Single-layer graphene oxide reinforced metal matrix composites by laser sintering: Microstructure and mechanical property enhancement

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Single-layer graphene oxide reinforced metal matrix composites by laser sintering: Microstructure and mechanical property enhancement

Dong Lin, C. Richard Liu, Gary J. Cheng

Abstract

This study investigates the integration of single-layer graphene oxide (GO) powders with iron matrix by laser sintering and its effects on mechanical strength and fatigue life. A laser-based additive manufacturing process is used to sinter GO and iron powders, and form GO–Fe nanocomposite materials. The aggregation of GO powders was prevented by the fast laser heating and cooling process. In addition, the evaporation of polyvinyl alcohol, which acted as a dispersing agent, from the cross-section helps align the GOs vertically in the cross-section. An energy-dispersive X-ray spectroscopy map from cross-sectional scanning electron microscopy images and Raman patterns together demonstrate the reduction of GOs after laser sintering. The GO–matrix interfacial structure was investigated by transmission electron microscopy. GOs were found to be stretched due to the rapid heating and cooling process during laser irradiation. Strengthening mechanisms of tensile strength and Young’s modulus were developed based on the laser sintering results. Surface microhardness was increased by 93.5% by laser sintering of 2 wt.% GO. The improvement in the fatigue life after laser sintering of GO-reinforced iron matrix nanocomposites was also investigated.

Keywords: Laser sintering (LS); Single-layer graphene oxide; Metal matrix nanocomposites; Strengthening; Fatigue life

1. Introduction

Enhancing the strength of metals through microstructure design is very important for structural materials [1]. Controlling the microstructures, including grain boundaries, precipitates, dislocation forests or solute atoms, plays a key role in the design of materials with desired properties [2]. In general, microstructures that impede dislocation glide can lead to a significant increase in metal strength because plastic deformation mainly occurs via dislocation movement [3]. Embedding nanomaterials into a metal matrix to hinder dislocation sliding has attracted much attention in recent years.

Graphene oxide (GO) is an important material widely used to synthesize graphene and is considered as graphene functionalized by oxygen-containing groups [4,5]. Different research groups have contributed to revealing the functional groups of GO [6–10]. GO possesses some unique properties, which are distinctly different from those of graphene due to the existence of surface functional groups. GO has the potential for application in many fields, including microelectronic and chemical devices [11–13], energy storage [14,15] and composite materials [16]. The mechanical properties of graphene and GO have been investigated extensively by both experimental and theoretical approaches [4]. Experiments on bulk graphite yield [17] 1.02 ± 0.03 TPa for the in-plane Young’s modulus. Lee
et al. [18] used nanoindentation to measure the elastic properties and intrinsic breaking strength of free-standing monolayer graphene membranes; the measured Young’s modulus was \( E = 1.0 \pm 0.1 \) TPa. Jiang et al. [19] investigated the Young’s modulus of graphene through the intrinsic thermal vibration and molecular dynamics simulation, and found that the Young’s modulus is in the range of 0.95–1.1 TPa at temperatures of between 100 and 500 K. Robinson et al. [20] measured the Young’s modulus of reduced GO as 185 GPa through thermal annealing and analysis of the frequency response of suspended membranes. Suk et al. [4] found that the Young’s modulus of graphene oxide relates to the number of layers: the measured Young’s modulus of single-layer, two-layer and three-layer GO membranes were 223.9 ± 17.7, 444.8 ± 25.3 and 665.5 ± 34.6 GPa, respectively. These experimental results demonstrate the superb mechanical properties of graphene and GO.

GO has been used in polymer and metal matrix composites to enhance their mechanical properties. For instance, Bortz et al. [21] studied the fatigue life and fracture toughness by adding GO to epoxy matrix composites. It was found that the crack was pinned by GO, which helps increase the fatigue life of epoxy matrix composites. Wang et al. [22] determined that the tensile strength of GO-reinforced aluminum matrix composites was enhanced by 62% with 0.3 wt.% GO. However, manufacturing high-quality graphene-reinforced metal composite is still a challenge due to the aggregation of graphene nanoplatelets with current techniques and our lack of understanding of the GO–matrix interface. Recently, the interaction of graphene with metals and its effects on mechanical property has been studied. The strength of graphene or GO-reinforced metal composites was investigated by Wang et al. [22]. The enhanced strength of graphene/copper was discussed by Hwang et al. [23] and by Pavithra et al. [24]. The mechanism of dislocation blocking by graphene was investigated recently in Kim et al. [1]. However, there has been no systematic study of the mechanical properties of graphene–metal nanocomposite, especially fatigue performance. In this paper, we study laser sintering of single-layer GOs and iron powders to make GO–Fe nanocomposites with GOs uniformly distributed in the matrix. The fundamental mechanism underlying the enhancement in mechanical properties, i.e. elastic modulus, strength and fatigue life, will be investigated. The chemical distribution, interfacial structure of GO–Fe and the atomic structure of GO after laser sintering will be studied to help understand the mechanical property enhancement.

2. Experimental method

Iron powders were mixed with GO using polyvinyl alcohol (PVA) as a dispersing agent. AISI 4140 plate was chosen as the substrate. The samples were first austenitized at 850 °C for 20 min followed by oil quench and then tempered at 450 °C for 2 h and naturally cooled down to room temperature in a vacuum furnace. The iron powders (average diameter 4 μm) and single-layer GO (from Cheaptube Inc.) were laser sintered. The thickness of GOs is 0.7–1.2 nm (by atomic force microscopy) and the sizes of single-layer GO are in the range of 300 nm to several micrometers in XY dimensions. The concentration of GO in the Fe–GO nanocomposites was 2 wt.%. GOs were separated in the coated layer by PVA and randomly distributed over the cross-section.

An IPG fiber laser was used as a laser sintering energy source; it was operated with a laser power of 100 W and a frequency of 50 kHz. The pulse duration and wavelength were 220 ns and 1064 nm, respectively. The beam size is 0.8 mm, while the scanning speed and step size were 2 mm s⁻¹ and 0.25 mm, respectively. Before laser sintering, the GO and iron powder were mixed together using a magnetic stirrer in water using PVA as a dispersing agent. PVA (4 wt.% of total solution) was used to separate GO [25,26]. After that, the mixed powders were coated on the sample surface. The substrate surface was mechanically polished with 0.05-μm grade aluminum oxide powder before coating [27–31].

Samples after laser sintering were prepared for Raman measurement. The surface and cross-sectional morphologies were characterized by a Hitachi S-4800 field emission scanning electron microscope and an FEI Philips XL-40 scanning electron microscope, respectively. A FEI Nova 200 focused ion beam (FIB) system was used to prepare transmission electron microscopy (TEM) samples by the lift-out method. The microstructure TEM images were obtained with an FEI Titan system operating at 300 kV.

Three-point bending fatigue test was performed in a 100 kN MTS servohydraulic fatigue test machine. In loading-control mode, a sine wave function with frequency of 10 Hz was loaded. The stress ratio \( R \) equals 0.1, where \( R = \sigma_{\text{min}}/\sigma_{\text{max}} \) (\( \sigma_{\text{min}} \) and \( \sigma_{\text{max}} \) are minimum and maximum stress, respectively). The maximum bending stress is \( \sigma = 3PL/2bh^2 \), where \( P \) is the applied load, \( L \) is the span for the bending fatigue test, \( b \) is the width of the specimen and \( h \) is the thickness of the specimen. All the tests were carried out at room temperature.

3. Results and discussion

3.1. Cross-sectional morphology and chemical analysis after laser sintering

During laser irradiation, iron powders were melted into liquid and PVA was evaporated from iron liquid as bubbles. These PVA bubbles helped to align the GOs vertically in the cross-section of the laser-sintered layer. The schematics of the aligning process before and after laser sintering are shown in Fig. 1a and b. The cross-sectional microstructure of the laser sintered layer is shown in Fig. 1c. Energy-dispersive X-ray spectroscopy (EDS) maps of carbon and iron are shown in Fig. 1d and e, respectively. It can be clearly seen in Fig. 1d that the GOs are vertically aligned in the cross-section of the iron matrix. A thin layer
of Fe–GO nanocomposites was coated on the substrate after laser deposition.

An enlarged view of GOs surrounded by matrix after laser sintering is shown in Fig. 2a. The EDS map of carbon, oxygen and iron in Fig. 2a is shown in Fig. 2b–d, respectively. The EDS map of carbon (yellow) in Fig. 2b shows the continuous shape of GO, which proves that GOs survived laser sintering. The yellow areas turn to be the dark region in the EDS map of iron, which is shown in Fig. 2d. The X-ray image result is shown in Fig. 2e. The “C” peak confirms the existence of carbon. Formation of GO involves reaction of graphite with strong oxidizers such as sulfuric acid, nitric acid, potassium chlorate and potassium permanganate [32]. The \( d \)-spacing of GO is increased by introducing oxygen-containing functional groups and the hybridization of oxidized carbon atoms is changed from planar \( sp^2 \) to tetrahedral \( sp^3 \) [5,32].

Thermal exfoliation and reduction of GO were conducted by heating GO in a furnace [32,36]. Exfoliation of the multilayer graphite structure occurred through generation of carbon dioxide by heating GO to 1050 °C [32]. Enormous pressure, 40 MPa at 300 °C and 130 MPa at 1000 °C, was created by the high-temperature gas [32]. The gas pressure was much larger than the pressure (2.5 MPa), which is generated by van der Waals force, needed to separate two stacked GO platelets [32]. Carbon oxide is released from decomposing functional groups on GO. This exfoliation mechanism can be also used to explain the lack of oxygen for GOs marked on the left in Fig. 2c. The oxygen for these GOs on the left side have escaped from the GO by rapid heating during laser sintering. The temperature during laser sintering was above the melting point of iron, which is \( \sim 1600 \) °C. Table 1 shows the weight ratio and atomic ratio of iron, carbon and oxygen in Fig. 3a. It also demonstrates the existence of GO with functional groups.

3.2. Thermal reduction of GOs by rapid heating and cooling

It is well known that melting of nanoparticles is different from melting of bulk crystals [27]. Melting of 2-D crystals is usually described in terms of the creation of topological defects, such as unbound disclinations and dislocations [37]. Based on simulations, the melting temperature of graphene is \( \sim 3200 \) °C, which due to a lack of experimental or simulation results is estimated to be close to graphene [38]. The melting temperature of GO is much higher than that of iron powders. This helps the GO to survive during the rapid heating process. With selected laser sintering conditions, iron powders were melted since iron has a low melting temperature of 1600 °C, i.e. much lower than the melting point of GOs [26].
Fig. 3 compares the Raman spectra of samples before and after laser sintering. The main features in the Raman spectra of the coated samples are $G$ and $D$ peaks, which are referred to GO. Raman spectra of laser sintered samples typically show the presence of the $G$, $D$ and $2D$ peaks, which link to reduced GO [39]. The $G$ peak is due to the bond stretching of all pairs of $sp^2$ atoms in both rings and chains, while the $D$ peak is related to the breathing modes of $sp^2$ atoms in rings [40]. The attachment of

![Fig. 2. (a) SEM of GOs in the cross-section of GO–Fe nanocomposites after laser sintering; (b) carbon, (c) oxygen and (d) iron EDS map of (a); and (e) X-ray spectrum of cross-section after laser sintering.](image)

![Table 1](table)

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<tr>
<td>FeK</td>
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<td>19.42</td>
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hydroxyl and epoxide groups on carbon basal plane causes the prominent D peak [39]. The variation of relative intensities of G and D bands of GO and reduced GO usually reveals the alternation of electronic conjugation states [41]. After laser sintering, the value of $I_D/I_G$ reduces from 2.886 (after coating) to 1.724, which means the defect density decreased after laser sintering and functional groups were partially released during laser sintering [32].

3.3. Interfacial microstructure between GO and iron matrix

Carbide is formed by metals reacting with carbon by the following [42]:

$$\frac{x}{y} M + C = \frac{1}{y} M_x C_y.$$  \hspace{1cm} (1)

Carbon nanotubes (CNTs) are exceptionally stable due to their near-perfect structure. They are also chemically stable since the carbon atoms are equally $sp^2$ bonded to the (0001) plane of graphite. The bonding between the in-plane carbon atoms in graphene is $\sigma$ bonding, which results in high mechanical strength [42]. The $\pi$ bond formed by overlapping of the out-of-plane orbitals enhances the thermal and electrical properties by ballistic transport [42]. Carbides form preferentially by $\sigma$ bond formation [43]. Weak interaction occurs in the side contact condition through weak bonds formed by out-of-plane orbitals [43]. Due to the stable nature of the basal plane of graphene, carbide formation is not favored at the side contact [42]. The end contact interaction, through the $\sigma$ bond formation, tends strongly to result in the formation of carbides at the interface [42]. Weak interaction occurs in side contact condition through weak bonds formed by out-of-plane orbitals [42]. The defects in CNTs with $sp^3$ bonded carbon atoms and exposed to (1010) planes may react with metals, forming side-contacted carbides [42].

An important issue for the fabrication of metal matrix nanocomposites is the wetting between metals and nanomaterials. According to Young’s equation, the contact angle is expressed as [44]:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{LV}},$$  \hspace{1cm} (2)

where $\theta$ is the wetting angle, and $\gamma_{SV}$, $\gamma_{LS}$ and $\gamma_{LV}$ are the surface energies at the solid–vapor, liquid–solid and liquid–vapor interfaces.

The Young–Dupre relation is given as follows [44]:

$$W_A = \gamma_{LV} (1 + \cos \theta).$$  \hspace{1cm} (3)

The smaller the contact angle, the better the wetting. The surface free energy at room temperature was derived as follows: graphite, 54.8 mJ m$^{-2}$; GO, 62.1 mJ m$^{-2}$; graphene, 46.7 mJ m$^{-2}$ [45].

The critical thickness for carbide formation is [42]:

$$t_{Crit} = -\frac{V_M}{\Delta y} \frac{\Delta G'}{\Delta G'},$$  \hspace{1cm} (4)

where $V_M$ is the molar volume of the carbide formed, $\Delta G'$ is the free energy of formation per mole of carbide, $\Delta y = \gamma_{MC}/CNT + \gamma_{MC}/Alloy - \gamma_{Alloy/Carbon}$ is the increase in the total surface energy as a result of the formation of new interfaces; subscript MC indicates metal carbide. The formation of carbide would decrease the contact angle of liquid alloy and CNT or GO, which will increase the wetting. Smaller $t_{Crit}$ value means easier formation of carbide and better wetting.

Figs. 4 and 5 represent TEM images and X-ray diffraction (XRD) results of a representative microstructure of the interface between GO and iron matrix after laser sintering. A bright-field high-resolution (HR) TEM image of a typical interfacial microstructure is shown in Fig. 4. It clearly demonstrates a distance of 0.25 nm in the parallel direction between each hexagonal cell of GO, which is marked at the upper right part of Fig. 4. For a body-centered cubic (bcc) crystal, $a = 0.29$ nm, which is also presented in the lower left part of Fig. 4. Cementite (Fe$_3$C) was generated by end contact interaction and is identified as a (202) plane with an atomic distance of 0.19 nm. The formation of cementite at the edge of GO proves the theoretical prediction of carbide generation occurring preferentially at the end side [42]. This is due to the stable nature of the basal plane of a graphene sheet [42]. The HRTEM image provides direct evidence of the survival of GOs after laser sintering. The XRD pattern was used to detect the generated iron carbide on the coated layer and after laser sintering. Cementite peaks were found on the XRD curve after laser sintering. These peaks further prove the theory that iron carbide is generated by the end side contact.

3.4. GO stretched by laser sintering due to rapid heating and cooling

Fig. 6 shows TEM images of GOs in the cross-section of the iron matrix after laser sintering. Single-layer GOs are
embedded into the iron matrix, as shown in Fig. 6a. The Fe–GO interfacial area is represented in Fig. 6b, and in Fig. 6c at higher magnification. The TEM images show that GO and iron matrix bond together coherently. Iron atoms present a rectangular shape because of the bcc structure \((a = 0.286 \text{ nm})\). Iron matrix is mainly located in the left area in Fig. 6a, while the GO is located in the right. The atomic distance of iron matrix in Fig. 6c is 0.20 nm, which is the \((110)\) direction of iron. The lattice structure of GO after laser sintering is also shown in the carbon hexagon unit (Fig. 6c). The distance between each grid of carbon atoms in the graphene plane is supposed to be 0.246 nm. However, the atomic distance in Fig. 6c is different from this value. The measured atomic distances in the \(a, b\) and \(c\) directions are 0.185, 0.195 and 0.278 nm, respectively. The reason for the alternation of atomic distance is the tension stress applied in the \(c\) direction (see Fig. 6d), which may be caused by fast heating and cooling during and after laser sintering. The defect due to the GO is also marked in Fig. 6c, and may be related to the decomposition of functional groups by laser sintering or rapid consolidation [32].

3.5. Tensile strength of GO-reinforced metal nanocomposites

Due to the reaction and new phase formation at the GO–Fe matrix interface, the strength of the nanocomposite is limited by the shear strength of the interfacial phase [42]. The strength of interphase would affect the load transfer from matrix to the GOs. In order to fracture a film fabricated from a nanocomposite, it is necessary to break the two components of the fracture surface [46]. The force, \(F_B\), required for the failure can be expressed as [46]:

\[
F_B = \sigma_p A_{bulk} + \sigma_{\text{shear}} A_{\text{interface}} = \sigma_C A, \tag{5}
\]

where \(\sigma_p\) is the matrix tensile strength, \(A_{bulk}\) is the area of bulk component of the fracture surface, \(\sigma_{\text{shear}}\) is the shear strength of metal carbide and \(A_{\text{interface}}\) is the area of the interface component of the fracture surface. In addition, \(\sigma_C\) is the tensile strength of nanocomposite and \(A\) is the cross-sectional area of the nanocomposite.

The volume fraction of GO can be written as:

\[
V_f = \frac{V_{GO}}{V} = \frac{N \pi r_{GO}^2 h}{V}, \tag{6}
\]

where \(V_{GO}\) is the total volume of GO, \(N\) is the total number of GO, \(r_{GO}\) is the average radius of GO, \(h\) is the average thickness of GO and \(V\) is the total volume of the nanocomposites.

In nanocomposite, each GO can be considered as occupying a certain volume; this volume per GO, \(V_{GO-M}\), can be found by rearranging Eq. (6):

\[
V_{GO-M} = \frac{V}{N} = \frac{\pi r_{GO}^2 h}{V_f}. \tag{7}
\]

If we model the volume per GO as a rectangular solid with height \(2r_{GO}\) \((z\) direction) and the values in the \(x, y\) directions are \(2r_{GO}\) and \(l\) when we assume the GOs are vertically aligned in the cross-section of the rectangular solid, then we have:

\[
V_{GO-M} = 4r_{GO}^2 l. \tag{8}
\]

Given

\[
l = \frac{\pi h}{4V_f}, \tag{9}
\]

we can assume there are \(n\) GOs in the cross-section, and \(n\) is given by:

\[
n = \frac{A}{2r_{GO} l} = \frac{2AV_f}{\pi hr_{GO}}. \tag{10}
\]

This allows us to calculate \(A_{bulk}\) and \(A_{\text{interface}}\) in Eq. (5). If we cut a certain volume of nanocomposite at \(z\) direction randomly, we would cut the GO from the cross-section with a value from 0 to \(2r_{GO}\). The average value of the cross-section is \(\pi r_{GO}/2\). The bulk component, \(A_{bulk}\), is given by the cross-section filled with metals:

\[
A_{bulk} = A - n\pi hr_{GO}. \tag{11}
\]

The interface area of all the GO protruding from the fracture surface is:

\[
A_{\text{interface}} = 2nh_{in}, \tag{12}
\]

where \(h_{in}\) is the thickness of the interfacial area.

Combining Eqs. (5), (10), (11) and (12) together, we have:

\[
\sigma_C = \left( \sigma_{\text{Shear}} \frac{2h_{in}}{r_{GO}} - \pi \sigma_p \right) \frac{2}{\pi} V_f + \sigma_p. \tag{13}
\]

3.6. Young’s modulus of GO-reinforced nanocomposites

Halpin and Tsai developed a model based on Hill’s model [47] in order to predict the Young’s modulus of nanocomposites. The Halpin–Tsai model can be modified
when considering randomly oriented CNT-enhanced composites [25, 48]:

\[
\frac{E_C}{E_M} = \frac{3}{8} \left[ 1 + \frac{(2l/D) \eta_L V_{CNT}}{1 - \eta_L V_{CNT}} \right] + \frac{5}{8} \left[ 1 + 2 \eta_T V_{CNT} \right],
\]

\[\eta_L = \frac{E_{CNT}/E_M - 1}{E_{CNT}/E_M + 2 l/D},\]

\[\eta_T = \frac{E_{CNT}/E_M - 1}{E_{CNT}/E_M + 2},\]

where \(l\), \(D\) and \(V_{CNT}\) are the length, diameter and volume fraction of CNTs, and \(E_C\), \(E_{CNT}\) and \(E_M\) are the tensile Young’s modulus of the composite, CNT and matrix, respectively.

In order to apply the Halpin–Tsai model to 2-D GO-enhanced metal matrix, the GO is considered to be circular in shape and of a certain thickness. The modified Halpin–Tsai model for 2-D enhanced nanocomposites can be written as:

\[
\frac{E_G}{E_M} = \frac{3}{8} \left[ 1 + \frac{(4r_{GO}/h) \eta_L V_{GO}}{1 - \eta_L V_{GO}} \right] + \frac{5}{8} \left[ 1 + 2 \eta_T V_{GO} \right],
\]

\[\eta_l = \frac{E_{GO}/E_M - 1}{E_{GO}/E_M + 4 r_{GO}/h},\]

where \(r_{GO}\) is the radius of GO.

Fig. 6. (a) TEM images of GOs in the cross-section; (b) HRTEM of GO and iron interface; (c) higher magnification of (b) showing the atomic arrangement; and (d) measured distance of the atomic layer in the a, b and c directions in (c).
\[ \eta_T = \frac{E_{GO}/E_M - 1}{E_{GO}/E_M + 2}, \quad (15) \]

where \( r_{GO}, h \) and \( V_{GO} \) are the average radius, average thickness and volume fraction of GO, and \( E_G, E_{GO} \) (444.8 GPa) and \( E_M \) (211 GPa) are the tensile Young's modulus of the composite, GO and matrix, respectively. This equation can be also applied to calculate the Young’s modulus of the graphene- and GO-enhanced metal matrix. The values of \( r_{GO} \) and \( h \) used for the calculation are 250 and 0.95 nm. The density of iron and GO are 7.874 and 2.28 g cm\(^{-3}\), respectively.

The Young’s modulus obtained by integrating different volume ratios of GO into iron matrix is calculated in Fig. 7. The Young’s modulus of the curve represents a linear relationship with volume ratio of GO, since the Halpin–Tsai model considers a uniform distribution of GOs in the matrix. It is necessary to add an exponent term to further modify the model when the weight ratio is higher than 2 vol.% because of the dispersing issues and voids in the nanocomposite model when the weight ratio is higher than 2 vol.% because of the dispersing issues and voids in the nanocomposite cross-section \([42,49]\). The exponent term needs to be adjusted for each material. However, the calculated results are still reliable when the volume ratio is \(<2\% \) (see Fig. 8).

3.7. Strengthening mechanism

Surface microhardness is related to dislocation density: \( H = H^* + \alpha G b / \rho \), where \( H^* \), \( \alpha \), \( G \) are material constants, \( b \) is the Burgers vector and \( \rho \) is the dislocation density \([50]\). The surface microhardness of the as-received material is 310 VHN. The scanning speed is fixed at 2 mm s\(^{-1}\). The surface hardness of laser-deposited iron increases with increasing laser intensity, which may be caused by the higher solidification rate. The surface hardness increases to 500 VHN when the laser intensity is 5000 W cm\(^{-2}\), which means a higher dislocation density was generated after laser sintering. The surface hardness of laser-deposited 2 wt.% GO is further increased to 600 VHN, which is \( \sim 93.5\% \) of the value of the base material.

\[ \Delta \sigma = \alpha \mu b \rho^{1/2}, \quad (16) \]

where \( \Delta \sigma \) is the increase in tensile strength, \( \mu \) is the shear modulus of matrix and \( \alpha \) is the geometric constant, which is normally 1.25. The density of dislocation is calculated by \([51]\):

\[ \rho = \frac{B V_{GO} \varepsilon}{b (1 - V_{GO})} \frac{1}{t}, \quad (17) \]

where \( B = 8 \) for the platelet, \( V_{GO} \) is the volume fraction of nanomaterials and \( t \) is the smallest dimension, here \( t = 2r_{GO} \), of the 2-D GO \([51]\):

\[ \varepsilon = \Delta CTE \times \Delta T, \quad (18) \]

where \( \Delta CTE \) is the difference between the thermal coefficients of the expansion of iron matrix \((11.8 \times 10^{-6} \text{K}^{-1})\) and GO \((-8.0 \pm 0.7) \times 10^{-6} \text{K}^{-1}) \) \([52]\) and \( \Delta T \) is the difference between the previous annealing and test temperatures. The estimation dislocation density generated by thermal mismatch is around \( 1.45 \times 10^{14} \text{m}^{-3}\).

3.8. Fatigue life enhancement

Stress–lifespan (S–N) tests were conducted for two process conditions: (i) laser-sintered iron; and (ii) laser-sintered 2 wt.% GO in the iron matrix. The effect of laser-sintered iron and laser-sintered 2 wt.% GO on fatigue performance were compared in terms of both fatigue strength and fatigue limit \([26,53,54]\). It can be clearly seen in Fig. 9 that laser sintering with 2 wt.% GO results in a better fatigue performance. For example, for a fatigue life of 300,000 cycles, the fatigue strength for laser-sintered iron and laser-sintered 2 wt.% GO is approximately above 500 and 600 MPa, respectively. In addition, for applied stress of 800 MPa,
the fatigue lives of laser-sintered iron and laser-sintered 2 wt.% GO are about 55,978 and 149,666 fatigue cycles. The fatigue life of laser-sintered 2 wt.% GO has increased 167% compared to laser-sintered iron. Along with other popular surface treatment techniques, such as laser shock peening, shot peening and deep rolling, the laser sintered Fe–GO nanocomposites also represents a great improvement in fatigue life for the high-cycle regime compared to the low-cycle regime [55].

Fatigue life until failure consists of two periods: the crack initiation period and the crack growth period [51]. Fatigue is a surface phenomenon when it is the crack initiation period, but is no longer a surface phenomenon when it transfers to the crack growth period. These two periods are a consequence of cyclic slip [51]. During fatigue test, plastic deformation occurs preferentially on the surface grains since it is less constrained. The cross-section after fatigue test of matrix and laser-sintered 2 wt.% GO were investigated in Fig. 10a and c, while Fig. 10b and d show their top surface, respectively. Fig. 10b clearly shows that cracks were initiated on the top surface of as-received sample after fatigue. However, the sample surface after laser sintering of 2 wt.% GO was strengthened and it was not easier for cracks to initiate from the surface, thus improving the fatigue life. The thickness of the laser sintering was ∼50 µm, which is not enough to affect the crack propagation process. The striations generated during the crack growth period are presented in Fig. 10a and c.

Fatigue life until failure consists of two periods: the crack initiation period and the crack growth period [56]. Fatigue is a surface phenomenon when it is the crack initiation period, but is no longer a surface phenomenon when it transfers to the crack growth period. These two periods are a consequence of cyclic slip [56]. During fatigue test, plastic deformation occurs preferentially on the surface grains since it is less constrained. The MMNCs strengthen metal matrix mainly by dislocation strengthening and blocking dislocation movement [57]. Laser-deposited nanocomposites also offer such advantages. This technique provides a greater hardness enhancement, higher dislocation density, and better dislocation pinning by embedding GO. Higher hardness results in higher dislocation density, due to the thermal mismatch of cooling after laser sintering. All of these help to increase resistance of crack
Crack pinning by GO was observed, which also helps to improve the fatigue life during the crack propagation period [21]. It is shown in Fig. 11 that cracks have been pinned at the normal direction of the shear direction. Fig. 11b shows the area marked in Fig. 11a, indicating that the GO plate was torn off from the iron matrix. The evenly distributed residue left on the GO surface indicates that the crack propagates along the GO–Fe interface and also that GOs were coherently integrated with the iron matrix after laser sintering. GO was torn into several small pieces, demonstrating the great strength of the interfacial area. Therefore, laser sintering of GO into metal matrix is proven to be an effective way to improve the fatigue life according to the three-point bending test.

4. Conclusion

In this paper we demonstrate the successful integration of single-layer GOs into iron matrix. The microstructures were characterized by SEM, TEM and Raman spectroscopy. The reduction of GO by laser sintering was demonstrated by EDS mapping and Raman spectroscopy. TEM images show coherent bonding between GOs and iron matrix, as well the stretch applied to the GO by the fast heating and cooling process. A model to calculate the tensile strength and Young’s modulus of GO–Fe nanocomposites has been developed. Surface hardness was improved greatly by laser sintering GO into iron matrix. Three-point bending fatigue life was also increased by integrating GO into iron matrix. The mechanisms of strengthening and fatigue life enhancement were investigated.

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