment can reduce the grain size of materials and improve the homogenization of surface chemical inhomogeneity, which can achieve high potential, so that the corrosion behavior tends to change from local to uniform modes. The precipitated phase or other impurities can also affect the electrochemical polarization of small areas on the surface and the formation of microelectrodes between impurities and matrix is also prone to pitting corrosion, leading to some conflicting results about the influence of gradient nanostructures on the corrosion performance<sup>[20, 96]</sup>. For example, it is found that pitting corrosion occurs around Fe-rich intermetallic particles in AA5083 after surface plastic deformation, which leads to anodic dissolution of the surrounding matrix and deterioration in corrosion resistance<sup>[105]</sup>. However, the USRP treatment on the surface of FeCoNiCrMn high-entropy alloy coatings can improve the corrosion resistance, which makes the surface phase composition more stable and the element distribution more uniform<sup>[106]</sup>. Additionally, another factor for corrosion resistance properties between mechanical turning and USRP

treatment is attributed to the surface roughness. The pitting potential significantly depends on the surface roughness and correspondingly increases with a decrease in surface roughness, and the corrosion resistance of materials is generally also more sensitive to the surface density of high-surface-energy sites (e. g. sharp edges and surface undulations), which increases the corrosion and local anodic attack might form in narrow depressions<sup>[53, 71, 107]</sup>. Notwithstanding that the improved surface roughness is achieved by the introduction of USRP according to many researches, there are remarkable results of the USRP-induced Ti6Al4V alloy which show surface delamination and fold defects on the treated surface due to the severe ultrasonic impacts and extrusions<sup>[94, 108]</sup>. The increased surface roughness may increase the corrosion area of the metal surface in contact with the solution, which leads to an enhancement in corrosion medium adsorption and diffusion. Nevertheless, according to the corrosion behavior of USRP-induced nickel aluminum bronzes<sup>[109]</sup>, the treated samples show superior corrosion resistance over untreated ones. The reduction in surface roughness and the improvement in surface quality improve the fluidity of the surface, and the elimination of turning furrows reduces the possibility of local damage on the surface, so that the surface is relatively uniformly damaged, while the relative surface area is reduced. Moreover, in chloride-containing electrolyte, the tendency of chloride ions to be preferentially adsorbed at defective sites yields non-homogeneous adsorption on the bare metal surface. The transport of both injected metal ions from the matrix and oxygen/chloride in solution to the passive film leads to inhomogeneous interface-movement rates and an undulating interface is formed<sup>[110]</sup>. As a result, due to the accumulation of corrosion products, the convex sites on the undulating interface are accompanied by the generation of internal tensile stress and prone to breakdown with the increase of tensile stress.

Correspondingly, the residual compressive stress induced by USRP can offset partial internal tensile stress generated by the growth of the oxide/passive film and resist the infiltration of corrosive agents at early stage of corrosion development. After USRP treatment, a gradient structure with a thickness of 425  $\mu\text{m}$  and a compressive residual stress field with a depth of 700  $\mu\text{m}$  are created, so that the corrosion rate of 7B50-T7751 aluminum alloy is reduced by 60.08% owing to the combined effect of compressive residual stress and surface nanocrystallization<sup>[111]</sup>. The residual compressive stress can also restrain the hydrogen diffusion and the crack propagation, which can decrease the stress corrosion cracking susceptibility of USRP-induced metals to a certain extent, and the passive film on the surface will be stably present<sup>[112]</sup>. In addition, the USRP also significantly helps protect metals from the cavitation erosion via introduction of deformation layers, phase transformation, formation of passivation film, grain refinement and the surface hardness as well as residual stress<sup>[113]</sup>. However, non-equilibrium grain boundaries exist in ultrafine-grained materials by severe plastic deformation and these specific grain boundaries possess an increased free



energy density, increased width, high density of dislocations (full or partial) associated with the near-boundary region<sup>[114]</sup>. Similarly, USRP treatment produces high densities of non-equilibrium grain boundaries and refines the grain size and distribution of second phases through fragmentation by intense shear. The large density of grain boundaries on the top surface created during USRP may enhance the atomic mobility, which can weaken the stability of passive film in active dissolution. In case of surface damage and grain boundary segregation, all these factors can simply promote the diffusion of solute elements and increase the corrosion rate. In summary, a comprehensive theory of USRP treatment and gradient grain refinement has to include all changes of the surface and subsurface, which may critically depend on processing regimes (temperature, strain rate, applied pressure, etc).

### 3.5 Properties of USRP-pretreated samples

The high diffusion rates of ultrafine grained structures are believed to be related to higher excess free energy of non-equilibrium grain boundaries in severely deformed metals. The excess free energy of non-equilibrium interfaces in ultrafine grained materials is larger than in coarse-grained materials<sup>[114]</sup>. The high grain boundary density after USRP treatment provides “short circuit diffusion” channels, which raise the number of enrichment sites and enhance the diffusion kinetics, and high dislocation density acts as fast paths, thus accelerating atomic diffusion<sup>[115]</sup>. It is found that elemental redistribution or/and realignment phenomena appear on the processed surface. Generalizing these findings, the high diffusion rates of gradient nanostructured materials created by USRP treatment may play a significant role in depositing films or coatings that are impossible to deposit at low temperature. She et al<sup>[116]</sup> demonstrated that USRP nanocrystallization pretreatment markedly decreases the optimized plasma nitriding temperature from 850 °C to 750 °C. The USRP pretreatment refines the mean surface grain size of Ti to about 38 nm and increases some microgrooves and defects on the surface. The surface hardness and vacuum tribological properties are enhanced by USRP pretreatment when the plasma nitriding temperature is below 750 °C, and the nitriding layer becomes thicker and harder with a reasonable gradient structure. Similarly, Ren et al<sup>[117]</sup> investigated the biocompatibility and osteogenesis performance of Ti6Al4V modified by USRP and plasma nitriding, and they concluded that the surface wettability of sample treated by USRP for 3 h present a water contact angle of 75.7°. As a long-term pretreatment process, USRP increases the surface chemical activity and surface roughness, so that USRP provides conditions for further plasma nitriding to form TiN/Ti<sub>2</sub>N layer and cell adhesion of MC3T3-E1 cells to induce osteogenesis. The nanostructured layer on the surface generated by repetitive severe plastic deformation enhances the subsequent nitriding kinetics, so that the nitriding temperature can be much lower than conventional nitriding temperature, which will demonstrate a new approach for nanomaterials in improving traditional processing

techniques<sup>[118]</sup>. In addition, Ren et al<sup>[119]</sup> tried to introduce deep cryogenic treatment on the basis of USRP to improve the mechanical properties of Cr12MoV steel. They found that the combined process promotes the phase transformation and the distribution of second phase is more homogenized. As a result, the surface mechanical properties, including smaller surface roughness, higher surface hardness and lower friction coefficient are achieved.

## 4 Summary and Conclusions

In general, the gradient nanostructure formation of metals by USRP treatment is a promising way to improve mechanical properties, and in recent years has become a subject of increasing scientific and technological fields. Previous work has proven the possibility of obtaining gradient nanostructured surfaces by USRP and assessed the deformation mechanism and microstructural characteristics of the obtained layers.

1) The USRP treatment enables the surface to obtain a gradient nanostructure through severe plastic deformation, which significantly reduces surface roughness, increases residual compressive stress, and obtains gradient ultrafine grains, compared to coarse-grained materials.

2) The effect of USRP treatment on the mechanical properties of the material are shown nearly without exceptions in the improvement of hardness, strength, wear resistance and fatigue properties while still maintaining high ductility. As the grain size decreases, the strength in most cases follows the classic Hall-Petch relationship.

3) USRP enhances the corrosion resistance through much better surface finish, beneficial residual compressive stresses and homogenization of chemical inhomogeneity by the ultrasonic vibration and mechanical rolling effects. Nevertheless, some researches demonstrate that change to more subsurface porosity and micro cracks is accompanied by grain size reduction and high densities of non-equilibrium grain boundaries may increase the corrosion rate in different solutions. Evidently, the literatures on corrosion properties of gradient nanostructured materials by USRP treatment are definitely insufficient to find the general trends, and more studies are needed.

4) USRP treatment can act as a pretreatment process for surface coatings or plasma nitriding, etc, which may markedly increase the corrosion resistance and preserve the improved mechanical characteristics.

In addition, about materials, some engineering materials processed by USRP, i.e. stainless steels, Ti alloys, Al alloys, have been investigated mostly while comprehensive studies of multi-kinds of steels, Ti alloys, pure metals like Cu and Ni are carried out by SSPD techniques. There are other materials that are currently used in engineering applications, which can be a potential object of research in this field, i.e. Mg alloys, U alloys, Be alloys, V alloys, low alloy steels, and also the pure metals. For these active materials, there are little data available but on the basis of the results shown in this work, a great improvement of their mechanical properties is expected while the corrosion/oxidation behavior should be systemically

studied. In summary, as more data are considered in the research and understanding in this area grows, it is worthwhile to revisit whether USRP treatment shows positive impacts on the service properties of different materials.

## References

- 1 Liu D, Liu D, Zhang X et al. *Materials Science & Engineering A* [J], 2018, 726: 69
- 2 Bagheri S, Guagliano M. *Surface Engineering*[J], 2009, 25(1): 3
- 3 Silvis-Cividjian N, Hagen C W, Kruit P. *Journal of Applied Physics*[J], 2005, 98: 84 905
- 4 Oboňa J V, Ocelík V, Rao J C et al. *Applied Surface Science*[J], 2014, 303: 118
- 5 Liu K Z, Wang X F, Liu J et al. *Progress in Surface Science*[J], 2018(93): 47
- 6 Zhang L, Ma A, Jiang J et al. *Surface & Coatings Technology*[J], 2013, 232: 412
- 7 Li X, Lu K. *Science*[J], 2019, 364(6442): 733
- 8 Li X, Lu K. *Nature Materials*[J], 2017, 16: 700
- 9 Valiev R Z, Islamgaliev R K, Alexandrov I V. *Progress in Materials Science*[J], 2000, 45: 103
- 10 Umemoto M. *Materials Transactions*[J], 2003, 44(10): 1900
- 11 Lu K, Lu J. *Journal of Materials Science & Technology*[J], 1999, 15(3): 193
- 12 Huang H W, Wang Z B, Lu J et al. *Acta Materialia*[J], 2015, 87: 150
- 13 Liu Y, Wang L, Wang D. *Journal of Materials Processing Technology*[J], 2011, 211: 2106
- 14 Waltz L, Retraint D, Roos A et al. *Scripta Materialia*[J], 2009, 60: 21
- 15 Zhao K, Liu Y, Yao T et al. *Materials Letters*[J], 2016, 166: 59
- 16 M Liu, Li J Y, Ma Y et al. *Surface & Coatings Technology*[J], 2016, 289: 94
- 17 Morita T, Noda S, Kagaya C. *Materials Science & Engineering A* [J], 2013, 574: 197
- 18 Li Y, Sun K, Liu P et al. *Vacuum*[J], 2014, 101: 102
- 19 Marteau J, Bigerelle M. *Tribology International*[J], 2015, 83: 105
- 20 Zhao W, Liu D, Zhang X et al. *International Journal of Fatigue* [J], 2019, 121: 30
- 21 Bagherifard S, Fernandez-Pariente I, Ghelichi R et al. *International Journal of Fatigue*[J], 2014, 65: 64
- 22 Bozdana A T, Gindy N N Z, Li H. *International Journal of Machine Tools & Manufacture*[J], 2005, 45: 713
- 23 Suh C M, Song G H, Suh M S et al. *Materials Science and Engineering A*[J], 2007, 443: 101
- 24 Mei G, Zhang K, Ding J. *Advanced Materials Research*[J], 2010, 102-104: 591
- 25 Cherif A, Pyoun Y, Scholtes B. *Journal of Materials Engineering and Performance*[J], 2010, 19: 282
- 26 Liu C, Liu D, Zhang X et al. *Materials*[J], 2017, 10: 833
- 27 Liu C, Liu D, Liu D et al. *Surface & Coatings Technology*[J], 2019, 370: 24
- 28 Zhang M, Liu Z, Deng J et al. *Applied Mathematical Modelling* [J], 2019, 76: 800
- 29 Kattoura M, Telang A, Mannava S R et al. *Materials Science & Engineering A*[J], 2018, 711: 364
- 30 Zhou X, Tamura N, Mi Z et al. *Physical Review Letters*[J], 2017, 118: 96 101
- 31 Margulies L, Winther G, Poulsen H F. *Science*[J], 2001, 291: 2392
- 32 Wang Y, Liao X, Zhu Y. *International Journal of Materials Research*[J], 2009, 100(12): 1632
- 33 Hughes D A, Hansen N. *Acta Materialia*[J], 1997, 45: 3871
- 34 Zhang Y, Lai F, Qu S et al. *Surface & Coatings Technology*[J], 2019, 366: 321
- 35 Ye Y, Kure-Chu S Z, Sun Z et al. *Materials and Design*[J], 2018, 149: 214
- 36 Ao N, Liu D, Zhang X et al. *Surface & Coatings Technology*[J], 2019, 361: 35
- 37 Ao N, Liu D, Xu X et al. *Materials Science & Engineering A*[J], 2019, 742: 820
- 38 Ye C, Telang A, Gill A S et al. *Materials Science & Engineering A*[J], 2014, 613: 274
- 39 Christian J W, Mahajan S. *Progress in Materials Science*[J], 1995, 39: 1
- 40 Li W L, Tao N R, Lu K. *Scripta Materialia*[J], 2008, 59: 546
- 41 Zhu Y T. *Journal of Materials Engineering and Performance*[J], 2005, 14: 467
- 42 Liu Y, Zhang Y, Zhao X. *Micro & Nano Letters*[J], 2017, 12(9): 585
- 43 Zhang Q, Hu Z, Su W et al. *Surface & Coatings Technology*[J], 2017, 321: 64
- 44 Wang Z, Gao C, Liu Z et al. *Materials Science & Engineering A* [J], 2020, 772: 138 696
- 45 Liu X C, Zhang H W, Lu K. *Science*[J], 2013, 342: 337
- 46 Mohamed F A. *Acta Materialia*[J], 2003, 51: 4107
- 47 Wang T, Wang D, Liu G et al. *Applied Surface Science*[J], 2008, 255: 1824
- 48 Ismail R, Tauviqirrahman M, Saputra E et al. *Procedia Engineering*[J], 2013, 68: 593
- 49 Zheng J, Hou Y, Ming P. *Key Engineering Materials*[J], 2016, 667: 29
- 50 Lu L X, Sun J, Li L et al. *The International Journal of Advanced Manufacturing Technology*[J], 2016, 87: 2533
- 51 Pyun Y S, Cho I H, Suh C M et al. *International Journal of Precision Engineering and Manufacturing*[J], 2013, 14(11): 2027
- 52 Cheng M, Zhang D, Chen H et al. *Journal of Materials Processing Technology*[J], 2014, 214: 2395
- 53 Li W, Li D Y. *Acta Materialia*[J], 2006, 54: 445
- 54 Wang H, Song G, Tang G. *Surface & Coatings Technology*[J], 2015, 282: 149
- 55 Ye Y, Li X, Sun Z et al. *Acta Metallurgica Sinica (English*

- Letters[J], 2018, 31: 1272
- 56 Lee C S, Park I G, Pyoun Y S et al. *International Journal of Modern Physics B*[J], 2010, 24(15): 3065
- 57 Liu Y, Wang L, Wang D. *Advanced Materials Research*[J], 2011, 189-193: 2112
- 58 Liu Y, Zhao X, Wang D. *Materials Science & Engineering A*[J], 2014, 600: 21
- 59 Zhao X, Liu Y. *Advanced Materials Research*[J], 2014, 834-836: 640
- 60 Zhou B, Fu X L, Xie A R et al. *Journal of Physics: Conference Series*[C], 2018, 1087(4): 42 068
- 61 Li F, Zhao B, Lan S et al. *The International Journal of Advanced Manufacturing Technology*[J], 2020, 106: 1893
- 62 Shi Y, Liu Y, Li X et al. *IOP Conference Series: Materials Science and Engineering*[J], 2018, 394(3): 32 058
- 63 Zhang P, Li S X, Zhang Z F. *Materials Science and Engineering A*[J], 2011, 529: 62
- 64 Estrin Y, Vinogradov A. *Acta Materialia*[J], 2013, 61: 782
- 65 Lu K, Lu L, Suresh S. *Science*[J], 2009, 324: 349
- 66 Toth L S, Gu C. *Materials Characterization*[J], 2014, 92: 1
- 67 Lu K. *Materials Science Forum*[J], 2005, 475-479: 21
- 68 Meyers M A, Mishra A, Benson D J. *Progress in Materials Science*[J], 2006, 51: 427
- 69 Zheng J, Liu H, Ren Y et al. *The International Journal of Advanced Manufacturing Technology*[J], 2020, 106: 503
- 70 Lu K. *Science*[J], 2014, 345(6203): 1455
- 71 Ye H, Sun X, Liu Y et al. *Surface & Coatings Technology*[J], 2019, 372: 288
- 72 Wang H, Song G, Tang G. *Materials Science & Engineering A* [J], 2016, 662: 456
- 73 Ao N, Liu D, Liu C et al. *Materials Characterization*[J], 2018, 145: 527
- 74 Panin A V, Kazachenok M S, Kozelskaya A I et al. *Materials Science & Engineering A*[J], 2015, 647: 43
- 75 Ye X, Ye Y, Tang G. *Journal of the Mechanical Behavior of Biomedical Materials*[J], 2014, 40: 287
- 76 Qin H, Ren Z, Zhao J et al. *Wear*[J], 2017, 392-393: 29
- 77 Wang Z B, Lu J, Lu K. *Surface & Coatings Technology*[J], 2006, 201: 2796
- 78 Li G, Qu S, Xie M et al. *Surface & Coatings Technology*[J], 2017, 316: 75
- 79 Wang Z, Xiao Z, Huang C et al. *Materials*[J], 2017, 10: 1203
- 80 Li G, Qu S G, Pan Y X et al. *Applied Surface Science*[J], 2016, 389: 324
- 81 Wang Z, Liu Z, Gao C et al. *Surface & Coatings Technology*[J], 2020, 381: 125 122
- 82 Amanov A, Cho I S, Kim D E et al. *Surface & Coatings Technology*[J], 2012, 207: 135
- 83 Padilla H A, Boyce B L. *Experimental Mechanics*[J], 2010, 50: 5
- 84 Dong J, Liu W C, Song X et al. *Materials Science and Engineering A*[J], 2010, 527: 6053
- 85 Xin C, Sun Q, Xiao L et al. *Journal of Materials Science*[J], 2018, 53: 12 492
- 86 Cheng M, Zhang D, Chen H et al. *The International Journal of Advanced Manufacturing Technology*[J], 2016, 83: 123
- 87 Zhao X, Xue G, Liu Y. *Results in Physics*[J], 2017, 7: 1845
- 88 Murakami Y. *Metal Fatigue: Effects of Small Defects and Nonmetallic Inclusions*[M]. Oxford: Elsevier Science Ltd, 2002
- 89 Zhang H, Chiang R, Qin H et al. *International Journal of Fatigue*[J], 2017, 103: 136
- 90 Cao X J, Pyoun Y S, Murakami R. *Applied Surface Science*[J], 2010, 256: 6297
- 91 Guo Y B, Warren A W, Hashimoto F. *CIRP Journal of Manufacturing Science and Technology*[J], 2010, 2: 129
- 92 Yasuoka M, Wang P, Zhang K et al. *Surface & Coatings Technology*[J], 2013, 218: 93
- 93 Liu C, Liu D, Zhang X et al. *International Journal of Fatigue*[J], 2019, 125: 249
- 94 Liu C, Liu D, Zhang X et al. *Journal of Materials Science & Technology*[J], 2019, 35: 1555
- 95 Yang J, Liu D, Zhang X et al. *International Journal of Fatigue* [J], 2020, 133: 105 373
- 96 Xu X, Liu D, Zhang X et al. *International Journal of Fatigue*[J], 2019, 125: 237
- 97 Wang Q, Sun Q, Xiao L et al. *Journal of Materials Engineering and Performance*[J], 2016, 25: 241
- 98 Hanlon T, Kwon Y N, Suresh S. *Scripta Materialia*[J], 2003, 49: 675
- 99 Miyamoto H. *Materials Transactions*[J], 2016, 57(5): 559
- 100 Ralston K D, Birbilis N, Davies C H J. *Scripta Materialia*[J], 2010, 63: 1201
- 101 Ralston K D, Birbilis N. *Corrosion*[J], 2010, 66: 75005
- 102 Xia T, Zeng L, Zhang X et al. *Surface & Coatings Technology* [J], 2019, 363: 390
- 103 Liu L, Li Y, Wang F. *Journal of Materials Science & Technology*[J], 2010, 26(1): 1
- 104 Chui P, Sun K, Sun C et al. *Applied Surface Science*[J], 2011, 257: 6787
- 105 Abdulstaar M, Mhaede M, Wollmann M et al. *Surface & Coatings Technology*[J], 2014, 254: 244
- 106 Cui Z, Qin Z, Dong P et al. *Materials Letters*[J], 2020, 259: 126 769
- 107 Shahryari A, Kamal W, Omanovic S. *Materials Letters*[J], 2008, 62: 3906
- 108 Wang H, Song G, Tang G. *Journal of Alloys and Compounds* [J], 2016, 681: 146
- 109 Sun Y, Wang H, Liu W et al. *Surface & Coatings Technology* [J], 2019, 368: 215
- 110 Zhang B, Wang J, Wu B et al. *Nature Communications*[J], 2018, 1: 1
- 111 Xu X, Liu D, Zhang X et al. *Journal of Materials Science & Technology*[J], 2020, 40: 88



- 112 Wang B, Yin Y, Gao Z et al. *RSC Advances*[J], 2017, 7: 36 876
- 113 Li C, Zhu R, Zhang X et al. *Surface & Coatings Technology*[J], 2020, 383: 125 280
- 114 Sauvage X, Wilde G, Divinski S V et al. *Materials Science and Engineering A*[J], 2012, 540: 1
- 115 Liu D, Liu D, Zhang X et al. *Materials Science & Engineering A*[J], 2020, 773: 138 720
- 116 She D, Yue W, Kang J et al. *Tribology Transactions*[J], 2018, 61(4): 612
- 117 Ren K, Yue W, Zhang H. *Surface & Coatings Technology*[J], 2018, 349: 602
- 118 Tong W P, Tao N R, Wang Z B et al. *Science*[J], 2003, 299: 686
- 119 Ren S, Zhang Y, Zhao Y et al. *Journal of Materials Engineering and Performance*[J], 2019, 28: 1132

## 超声表面滚压技术制备梯度纳米结构材料

陈道明<sup>1,2</sup>, 刘涇源<sup>2</sup>, 陈德华<sup>2</sup>, 苏 斌<sup>2</sup>, 刘柯钊<sup>2</sup>

(1. 表面物理与化学重点实验室, 四川 绵阳 621908)

(2. 中国工程物理研究院材料研究所, 四川 绵阳 621907)

**摘 要:** 介绍了超声表面滚压技术 (USRP) 在制备梯度纳米结构材料中的应用。USRP 技术能在材料表面构建梯度纳米结构层并引入残余压应力, 同时显著降低材料表面粗糙度并提升表面均匀性。讨论了与 USRP 加工工艺及过程密切相关的微观结构演变和表面特性, 分析了不同材料体系及工艺参数对 USRP 处理的影响规律。研究表明, 采用合适的 USRP 处理工艺可改善材料表面的力学性能, 即硬度, 强度, 耐磨性及抗疲劳性能等, 而腐蚀/氧化行为则更依赖于材料的组织结构、表面完整性、应力状态、不同的腐蚀介质及服役环境等因素的综合作用。此外, 对 USRP 制备梯度纳米结构材料面临的一些基础科学问题和工业应用探索进行了讨论和展望。

**关键词:** 超声表面滚压; 梯度纳米结构; 表面特性; 力学性能; 腐蚀行为

---

作者简介: 陈道明, 男, 1988 年生, 博士, 中国工程物理研究院材料研究所, 四川 绵阳 621907, 电话: 0816-3626728, E-mail: chendaominght@126.com