Original Article

Thermal relaxation of residual stress in shot-peened CNT/Al–Mg–Si alloy composites

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ABSTRACT

A carbon nanotubes (CNTs)-reinforced Al–Mg–Si alloy composite was made and shot peened. After shot peening, a compressive residual stress field was generated in shot peened layer. The change law of residual stress and microhardness with annealing time at elevated temperatures (150 °C, 200 °C, and 250 °C) was investigated. An Al–Mg–Si alloy without CNT addition is prepared in the same process to compare with the CNTs/Al–Mg–Si alloy composite to verify the effect of CNTs on residual stress relaxation. Results showed that for the both materials, macro and micro residual stresses in the shot-peened layers decreased firstly due to thermal recovery and then trend to be stable during annealing process. Increasing the annealing temperature could accelerate the speed of stress release and increase the decrement rate. Specially, the addition of CNTs could improve the thermal stability of the macro residual stress created by shot peening.

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1. Introduction

Shot peening (SP) is a forceful and low cost method to improve the superficial properties of metals [1–5]. During shot peening treatment, a massive amount of high-speed “shots” impacted the surface of a part or member. The plastic deformation resulted by shots is resisted by the surrounding material. Consequently, a compressive residual stress field is created in the near-surface region. The performance of shot-peened layers [6–8], such as fatigue strength, stress corrosion property, and microhardness, could be singularly enhanced by the induced compressive residual stress field and changed microstructure [9,10].

Recently, carbon nanotubes (CNTs)-reinforced aluminum matrix composites have attracted increasing effort [11–15] to develop a new generation of lightweight, high-strength, high-stiffness materials. Many methods have been developed to fabricate CNT/Al, such as friction stir-processing (FSP), accumulative roll bonding (ARB) [10–13], nano-scale dispersion (NSD), etc. Meanwhile, many researchers, like Xu, Jiang et al. [11,12] have also paid attention to develop flake powder metallurgy (flake PM) route, which used the CNT/Al flake powders achieved from slurry mixing to fabricate CNT/Al composites with laminate structures of 2D aligned CNT and planar Al grains, to increase the strength and ductility simultaneously. In fields of military devices, electronic and high-speed transportation [16,17], components made by the new material
usually need to be treated by shot peening to further improve the surface properties [18]. Our previous work has investigated the effect of the peening intensity and peening method on compressive residual stress field and microstructure of the peened layer.

As a beneficial factor, the residual stress field induced by SP could be diminished partly in high-temperature environments which is not beneficial for its application. Specially, the relaxation of residual stress would reduce the fatigue performance and work hardening rate of the peened layer. Hence, the residual stress stability in CNTs/Al composites at elevated temperatures must be investigated for its further application. Currently, few investigations have been conducted on the thermal relaxation of the residual stress in the new material. In this study, a CNTs/Al-Mg-Si alloy composite was made and then treated by SP. After SP, its residual stress stability behavior was analyzed. An Al-Mg-Si alloy was prepared in the same way for comparison to investigate the effect of CNTs addition on the thermal stability of residual stress.

2. Experimental methods

In this study, a 1.5-wt.% CNTs-reinforced Al-Mg-Si alloy composite (0.92 wt.% Mg, 0.41 wt.% Si, and 0.21 wt.% Cu) [19] was made by flake powder metallurgy. The multiwall CNTs (~1-2 μm in length and 25 nm in diameter and; Cano [Zhenjiang] Technology Ltd., China) were premixed with ~32 μm diameter near-spherical Al alloy powder for 20 min at 2100 rpm by a high-speed mechanical powder processor. The CNTs were further dispersed by shift-speed ball milling. Ball milling for 9 h at 150 rpm was then conducted to flatten Al powders to flakes with 600 nm in thickness. After that the premixed powders with 1 wt.% stearic acids were initially cold welded to particles with ball milling speed of 250 rpm for 2 h via an attritor. Additional details about the preparation for the composite powder could be found in our recent publications [19,24].

After storage in a vacuum furnace for 2h at 450 °C to eliminate stearic acid, the composite powders were compacted into billets of 80 mm diameter and 120 mm length at 500 MPa. They were then sintered in flowing Ar atmosphere at 510 °C for 3 h and hot extruded into a plate with a 25 mm × 15 mm section with a ram speed of 12 mm min⁻¹ and 450 °C.

Peening treatment was conducted to an Almen intensity of 9 A relative to the SAE-J442 standard by an air blast machine (Catching Machinery Company, China). The diameter and hardness of the ceramic shot are 0.305 mm and 50 HRC (i.e., Rockwell hardness). After peening, isothermal annealing treatment was performed at elevated temperatures (150 °C, 200 °C, and 250 °C). The variance of residual stress fields in the specimens at the elevated temperatures was measured at specific time intervals (i.e., 1, 2, 4, 8, 15, 30, 60, and 120 min). Thin surface layers of the specimens were removed individually via chemical etch method.

Fig. 1(a) and (b) shows the microstructure of the CNTs/Al-Mg-Si composite characterized by transmission electron microscopy (TEM). As shown in Fig. 1(a) and (b), CNTs with diameter around 20 nm and an average length of 80 nm, are uniformly distributed along the near equiaxed-grained grain boundary. Graphitic layers of the CNTs with spacing between two neighboring lattice fringes of ~0.34 nm were shown in Fig. 1(b), which is consistent with the (002) plane of graphite. Fig. 1(c) shows the photo of blocky specimens after shot peening. As can be seen, the surface layer impacted by shots was transformed from smooth to coarse after SP.

X-ray diffraction (XRD) was conducted by the sin^2 θ method to determine the residual stress by measuring the crystal plane spacing of specific planes (usually the {220} planes for Al) using an X-ray stress analyzer (Proto, Ni filter, Cr–K, voltage of 20 kV and current of 15 mA). The XRD analysis of specimens was conducted using the SmartLab X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å) and a scan step of 2° min⁻¹. The microplastic strain was quantified by measuring the fit of the peak profiles of Al in XRD via Rietveld refinement. Specifically, the peak patterns can be fitted via a pseudo-Voigt (PV) function as follows:

\[ I = \sum_{\alpha \in \{a, b, c\}} \frac{I_{0\alpha} \sin^2 \theta}{(1 + \Delta_{\alpha}) \left(1 + \frac{2\pi}{\lambda} d_{\alpha} \sin \theta \right)^2} \left(1 + \frac{2\pi}{\lambda} d_{\alpha} \sin \theta \right)^2 \]

where \( \beta \), \( \Delta \), and \( I_0 \) are the FWHM, Gaussian component, and scale parameters of the PV function, respectively. In addition, \( S = (2\pi - 2\theta) / \beta \), \( \theta \) is the Bragg angle of Kα₁ radiation. The fitting error was refined to be less than 1.5%.

Microhardness was determined using a micro sclerometer with 500 g load and loading time of 15 s. The indenter used was a Vickers diamond pyramid. The microhardness at each time and depth was obtained 10 times, and the average value was determined.

Fig. 1 – The microstructure and photographs of samples before and after shot peening are shown in (a) and (b). Photographs of the composite are shown in (c).
3. Results

3.1. Surface topography after shot peening

3D reconstructions of the surface topography of the specimens after peening are presented in Fig. 2(a) and (b). As can be seen in Fig. 2, after peening treatment the surface roughness of the specimens were changed due to the impact of the shots. The value of $R_a$ of CNT/Al–Mg–Si composite was 65 μm, which was 15% less than that of the Al–Mg–Si alloy.

Higher microhardness usually implied less radius and depth of the crater under the same peening condition. In this study, the initial microhardness of the CNTs/Al–Mg–Si composite was 106 HV higher than that of the Al–Mg–Si alloy (93 HV) because of the dispersion strengthening ability and bearing capacity of CNTs [19]. So the surface topography of CNTs/Al–Mg–Si alloy composite was more smooth than the Al–Mg–Si alloy after SP.

3.2. Residual stresses variations after isothermal annealing

Fig. 3 shows the stabilized residual stress fields at elevated annealing temperatures (i.e., 150 °C, 200 °C and 250 °C). The maximum of CRS was found in the substrate layers consistently but the value decreased rapidly with the rising annealing temperature. Notably, the depths of the maximum compressive residual stress in the two materials were almost constant after annealing. The descending rates of the maximum residual stress were 16% (150 °C), 42% (200 °C), 70% (250 °C) in the CNT/Al–Mg–Si composite and 30% (150 °C), 61% (200 °C), 85% (250 °C) in the Al–Mg–Si alloy.

Fig. 3(c) and (d) shows the statistical analysis of the total distributions of the maximum compressive residual stress in the shot-peened regimes of the two materials fitted by normal distribution functions. This result provided further insight into the difference of the macro residual stresses in the two materials under a close stress level. As can be seen from Fig. 3(c) and (d), the residual stress in CNT/Al–Mg–Si alloy composite and Al–Mg–Si alloy was distributed in Gaussian distribution. The peak of CNTs/Al–Mg–Si alloy composite was much narrower compared with Al–Mg–Si alloy. It indicated that the addition of CNTs could also be the cause of the uniformity in macro residual stress.

To further analyze the stress relaxation behavior during heat treatment, the variance of the maximum residual stress with annealing time of the two materials is measured and plotted in Fig. 4. The results showed that stress relaxation occurred particularly in the first few minutes, and the relaxation rate reached a stable state after 120 min.

Many researchers revealed that the thermally activated mechanism may be expressed via the Zener–Wert–Avrami function, as shown in Eq. (2) [21]:

$$\frac{\sigma_{r}^{S}}{\sigma_{0}^{S}} = \exp[-(At)^{m}]$$

where $m$ is the numerical parameter depended on the relaxation mechanism, $\sigma_{0}^{S}$ is the residual stress of the as-peened samples, $\sigma_{r}^{S}$ is the residual stress after exposure to temperature $T$ for time $t$, and $A$ is the function in the correlation of the elevated temperature. $A$ is expressed as follows:

$$A = B \exp \left( -\frac{\Delta H}{kT} \right)$$

where $k$ is the Boltzmann constant, $B$ is the material constant, $\Delta H$ is the activation enthalpy for residual stress relaxation.

The value of the numerical parameter $m$ could be calculated via fitting the experimental data $\ln(\frac{\sigma_{r}^{S}}{\sigma_{0}^{S}})$ as a linear function of $\ln(t)$ based on Eq. (2). $m$ is the slope of the straight lines, and the activation enthalpy for the residual stress relaxation, $\Delta H$ was identified via regression analysis based on the intercept.

As shown in Fig. 5, the experimental data were nearly linear at each fixed temperature and displayed a good fit. The values of the slope of the two materials were almost constant under elevated temperatures. $\Delta H$ for the CRS relaxation of the two materials was determined to be 1.35 eV and 1.12 eV, respectively. The residual stress of CNT/Al–Mg–Si composite showed a higher stability than that of Al–Mg–Si alloy.

3.3. Dislocation density variations after isothermal annealing

During the SP process, domain sizes were refined and many dislocations were induced in the surface layers due to severe deformation. The micro residual stress (the second and third types of internal residual stress) was mainly resulted by local lattice distortions, and could be reflected by the dislocation density. As a statistical average value, the dislocation density acquired via Rietveld refinement based on the XRD patterns was appropriate. Fig. 6(a) and (b) shows the variation in the XRD pattern and dislocation density—depth distribution of the two materials. The maximum dislocation density was

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**Fig. 2** – 3D reconstructions of surface topography ((a) CNTs/Al–Mg–Si composite and (b) Al–Mg–Si alloy).
Fig. 3 – Residual stress along with depth ((a) CNT/Al–Mg–Si composite and (b) Al–Mg–Si alloy) and statistical analysis of the initial surface residual stress distributions by using normal distribution functions ((c) CNT/Al–Mg–Si composite and (d) Al–Mg–Si alloy).

Fig. 4 – Maximum residual stress relaxation with annealing time at elevated temperatures: (a) Al–Mg–Si alloy and (b) CNT/Al–Mg–Si composite.
observed at the surface layer. Moreover, the values decreased gradually with depth. The depth of work hardening layers was around 200 μm where the residual stresses reached their maximum value.

The variation in surface dislocation density during thermal treatment (Fig. 7) was analogous to that of residual stress; it initially decreased and then became stable with increasing annealing time and temperature. The Zener–Wert–Avrami function [21–23] could be applied again to calculate the activation enthalpy of the dislocation density throughout the annealing process.

The dislocation density values of the samples during annealing substituted the ratio $\frac{\sigma_{\text{RS}}}{\sigma_0}$ in Eq. (1). Subsequently, $m_{\text{composite}} = 0.53$ and $m_{\text{alloy}} = 0.51$ for the composite and alloy, respectively, could also be achieved via regression analysis. The activation enthalpy of the dislocation density during annealing could be acquired by measuring the slope of $\lg(t)$ versus $1/T$. The activation enthalpies for the composite and alloy were 1.12 eV and 1.09 eV, respectively. As can be seen, the activation enthalpy for the dislocation density relaxation was smaller than that of the macro residual stresses of the materials. Meanwhile, the addition of CNTs could only slightly be contributed to the stability of the micro residual stress/dislocation density.

### 3.4. Microhardness variations after isothermal annealing

A similar reduction occurred with the annealing time between the microhardness profiles and dislocation density. The work hardening levels based on macro and micro residual stress were correlated with the local yield strength and could be generally indicated by the variation in microhardness. As shown in Fig. 8, the microhardness profiles dropped at elevated temperatures for 120 min, and the detected maximum microhardness was observed in the initial time and almost 68% higher than the final value. This result was in good agreement with the trends of the dislocation density and CRS. Moreover, the microhardness became stable with increasing time. In general, the decrease rate of the highest value was approximately 23% (150°C), 29% (200°C), and 35% (250°C) for the CNTs/Al–Mg–Si composite and 27% (150°C), 32% (200°C), and 38% (250°C) for the Al–Mg–Si alloy.

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**Fig. 5** – Influences of annealing temperature and exposure time on residual stresses in $\lg(-\ln \frac{\sigma_{\text{RS}}}{\sigma_0})$ vs. $\lg(t)$ diagram. (a) CNTs/Al–Mg–Si composite and (b) Al–Mg–Si alloy.

**Fig. 6** – Dislocation density variance in the maximum residual stress layer with annealing time and depth distribution after annealing treatment.
4. Discussion

Shot peening could result repeated dimpling at the surface with uniform surface coverage, severe deformation happens during the process, and thereby a cold-worked layer with residual stress field and high dislocation density is generated. The induced compressive residual stress field and dislocations are also the main reasons why microhardness increased.

During shot peening, the CNTs dispersed in the grain boundary could bear the impact load of the shots and hinder the grain boundary rotation. Thus, the maximum residual stress of CNT/Al-Mg-Si alloy composite was lower than Al-Mg-Si alloy under the same peening intensity. In annealing process, grain boundary sliding and dislocation motion were caused by thermal activity resulting in the macro residual stress relaxation of the two materials [25–27]. Meanwhile, increased residual stress relaxation occurs at a high applied temperature and remarkable reduction in yield stress was generated. Therefore, the decrease in the macro residual stress was strongly correlated with the annealing temperature and exposure time. With increasing annealing and exposure times, the decrement of the macro residual stress increased. The final relaxation rate is mostly subjected to thermal activation energy [28]. It is often independent of temperature but dependent on the relaxation mechanism. High thermal activation energy generally indicates high stress stability. Hence, the difference in the thermal relaxation mechanism and thermal stability on the macro residual stress of the two materials in this study could be presented by the thermal activation energy. Compared with the Al-Mg-Si alloy, the CNT/Al-Mg-Si alloy composite demonstrated that thermal stability of residual stress could be enhanced with CNT addition, by hindering the rotation of grain boundary.
Meanwhile, after annealing treatment, the completely diminished macro residual stress did not indicate the complete disappearance of dislocation. The macro stress was in an unstrained state, whereas the micro stress persisted in the grain dimension equilibrium. Thus, the dislocation density showed higher thermal stability than the macro residual stress. Grain boundary sliding could also accelerate the reduction in the macro residual stress.

5. Conclusions

The residual stress relaxation of a CNTs/Al–Mg–Si alloy composite treated by SP was investigated at elevated annealing temperatures. The residual stress could be categorized into macro stress (type I) and micro stress (types II and III). These stresses decreased firstly and trend to be stable during annealing treatment. The decreased rate of micro residual stress characterized by the dislocation density is higher than the macro residual stress under the same annealing temperature. This result could be explained by comparing the thermal activation enthalpies. Meanwhile, the addition of CNTs could improve the thermal stability of the macro residual stress but only slightly contributed to the relief of micro residual stress.

Conflicts of interest

The authors declare no conflicts of interest.

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