Tensile properties and surface nanocrystallization analyses of H62 brass subjected to room-temperature and warm laser shock peening

J.Z. Lu*, H.F. Duan, K.Y. Luo, L.J. Wu, W.W. Deng, J. Cai

School of Mechanical Engineering, Jiangsu University, Zhenjiang, 212013, People's Republic of China

Abstract: The effects of coverage layer and temperature on the tensile properties and surface microstructure of H62 brass subjected to laser shock peening (LSP) were systematically investigated. Ultimate tensile strength, elongation rate, and in-depth microstructural evolutions of three kinds of LSPed specimens, including LSPed specimens with one coverage layer and three coverage layers at room temperature, and one coverage layer at dynamic strain aging temperature, were subsequently measured and characterized. Special attentions were paid to surface nanocrystallization and amorphization of H62 brass subjected to room-temperature LSP and warm LSP technologies for the first time. The formation mechanisms of surface nanocrystallization and amorphization induced by room-temperature LSP and warm LSP were also discussed and completely revealed, and surface nanocrystallization contributed to the improvement of ultimate tensile strength and elongation rate of H62 brass subjected to LSP.

Keywords: Laser shock peening; H62 brass; Tensile property; Nanocrystallization; Amorphization; TEM observation

Corresponding author: Xuefu Road 301, Jingkou District, Zhenjiang 212013, People's Republic of China
Email address: jzlu@ujs.edu.cn (J.Z. Lu)
Tel.: +86-511-88797198; Fax: +86-511-88780352

Page -1-

1. Introduction

Over the past several decades, nanocrystalline materials have attracted considerable interests because of their higher heat capacity, better fatigue properties, improved tribological properties compared with their coarse-grain polycrystalline counterpart [1, 2]. Profiting from these outstanding properties, nanocrystalline materials are used in many engineering fields. Surface nanocrystallization is produced on the surface layer of metallic materials and alloys by traditional treatment technologies, including surface mechanical attrition treatment [3], ultrasonic shot peening [4], high-energy shot peening [5], and accumulative roll bonding [6], under low temperatures and high strain rates.

Laser shock peening (LSP) is an effective surface-strengthening technology that can produce nanocrystalline in the surface layer of metallic materials and alloys because of its four remarkable characteristics, namely, high pressure (in the scale of GPa), high energy (more than 1 GW/cm²), ultrafast (several tens of nanoseconds), and ultrahigh strain rate (more than 10⁷ s⁻¹) [7, 8]. For example, a nanocrystalline surface layer was successfully fabricated on an AZ91D magnesium alloy through LSP with different pulse energies, and the generation of nanocrystallization can be attributed to the dislocation glide by severe plastic deformation. Moreover, surface nanocrystallization has a significant contribution to the increased surface micro-hardness of AZ91D magnesium alloy [9]. At room temperature, adequate laser parameters caused nanocrystalline formation on the surface of TC6 titanium alloy and AISI 304 stainless steel. In the direction of shock wave decay, refined grain, dislocation structures were presented from the surface to the matrix of TC6 titanium alloy. However, mechanical twinning was prevalent during surface nanocrystallization on the surface layer of AISI 304 stainless steel [10]. High-density dislocations and nanostructures with an average size of 40 nm were also observed in the surface layer after multiple LSP impacts, leading to the high cycle fatigue

(HCF) performance of TC11 and TC6 titanium alloys [11, 12]. These investigations mainly focused on surface nanocrystallization and mechanical properties (residual stress, microhardness, and HCF life). Although surface nanocrystallization can effectively improve mechanical properties of the metallic materials and alloys, the surface nanocrystallization mechanism and its effect on mechanical properties of metallic materials induced by laser shock wave lag well behind so far.

Temperature is also an important factor in the refinement of coarse grains in the surface layer during LSP. Performed under elevated temperatures, warm laser shock peening (WLSP) is an innovative surface treatment process that combines the advantages of LSP and dynamic strain aging (DSA) [13]. Through DSA, WLSP of steel increases the dislocation density and stabilizes the dislocation structure through pinning of the mobile dislocations by the carbon atoms, resulting in the increased stability of the compressive residual stress [14]. Similar results can also be found in the literature [15]. However, after WLSP, nanostructures were not observed on the top surface of AISI 4140 steel and 7075 aluminum alloy [14, 15]. Amorphous solids, unlike crystals, lack long-range order among their atomic configurations. Amorphous solids also have excellent mechanical properties. At room temperature, laser shock compression can generate two distinct amorphous regions, namely, a bulk amorphous layer near the surface and amorphous bands, which are initially aligned with the {111} slip planes. This amorphization was generated by the combined effect of high-magnitude hydrostatic and shear stresses under dynamic shock compression [16]. However, reports on surface amorphization of metallic materials and alloys induced by LSP and the corresponding formation mechanism were few.

This study aims to investigate the effects of coverage layer and temperature on the tensile properties and surface microstructure of H62 brass subjected to LSP. Special attentions are focused

on the characterization of surface nanocrystallization and amorphization, and the in-depth microstructural evolution of H62 brass under three kinds of LSP conditions. The formation mechanisms of surface nanocrystallization and amorphization induced by RTLSP and WLSP are also discussed and revealed. Furthermore, the contribution of surface nanocrystallization and amorphization to the improvement in tensile properties of H62 brass is analyzed.

2. Experimental procedures

2.1. Material and specimen preparation

A 2 mm-thick H62 brass plate was used in the present study, and its chemical composition was 62 wt.% Cu, 0.006 wt.% Fe, 0.08 wt.% Pb, 0.005 wt.% Sb, 0.002 wt.% Bi, and balanced Zn. All dog-bone shaped tensile specimens were cut from the same plate, and their dimensions were shown in [Fig. 1\(a\)](#). Prior to the LSP treatment, both sides of each as-machined specimen were progressively polished by SiC paper with different grades of roughness (500#, 800#, 1,000#, 1,200#, 1,600#, 2,000#, and 2,500#) to obtain near scratch-free specimens. Then, the specimens were cleaned with deionized water. Subsequently, these specimens were immersed in acetone to degrease their surfaces through ultrasound wave.

2.2 Laser shock peening experiments

LSP experiments were performed using a Q-switched Nd: YAG laser operating at 1 Hz repetition with an irradiation wavelength of 1,064 nm. The focused diameter of the laser beam was 3 mm, whereas the full width at half maximum of the Gaussian intensity pulses was 10 ns. For all of the specimens that underwent LSP at room and DSA temperatures, the front surface of the gauge part (30 mm × 6 mm) was treated by massive LSP treatment and the opposite surface of the gauge part was subjected to the same treatment. The overlapping rates between the two adjacent spots in the

transverse and longitude directions were maintained at 50% [7, 17]. As shown in Fig. 1(b), massive LSP treatment was performed from the starting point (blue point), then along the LSP scanning path, and finally to the end point (red point). We defined this specimen as the LSPed specimen with one coverage layer. Specimen surface treated three times by massive LSP treatment was defined as LSPed specimen with three coverage layers. During massive LSP treatment at room temperature (RTLSP), a 1 mm-thick water layer was used as the transparent confining layer, and a 100 μm professional Al tape (made in USA) was used as the absorbing layer to protect the surface of the specimen from thermal damage. The Al foil was replaced after each coverage layer. The laser beam was always maintained to be perpendicular to the specimen surface. For massive WLSP treatment at DSA temperature, a 1 mm-thick water layer was replaced with silicone oil, which has a high vapor point of approximately 300 °C, as the transparent confining layer. The other processing parameters were same to those at room temperature.

In the present work, three kinds of LSPed specimens were considered as follows. The RTLSPed specimen with one coverage layer (the RTLSP-1 specimen) is an LSPed specimen containing one coverage layer at room temperature. The RLSPed specimen with three coverage layer (the RTLSP-3 specimen) is a LSPed specimen with three coverage layers at room temperature. The WLSPed specimen with one coverage layer (the WLSP-1 specimen) is a LSPed specimen with one coverage layer at DSA temperature.

2.3 Tensile experiments

Tensile properties of as-machined specimen and three kinds of LSPed specimens were measured on a MTS880-10 servo-hydraulic material testing machine system at RT with a constant strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. To obtain the reproducing tensile properties, the tensile tests of each specimen are carried

out at least four times. For each kind of specimen, the yield strength measured on the second test was varied by less than 2% from the value measured on the first test. An extensometer with a gauge length of 25 mm was used to measure the strain during the test. The UTS and ductility (percent elongation) were evaluated.

2.4 Microstructural observations and characterization

In-depth microstructural characterizations at surface layers of LSPed specimens were performed using a JEM-2100 transmission electron microscope (TEM) operated at a voltage of 200 keV. For the TEM observations, thin TEM foils at different depths in the deformation layer were prepared through ion milling at a low temperature. Schematic illustration of TEM observation locations taken from three kinds of LSPed specimens is shown in [Fig. 2](#) in details, where the red points represent

3. Results and discussion

3.1 Engineering stress-strain curves

[Fig. 3\(a\)](#) shows the engineering stress-strain curves of as-machined specimen and three kinds of LSPed specimens manufactured by H62 brass, and [Fig. 3\(b\)](#) is the high-magnification of different UTS values for the corresponding tensile specimens. From [Fig. 3\(a\)](#), it can be found that the engineering stress has a similar relationship with the engineering strain when the engineering strain is under 0.04% for all specimens. Moreover, no significant change is observed in the rake ratio of the linear region for three kinds of LSPed specimens. This phenomenon suggests that the number of coverage layer and temperature have little effect on the elastic deformation behavior of the H62 brass subjected to LSP treatment.

The UTS values of as-machined specimen and three kinds of LSPed specimens can also be clearly obtained from [Fig. 3\(b\)](#). Comparing with the UTS value of 311 MPa for the as-machined

specimen, the WLSP-1 specimen exhibits a highest UTS value of 389 MPa, while those of the RTLSP-1 and RTLSP-3 specimens are 368 MPa and 372 MPa, respectively. At room temperature, LSP with one and three coverage layers generates an increase of 18.3% and 19.6% in UTS of H62 brass, respectively. In contrast, at DSA temperature, LSP with one coverage layer also causes an increase of 25.1% in UTS of H62 brass.

It is worth noting that the UTS value of the RTLSP-3 specimen is slightly higher than that of the RTLSP-1 specimen, indicating that the number of coverage layer has little influence on the UTS of H62 brass. The strain up to plastic instability point of the RTLSP-1 and RTLSP-3 specimens are increased by 2.3% and 6.7% comparing with that of the as-machined specimen, respectively. Meanwhile, the strain up to plastic instability point of the WLSP-1 specimen has an improvement of 27.4% comparing with that of the as-machined specimen. Therefore, it can be concluded that the RTLSP treatment improves the elongation of H62 brass, and the RTLSP treatment with multiple coverage layers results in a larger elongation. Furthermore, service temperature is also an important factor to influence the elongation of H62 brass subjected to massive LSP treatment. In generally, the ductility of alloys and metallic materials usually decreases with increasing the ultimate tensile strength [18]. It is interesting to note that three kinds of LSPed specimens, including the RTLSP-1 and RTLSP-3 specimens, and the WLSP-1 specimen, exhibit a good combination of UTS and ductility.

3.2 Microstructural observations of LSPed specimens at room temperature

Fig. 4 presents typical TEM observations at different depths to the top surface of the RTLSP-1 specimen, which are taken from Points A, B, C, D, and E in Fig. 2(a). The original features of the substrate located at a depth of ~1500 μm below the shocked zone induced by the RTLSP treatment

are shown in Fig. 4a. The original coarse grain in the substrate is estimated at several micrometers, and some dislocation lines (DLs) inside the original grain are located at this layer. The DLs can be considered growth dislocations because no plastic deformation has occurred in the substrate. The uniformly distributed DLs or dislocation accumulations can be observed in these grains. Figs. 4b and 4c show the typical TEM images in the MPD layer at the depths of 260 μm and 200 μm to the top surface, respectively. Several DLs arranged randomly in the grain of the MPD layer are observed. The dislocation generates and grows when the pressure of the shock wave induced by LSP is higher than the dynamic yield strength of H62 brass. The dense DLs accumulate and are transformed into dislocation tangles (DTs). The dislocation walls (DWs) and dislocation cells (DCs) by slip, accumulation, and interaction with increasing strain in the MPD layer of H62 brass can be observed when the distance to the top surface decreases. Fig. 4d shows a typical TEM image in the SPD layer at a depth of 60 μm to the top surface, and some DCs with an average size ranging from 100 nm to 400 nm can be obviously identified, which are smaller than the average size of the original coarse grain in the substrate. In this layer, some complex dislocation structures, such as DLs and DWs, can also be identified. Fig. 4e shows a typical TEM image at a depth of 30 μm to the top surface, and the microstructural evolution along the depth direction is presented. As illustrated in Ellipse [A] and Ellipse [B], some equiaxed nanograins with grain size of approximately 15 nm to 30 nm can be observed in areas where the strain and strain rate induced by LSP reached the maximum. The corresponding selected area electron diffraction (SAED) pattern taken from Ellipse [A] is shown in Fig. 4f. This SAED pattern is composed of discontinuous diffraction spots which are elongated gradually into a circular shape. This finding confirms the refinement of the coarse grains at a depth of 30 μm and their disintegration into nanograins with random crystallographic orientations.

TEM images in Fig. 5 show the typical microstructures at different depths to the top surface of the RTLSP-3 specimen, taken from Point A, B, D, E, and F in Fig. 2b, respectively. The average size of the coarse grain in the substrate is approximately several micrometers, and some growth dislocations are observed in some grains, as shown in Fig. 5a. Fig. 5b shows the typical TEM images in the MPD layer at a depth of 260 μm to the top surface, and Fig. 5c shows a high-magnification image of Ellipse [A] in Fig. 5b. Some dislocation structures, such as dense and randomly distributed DLs and DTs, are observed inside refined grains, as shown in Fig. 5c. DWs can also be observed (Fig. 5b), which may be transformed into subgrain boundaries to minimize the total energy through dislocation accumulation and rearrangement [19]. Fig. 5d illustrates the typical TEM image in the SPD layer at a depth of 60 μm to the top surface, and some nanostructures with an average size ranging from 50 nm to 150 nm emerge after RTLSP treatment with three coverage layers. Mechanical twins with some dislocation structures are observed inside these refined grains, which are not observed in the RTLSP-1 specimen. Some subgrains are also observed in the SPD layer, and these substructures will further be subdivided into smaller blocks, marked by a red arrow in Fig. 5d. This finding reveals that the grain can be refined further with increasing the strain and strain rate. Figs. 5e and 5f show the typical TEM images at a depth of 30 μm to the top surface, and the average size of the refined grains further decreases with decreasing the depth to the top surface. Some nanograin arrays are observed on the right side, whereas relatively large nanograins and dislocation accumulations can be observed on the left side, as shown in Fig. 5e. From Fig. 5f, the grain size on the lower right corner ranges from 10 nm to 25 nm, and some dislocation structures, including dislocation accumulations and DTs, can be observed on the upper left corner.

3.3 Microstructural observations of LSPed specimen at DSA temperature

Fig. 6 shows typical TEM images of different depths of the WLSP-1 specimen. After H62 brass was subjected to WLSP with one coverage layer, the average size of the formed grains in the substrate (taken from Point A in Fig. 2c) varied from 2 μm to 4 μm , as shown in Fig. 6a. Moreover, few growth dislocations appear inside coarse grains, and some growth DLs accumulate and cause the formation of DTs.

Figs. 6b and 6c show typical TEM images in the MPD layer at the depths of 260 μm and 200 μm to the top surface (taken from Points B and C in Fig. 2c), respectively. Dense dislocations are irregularly distributed inside coarse grains. The interaction between the dislocations generated by the WLSP and the growth dislocations results in DTs with relatively high densities, which are more stable than the dislocation accumulations [14]. Notably, a piece of 0.5 μm -thick mechanical twin, with some dislocations, can be observed. Meanwhile, high-density dislocations are generated around the twin boundary. As shown in Fig. 6c, the dense dislocations are generated in the deformation region and interlaced into a mesh structure, forming a large number of DTs and DCs with various sizes. A few dislocation structures can also be observed inside DCs.

Typical TEM observations in the SPD layer at a depth of 60 μm to the top surface (taken from point D in Fig. 2c) are shown in Fig. 6d. Some refined grains with sizes ranging from 30 nm to 200 nm are generated in this layer. High-density dislocations are unevenly distributed, and the maximum dislocation density is observed around the grain boundary. Some refined nanocrystallines with an average size of 40 nm can be observed in Ellipse [A]. Fig. 6e shows the SAED pattern taken from Ellipse [B] in Fig. 6d. A ring formed by the elongation of the discontinuous diffraction spots reveal the nanocrystallines generated in the region of Ellipse [B].

Typical TEM image at a depth of 30 μm to the top surface (taken from Point F in Fig. 2c) is

shown in Fig. 6f, and an evidence of grain refinement can be observed clearly in the generated nanocrystalline. After the WLSP treatment with one coverage layer, a large number of nanocrystallines with several nanometers form at a depth of 30 μm to the top surface. The SAED pattern in the inset of Fig. 6f presents the continuous and homogeneous concentric rings containing some crystalline diffraction spots, and these observed features indicate that the grain size is small and the grains exhibit a random crystallographic orientation [10].

3.4 Strain-induced surface nanocrystallization and amorphization by RTLSP and WLSP

The typical microstructures on the top surfaces of the LSPed specimens are presented in Figs. 7, 8, and 9. Fig. 7a shows the equiaxed grain with average size ranging from 5 nm to 15 nm on the top surface of the RTLSP-1 specimen. No amorphous phase is observed in the interface region between the two adjacent grain boundaries. Fig. 7c shows the corresponding SAED pattern taken from Ellipse [A] in Fig. 7a, and the homogeneous and continuous diffraction ring with crystalline spots is presented. Moreover, the $\{111\}$, $\{200\}$, $\{220\}$, and $\{311\}$ planes are observed. These planes indicate the refinement of the grains on the top surface into nanograins and the absence of amorphization. After the RTLSP treatment with three coverage layers, a large number of equiaxed grains with average size ranging from 3 nm to 10 nm form on the top surface, as shown in Fig. 8a. In addition, some amorphous phases are also observed on the top surface. Fig. 8c shows the corresponding SAED pattern taken from Ellipse [A] in Fig. 8a, indicating continuous and homogeneous rings with exiguous crystalline diffraction spots [20]. The nanocrystalline phase remains dominant. However, the $\{200\}$ plane expands and tends to transform into an amorphous state, and the other lattice planes are more homogeneous and continuous.

A large number of amorphous phases occur on the top surface of the WLSP-1 specimen, leading

to increased intervals among the adjacent nanocrystallines with grain sizes of 2-10 nm, as shown in Fig. 9a. Fig. 9c shows the corresponding SAED pattern taken from Ellipse [A] in Fig. 9a, wherein broad halo rings without crystalline diffraction spots within the SAED pattern and the {111} plane can be observed. These observed features indicate that an amorphous phase is formed, which is more evident on the top surface.

High-resolution TEM (HRTEM) images of Ellipse [A] in Figs. 7a, 8a, and 9a are shown in Figs. 7b, 8b, and 9b, respectively. The variations in the nanocrystalline sizes and the numbers of structures with amorphous phase are evident in the HRTEM images. For the RTLSPed specimens, the average size of the nanograins on the top surface decreases from ~8 nm (Fig. 7b) to ~5 nm (Fig. 8b) when the number of coverage layers varies from one to three layers. Relative to those of RTLSP-1 specimen, the nanograins induced by WLSP shows an apparent decrease in the average size, varying from ~8 nm (Fig. 7b) to ~2 nm (Fig. 9b) on the top surface of H62 brass. Meanwhile, the increase in the number of amorphous phases is observed in Figs. 7c, 8c, and 9c. This finding is in accordance with the results obtained from the TEM images and SAED patterns on the top surface. Thus, the degree of amorphization increases gradually in the RTLSP-1, RTLSP-3, and WLSP-1 specimens.

3.5 Formation mechanism of surface nanocrystallization and amorphization

Microstructural evolution of H62 brass specimens subjected to RTLSP and WLSP are schematically illustrated in Fig. 10. Each state shown in Figs. 10a and 10b will be discussed in terms of the above-mentioned experimental observations. The formation process of surface nanocrystallization and amorphization induced by RTLSP and WLSP on the top surface of H62 brass can be described as follows:

Some growth dislocations (State [I] in Fig. 10a) occur in the substrate of H62 brass (Fig. 4a).

After the RTLSP treatment with one coverage layer, a shock wave with ultrahigh pressure induced by LSP propagates into the surface layer, and the dislocation movement in the MPD layer results in the formation of high-density DLs (Fig. 4c). When the strain and strain rate increase, the dislocation plane and cross slips are generated and result in the significant accumulation of DLs. Subsequently, the accumulation of DLs causes the formation of complex and random dislocation structures in the MPD layer, for example, DTs and DWs. Then, the original coarse grain is subdivided by the formation of the DCs (Fig. 4d). When the strain increases to a certain level, DCs are converted to ultrafine equiaxed grains at a nanometer scale, as shown in Fig. 4e. A small grain size indicates an increased number of grain boundaries, which disrupts dislocation motion and thus improves the strength of metallic materials [21]. A nanostructured layer with an average size of ~8 nm is formed on the top surface of the RTLSPed specimen with one coverage layer, as shown in Fig. 7.

When the coverage layer increases to three during RTLSP treatment, the top surface of H62 brass suffers from severe plastic deformation induced by the pulse laser beams with several times. With repeated RTLSP treatment, the subdivision process occurs at a finer scale inside the refined grains. Until the dislocation multiplication rate is balanced by the dislocation annihilation rate, a large number of ultrafine equiaxed grains with an average size of ~5 nm have been produced on the top surface (State [II] in Fig. 10a), as shown in Fig. 8. The increased strain does not reduce the grain size from this point, and a stabilized grain size occurs on the top surface. This finding may be attributed to the inhibited production of new DTs and DWs inside the refined grains that undergo a subsequent RTLSP treatment [22]. Thus, both RTLSPed specimens generate surface nanocrystallization and amorphization on the top surface of H62 brass because dislocation motions, DLs, DTs, and DWs are produced and accumulated and then cause the formation of DCs and

subgrains, as shown in Figs. 5b, 5c, 5d, and 5e.

Under the mechanical effect of ultra-strong laser-induced shock wave, the dislocation density at the shock front can be calculated as follows [16]:

$$\rho_d = \frac{2\pi^2}{0.8(1-\nu)k^3b_0^2} \left(\frac{V}{V_0}\right)^{-2/3} \left[1 - \left(\frac{V}{V_0}\right)^{1/3}\right]^3, \quad (1)$$

where k is the orientation factor, b_0 is the Burgers vector, V is the compressed specific volume, and V_0 is the specific volume in the relaxed state. Notably, the LSP treatment results in the decrease in volume on the surface layer of metallic materials and alloys [23]. According to Equation (1), the dislocation density at the shock front (ρ_d) is inversely proportional to the volume ratio V/V_0 . This relationship can explain the formation of high-density dislocation structures induced by RTLSP.

Microstructural evolution also has a relationship with the decay of the shock wave along the depth direction [24]. Particularly, the strain rate decreases remarkably with increasing the depth to the top surface. This relationship is an important factor that influences the microstructure and the grain arrangement on the top surface of H62 brass.

At a DSA temperature of 180 °C, a large number of coarse grains with average size ranging from 2 μm to 4 μm and with a few growth dislocations, accompanying with some diffusive solute atoms (marked by blue points in Fig. 10b), are observed in the substrate of H62 brass (State [I] in Fig. 10b), as shown in Fig. 6a. When H62 brass is subjected to WLSP treatment with one coverage layer, high-density DTs and mechanical twin instead of dislocation accumulations form on the top surface, as shown in Figs. 6b and 6c. This finding indicates that the dislocation slip and mechanical twinning may dominate during plastic deformation of H62 brass subjected to WLSP. These structures interlace into DCs and even into subgrains in the SPD layer, as shown in Figs. 6c and 6d. At this point, the

increased temperature promotes the diffusion of solute atoms to the growth dislocation cores in the untreated specimen and forms the Cottrell clouds [14]. The Cottrell clouds produce a pinning force on the dislocations and hinder dislocation movement at the initial stage of the later plastic deformation induced by LSP. Under the combined effect of the laser shock wave and DSA temperature, the interaction between the diffusive solute atom and the mobile dislocation significantly increases. New dislocations are generated to accumulate the plastic deformation, and the increased stress is also needed to detach the pinned dislocation from the solute atoms because the dislocations are pinned by the diffusive solute atoms. In this condition, other dislocation sources will be activated and more mobile dislocations will be generated [14, 15]. Meanwhile, increased temperature promotes dislocation activities, which further causes dislocation multiplication and annihilation. Moreover, the increased temperature decreases the yield stress of the material [15]. The above-mentioned factors result in a higher dislocation density compared with the RTLSP. Thus, more dislocations and more complex dislocation structures will be formed inside the produced grains.

The surface amorphization is observed at the local area of the RTLSP-3 specimen and the WLSP-1 specimen. Generally, amorphization is accompanied by the generation of ultrafine grains with sizes of several nanometers (State [II] in Fig. 10b), as shown in Fig. 9b. Thus, surface amorphization can be regarded as an extreme process of grain refinement. In fact, the increase in the free energy of the crystalline directly leads to amorphization, which results from the accumulation of the defects and the generation of chemical disorder due to plastic deformation [25]. Furthermore, the Gibbs free energy is related to the temperature and applied stress. When the Gibbs free energy of the amorphous phase and the liquid phase are assumed to be equal, the energy barrier (ΔG_{c-a}) of the transformation from the crystal state (c) to the amorphous phase (a) can be expressed as follows [16]:

$$\Delta G_{c-a}(T; P, \tau = 0) = P\varepsilon_v + \tau\gamma + \Delta G_{c-a}(T; P, \tau), \quad (2)$$

where P is the hydrostatic stress, ε_v is the volumetric strain, τ is the deviatoric shear stress, and γ is the shear strain. The Gibbs free energy as a function of temperature without the existence of applied stress can be expressed as follows [16]:

$$\Delta G_{c-a}(T) = \Delta G_{c-a}(300K) \left(1 - \frac{T-300}{T_m-300} \right), \quad (3)$$

where T_m is the temperature of the Gibbs free energy of the crystalline that is equal to that of the amorphous phase. According to Equation (3), when the temperature increases, the energy barrier (ΔG_{c-a}) for c-a transformation decreases. In addition, compared with the movement speed (V_1) of solute atom at room temperature, the DSA temperature causes a faster movement speed (V_2) of solute atoms inside coarse grain, as schematically shown in Fig. 10. Thus, in this case, the DSA temperature promotes the transformation from nanocrystal state to amorphous phase on the top surface of H62 brass subjected to LSP.

From these experimental data, relatively more DTs and smaller DCs will be generated, as shown in Fig. 6c. When the strain increases further, the small high-density DCs are transformed into subgrains with low-angle grain boundaries. When the strain increases to a certain value at DSA temperature, the pinning dislocations caused by the solute atoms serve as a new dislocation source, and new dislocations are generated from these pinning dislocations under ultrahigh pressure. Meanwhile, the activity of these pinning dislocations detaches from the solute atoms, which requires a large amount of stress. Both factors lead to a high dislocation density and increased uniform distribution of the dislocation structure, which contributes to the formation of nanocrystallization and amorphization on the top surface. Increased temperature relative to room temperature also facilitates the dynamic recrystallization of the subgrain boundaries. Thus, increased formation of relatively

smaller nanocrystallines is observed on the top surface of the WLSP-1 specimen relative to those of the RTLSP-1 and RTLSP-3 specimens, as illustrated in State [II] in Fig. 10b.

Fig. 6 shows the interaction between the mechanical twin and the dislocation motion, which plays an important role in the refinement of the coarse grain in the surface layer of H62 brass subjected to WLSP. At the start of the plastic deformation induced by WLSP, the mechanical twins are generated when the grain size is reduced into submicroscale or nanoscale. The similar finding can also be observed in pure Al in which deformation twinning occurs in the nanometer scale [26]. Furthermore, some dislocation structures can be observed in the mechanical twins, as shown in Fig. 6b. Most T/M lamellae accommodate plastic strain mainly through manipulation and interaction of the dislocations. During plastic deformation, numerous dislocations can accumulate within the thin T/M layers or at the vicinity of the substantial twin boundaries. Then, the dislocations arrange themselves into interconnecting boundaries to minimize the total energy state, thereby subdividing the T/M lamellae into refined blocks. With the accumulation of plastic strain, the original coarse grain is refined into nanocrystalline through the refinement mechanism discussed previously.

The majority of the failures in engineering materials are sensitive to the microstructure on the material surface, and most such failures are also initiated at the surface. The previous results showed that surface nanocrystallization [27] can improve the overall properties and behaviors of metallic materials, such as 316L stainless steel [4] and Mg-Al alloy [9, 28]. From above-mentioned experimental results, it can be found that all three kinds of massive LSP treatment lead to functional gradient nano-materials in the surface layer of H62 brass. As we known, combined DSA effect with the mechanical effect of laser shock wave, there exists a functional gradient nano-material layer with smaller grain size in the surface layer of H62 brass. In fact, functional gradient nano-materials

exhibit some unique structural characteristics and novel properties which are fundamentally different from those of the conventional coarse-grained polycrystalline materials, including microhardness and creep rate [29]. Also, from the literature [30], it can be seen that after 93% CW at 180 °C (curve D), the UTS is much higher than that of the coarse-grained Cu (curve A), which can be attributed to the nanocrystalline/ultrafine grains that reduce the size of nucleating flaws and increase the resistance to crack propagation, leading to a higher fracture stress.

In the present work, RTLSP and WLSP generate a nanostructured surface layer with average sizes of 5 nm and 2 nm on a H62 brass plate, directly contributing to the improvement in the UTS (strengthen) and elongation rate (ductility) of H62 brass.

4. Conclusions

(1) In-depth microstructural evolutions of three kinds of LSPed specimens, including the RTLSP-1 specimen, the RTLSP-3 specimens, and the WLSP-1 specimen, were characterized and analyzed. Nanograins with an average size of less than 10 nm were observed on the top surfaces of all the LSPed specimens. Particularly, surface amorphization can be observed at a localized area on the top surfaces of the RTLSP-3 specimen and the WLSP-1 specimen for the first time.

(2) At DSA temperatures, the motion of the solute atom pinning dislocations and the detachment of these dislocations from the solute atoms lead to increased dislocation density and enhanced uniform distribution of the dislocation structure. These results contribute to the formation of nanocrystallization and amorphization on the top surface of H62 brass subjected to massive LSP treatment with one coverage layer.

(3) The formation mechanisms of surface nanocrystallization and amorphization induced by RTLSP and WLSP were completely revealed, and the ultrahigh strain rate and DSA temperature are

essential to surface nanocrystallization and amorphization of H62 brass.

(4) Comparing with the as-machined specimens, three kinds of LSPed specimens, including the RTLSP-1 and RTLSP-3 specimens, and the WLSP-1 specimen, exhibited a good combination of UTS and ductility. RTLSP and WLSP generate a nanostructured surface layer with average sizes of 5 nm and 2 nm on a H62 brass plate, directly contributing to the improvement in the UTS (strengthen) and elongation rate (ductility) of H62 brass.

Acknowledgements

The authors are grateful for the support provided by National Natural Science Foundation of China (Nos. 51275220 and 51575242), Jiangsu Provincial Natural Science Foundation for Distinguished Young Scientists (Nos. BK20140012/BE2016148/BK20151341), Major programs of Natural Science Foundation of the Jiangsu Higher Education Institutions (No. 14KJA460002), National Science Foundation for Post-doctoral Scientists of China (No. 2015T80504), Six Major Talent Peak of Jiangsu Province (2014-ZBZZ-015), and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

- [1] N. Argibay, T.A. Furnish, B.L. Boyce, B.G. Clark, M. Chandross, Stress-dependent grain size evolution of nanocrystalline Ni-W and its impact on friction behavior, *Scr. Mater.* 123 (2016) 26–29.
- [2] T. Balusamy, S. Kumar, T.S.N.S. Narayanan, Effect of surface nanocrystallization on the corrosion behavior of AISI 409 stainless steel, *Corros. Sci.* 52 (2010) 3826–3834.
- [3] X. Wang, L. Jiang, A. Luo, J. Song, Z. Liu, F. Yin, Q. Han, S. Yue, J.J. Jonas, Deformation of twins in a magnesium alloy under tension at room temperature, *J. Alloy. Compd.* 594 (2014) 44–47.
- [4] G. Liu, J. Lu, K. Lu, Surface nanocrystallization of 316L stainless steel induced by ultrasonic

shot peening, *Mater. Sci. Eng. A* 286 (2000) 91–95.

[5] L.F. Hou, Y.H. Wei, X.F. Shu, B.S. Xu, Nanocrystalline structure of magnesium alloys subjected to high energy shot peening, *J. Alloy. Compd.* 492 (2010) 347–350.

[6] P.J. Hsieh, Y.P. Hung, S.I. Chou, J.C. Huang, Nanocrystallization and Amorphization Mechanisms in Zr-X Alloys during the ARB Process, *Mater. Trans.* 45 (2004) 2686–2692.

[7] K.Y. Luo, J.Z. Lu, Q.W. Wang, M. Luo, H. Qi, J.Z. Zhou, Residual stress distribution of Ti-6Al-4V alloy under different ns-LSP processing parameters, *Appl. Surf. Sci.* 285P (2013) 607–615.

[8] K.Y. Luo, X. Jing, J. Sheng, G.F. Sun, Z. Yan, J.Z. Lu, Characterization and analyses on micro-hardness, residual stress and microstructure in laser cladding coating of 316L stainless steel subjected to massive LSP treatment, *J. Alloy. Compd.* 673 (2016) 158–169.

[9] X.D. Ren, J.J. Huang, W.F. Zhou, S.D. Xu, F.F. Liu, Surface nano-crystallization of AZ91D magnesium alloy induced by laser shock processing, *Mater. Des.* 86 (2015) 421–426.

[10] S. Lou, Y. Li, L. Zhou, X. Nie, G. He, Y. Li, W. He, Surface nanocrystallization of metallic alloys with different stacking fault energy induced by laser shock processing, *Mater. Des.* 104 (2016) 320–326.

[11] X.F. Nie, W.F. He, S.L. Zang, X.D. Wang, J. Zhao, Effect study and application to improve high cycle fatigue resistance of TC11 titanium alloy by laser shock peening with multiple impacts, *Surf. Coat. Technol.* 253 (2014) 68–75.

[12] X.F. Nie, W.F. He, L.C. Zhou, Q.P. Li, X.D. Wang, Experiment investigation of laser shock peening on TC6 titanium alloy to improve high cycle fatigue performance, *Mater. Sci. Eng. A* 594 (2014) 161–167.

- [13] C. Ye, Y.L. Liao, G. J. Cheng, Warm laser shock peening driven nanostructures and their effects on fatigue performance in aluminium alloy 6160, *Adv. Eng. Mater.* 14 (2010) 291–297.
- [14] C. Ye, S. Suslov, B.J. Kim, E.A. Stach, G.J. Cheng, Fatigue performance improvement in AISI 4140 steel by dynamic strain aging and dynamic precipitation during warm laser shock peening, *Acta Mater.* 59 (2011) 1014–1025.
- [15] C. Ye, Y.L. Liao, S. Suslov, D. Lin, G.J. Cheng, Ultrahigh dense and gradient nano-precipitates generated by warm laser shock peening for combination of high strength and ductility, *Mater. Sci. Eng. A* 609 (2014) 195–203.
- [16] S. Zhao, E.N. Hahn, B. Kad, B.A. Remington, C.E. Wehrenberg, E.M. Bringa, M.A. Meyers, Amorphization and nanocrystallization of silicon under shock compression, *Acta Mater.* 103 (2016) 519–533.
- [17] K.Y. Luo, T. Lin, F.Z. Dai, X.M. Luo, J.Z. Lu. Effects of overlapping rate on the uniformities of surface profile of LY2 Al alloy during massive laser shock peening impacts, *Surf. Coat. Technol.* 266 (2015) 49–56.
- [18] S.G. Irizalp, N. Saklakoglu, High strength and high ductility behavior of 6061-T6 alloy after laser shock processing, *Opt Laser Eng* 77 (2016) 183–190.
- [19] X.D. Ren ,W.F. Zhou, Y.P. Ren , S.D. Xu, F.F. Liu, S.Q. Yuan, N.F. Ren, J.J. Huang, Dislocation evolution and properties enhancement of GH2036 by laser shock processing: Dislocation dynamics simulation and experiment, *Mater. Sci. Eng. A* 654 (2016) 184–192.
- [20] T. Nagase, Y. Umakoshi, Amorphous phase formation in Co–Cu–Zr–B-based immiscible alloys, *J. Alloy. Compd.* 649 (2015) 1174–1181.
- [21] L. Lu, Y.F. Shen, X.H. Chen, L.H. Qian, K.Lu, Ultrahigh strength and high electrical

conductivity in copper, *Science* 304 (2004) 422–426.

[22] J.Z. Lu, K.Y. Luo, Y.K. Zhang, C.Y. Cui, G.F. Sun, J.Z. Zhou, L. Zhang, J. You, K.M. Chen, J.W. Zhong, Grain refinement of LY2 aluminum alloy induced by ultra-high plastic strain during multiple laser shock processing impacts, *Acta Mater.* 58 (2010) 3984–3994.

[23] C.S. Montross, T. Wei, L. Ye, G. Clark, Y.W. Mai, Laser shock processing and its effects on microstructure and properties of metal alloys: a review, *Int. J. Fatigue* 24 (2002) 1021–1036.

[24] K. Lu, J. Lu, Nanostructured surface layer on metallic materials induced by surface mechanical attrition treatment, *Mater. Sci. Eng. A* 375–377 (2004) 38–45.

[25] C. Ye, S. Suslov, X.L. Fei, G.J. Cheng, Bimodal nanocrystallization of NiTi shape memory alloy by laser shock peening and post-deformation annealing, *Acta Mater.* 59 (2011) 7219–7227.

[26] X.Z. Liao, F. Zhou, E.J. Lavernia, S.G. Srinivasan, M.I. Baskes, D.W. He, Y.T. Zhu, Deformation mechanism in nanocrystalline Al: Partial dislocation slip, *Appl. Phys. Lett.* 83 (2003) 632–634.

[27] K. Lu, J. Lu, Surface nanocrystallization of metallic materials-presentation of the concept behind a new approach, *J. Mater. Sci. Technol.* 15 (1999) 193–197.

[28] L.H. Zhang, Y. Zou, H.T. Wang, L. Meng, J.B. Liu, Z.W. Zhang, Surface nanocrystallization of Mg-3 wt.% Li-6 wt.% Al alloy by surface mechanical attrition treatment, *Mater. Charact.* 120 (2016) 124–128.

[29] K. Lu, Nanocrystalline metals crystallized from amorphous solids: nanocrystallization, structure, and properties, *Mater. Sci. Eng. R* 16 (1996) 166–221.

[30] Y.M. Wang, M.W. Chen, F.H. Zhou, E. Ma, High tensile ductility in a nanostructured metal, *Nature*, 419 (2002) 912–915.

NOTE: Movement speed, $\rightarrow V_1$, $\rightarrow V_2$, $v_1 < v_2$

Room temperature DSA temperature • Solute atom

List of Figure Captions

Fig. 1 (a) The dimensions of the dog-bone shaped tensile specimen, and (b) partial enlargement drawing of LSPed region showing the starting point, the LSP scanning path and the end point. (Unit: mm).

Fig. 2 Schematic illustration of TEM observation locations taken from three kinds of LSPed specimens. (a) RTLSP-1 specimen, (b) RTLSP-3 specimen, and (c) WLSP-1 specimen.

Fig. 3 (a) Engineering stress-strain curves of as-machined specimen and three kinds of LSPed specimens, and (b) the high-magnification of different UTS values corresponding the gray region in (a).

Fig. 4 Typical TEM images at different depth of the RTLSP-1 specimen. (a) in the substrate, (b) and (c) in the MPD layer, (d) in the SPD layer, (e) at a depth of 30 μm to the top surface in the SPD layer, (f) the corresponding SAED pattern of Ellipse [A] in (e).

Fig. 5 Typical TEM images at different depths of the RTLSP-3 specimen. (a) in the substrate, (b) in the MPD layer, (c) a magnified image of Ellipse [A] in (b), (d) in the SPD layer, (e) and (f) at a depth of 30 μm to the top surface in the SPD layer.

Fig. 6 Typical TEM images at different depths of the WLSP-1 specimen. (a) in the substrate, (b) and (c) in the MPD layer, (d) in the SPD layer, (e) the SAED pattern of Ellipse [B] in (d), (f) at a depth of 30 μm to the top surface in the SPD layer.

Fig. 7 (a) Typical TEM image on the top surface of the RTLSP-1 specimen, (b) HRTEM image of Ellipse [A] in (a), and (c) the corresponding SAED pattern of Ellipse [A] in (a).

Fig. 8 (a) Typical TEM image on the top surface of the RTLSP-3 specimen, (b) HRTEM image of Ellipse [A] in (a), and (c) the corresponding SAED pattern of Ellipse [A] in (a).

Fig. 9 (a) Typical TEM image on the top surface of the WLSP-1 specimen, (b) HRTEM image of

Ellipse [A] in (a), and (c) the corresponding SAED pattern of Ellipse [A] in (a).[Fig. 10](#) Schematic illustration on microstructural evolution of RTLSPed specimen and WLSPed specimen showing the formation of surface nanocrystallization and amorphization.

[Fig. 10](#) Schematic illustration on microstructural evolution of RTLSPed specimen and WLSPed specimen showing the formation of surface nanocrystallization and amorphization.

Fig. 1 (a) The dimensions of the dog-bone shaped tensile specimen, and (b) partial enlargement drawing of LSPed region showing the starting point, the LSP scanning path and the end point. (Unit: mm).

Note: The red points represent TEM observation locations away from the top surfaces.

Fig. 2 Schematic illustration of TEM observation locations taken from three kinds of LSPed specimens. (a) RTLSP-1 specimen, (b) RTLSP-3 specimen, and (c) WLSP-1 specimen.

Fig. 3 (a) Engineering stress-strain curves of as-machined specimen and three kinds of LSPed specimens, and (b) the high-magnification of different UTS values corresponding the gray region in (a).

Fig. 4 Typical TEM images at different depth of the RTLSP-1 specimen. (a) in the substrate, (b) and (c) in the MPD layer, (d) in the SPD layer, (e) at a depth of 30 μm to the top surface in the SPD layer, (f) the corresponding SAED pattern of Ellipse [A] in (e).

Fig. 5 Typical TEM images at different depths of the RTLSP-3 specimen. (a) in the substrate, (b) in the MPD layer, (c) a magnified image of Ellipse [A] in (b), (d) in the SPD layer, (e) and (f) at a depth of 30 μm to the top surface in the SPD layer.

Fig. 6 Typical TEM images at different depths of the WLSP-1 specimen. (a) in the substrate, (b) and (c) in the MPD layer, (d) in the SPD layer, (e) the SAED pattern of Ellipse [B] in (d), (f) at a depth of 30 μm to the top surface in the SPD layer.

Fig. 7 (a) Typical TEM image on the top surface of the RTLSP-1 specimen, (b) HRTEM image of Ellipse [A] in (a), and (c) the corresponding SAED pattern of Ellipse [A] in (a).

Fig. 8 (a) Typical TEM image on the top surface of the RTLSP-3 specimen, (b) HRTEM image of Ellipse [A] in (a), and (c) the corresponding SAED pattern of Ellipse [A] in (a).

Fig. 9 (a) Typical TEM image on the top surface of the WLSP-1 specimen, (b) HRTEM image of Ellipse [A] in (a), and (c) the corresponding SAED pattern of Ellipse [A] in (a).

Fig. 10 Schematic illustration on microstructural evolution of RTLSPed specimen and WLSPed specimen showing the formation of surface nanocrystallization and amorphization.