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Laser induced domino exfoliation of graphite to graphene in spheroidal graphite cast iron

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ABSTRACT

A Fe-based coating of 400–500 μm thickness was achieved after laser surface irradiation of spheroidal graphite cast iron, and the volume loss of spheroidal graphite cast iron was 4.4 times of Fe-based coating. It was demonstrated that, spheroidal graphite was domino exfoliated to spirally assembled graphene after laser irradiation. Owing to the good laser absorptivity of graphene, laser induced selective photothermolysis of graphene occurred. The heat of photothermolysis was transferred to graphite, due to the good thermal conductivity of graphene. Continuous selective photothermolysis and heat transfer led to the domino exfoliation of graphite to graphene. Induced by heat flow force and exfoliation force, the exfoliated graphene was spirally assembled.

1. Introduction

Ever since the first invention in 1943, spheroidal graphite cast iron has been widely used for almost one century. Because of the spherical morphology of graphite in spheroidal graphite cast iron, a combination of good strength, ductility and toughness has been achieved. Due to the low strength nature of graphite, however, its wear resistance is still not satisfactory.

More recently, the excellent mechanical properties of graphene have drawn numerous attentions [1,2]. Structurally, graphene is the mother of graphite. Graphene has been synthesized from chemical or mechanical exfoliation of graphite [3,4], and laser induced graphene growth from graphite has been reported [5]. Induced by laser irradiation, exfoliation of graphite to graphene in spheroidal graphite cast iron may be feasible.

However, the graphite and iron base of cast iron exhibit largely different melting points. The melting point of iron base is 1808 K, much lower than 3773 K of graphite. High temperature exfoliation of graphite by laser irradiation may destroy the iron base of spheroidal graphite cast iron. Furthermore, graphene is easily oxidized by oxygen under air conditions. Up to now, graphene is rarely found during conventional laser surface treatment of irons and steels.

Selective photothermolysis is defined as the precise targeting of structures or tissues by a specific wavelength of light, and it has been adopted for cancer treatment, to selectively remove the pathological changes of human bodies [6,7]. By absorbing light into the target alone, sufficient heat is produced to damage the target, with the surrounding region remaining undamaged. Because graphite exhibits a much higher ratio of laser absorption than iron base [8], laser selective photothermolysis may occur, exfoliating graphite to graphene and avoiding the destruction of the surrounding iron base during laser irradiation.

Herein, domino exfoliation of graphite to graphene was achieved during laser surface irradiation of spheroidal graphite cast iron under argon atmosphere, and the influence of laser selective photothermolysis upon domino exfoliation of graphite to graphene was discussed. The graphite to graphene domino exfoliation approach will provide some new insights for the surface treatment of cast irons.

2. Experimental

Specimens with dimensions of $100 \times 20 \times 20$ mm^3 were used as substrates. Then, the spheroidal graphite cast iron samples were pretreated by H_2SO_4, HCl solution and sandblast treatment. Afterwards, laser irradiation under argon atmosphere was applied by a 6 kW transverse-flow fiber laser (YLS-6000). The laser irradiation parameters were used as in the following: laser power 0.5–2.0 kW, laser beam diameter 6.0 mm, scanning speed 2 mm/s, and ratio of overlapping 30%. The first treatment of spheroidal graphite cast iron at slow scanning speed is to provide enough reaction time for exfoliation of graphite. In order to solve the coarse grain problem during the first treatment of spheroidal graphite cast iron, subsequently, the surface of the above

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Fe-based coating was further laser irradiated with a rapid scanning speed of 30 mm/s.

After laser irradiation, the samples were sectioned, polished, and etched with etchants of 6–8% HNO_3 ethanol solution for optical microscopy (OM, Keyence 1000E) and scanning electron microscopy (SEM, JSM-6360LV, with an accelerating voltage of 20 kV, secondary electron image) observations. The crystallographic characterization was performed by an X-ray diffraction (XRD, D/Max-Ultima$^+$, with an accelerating voltage of 40 kV) with Cu Kα radiation at a scan speed of 6°/min. High resolution transmission electron microscopy (HRTEM, JEOL 2010F) characterization of the samples was performed after polished and ion-reduced to nanometer scale thickness.

The surface microhardness of the samples was measured using a FM-700 Vickers microhardness instrument at a load of 100 g for a loading time of 15 s. A rhombic diamond indenter was used in our experiment, with three indentations for each load, and the other parameters were adopted according to ASTM E384-08.

In reference of previous work [9], unlubricated sliding wear tests were conducted with a pin-on-disk apparatus (MG-2000 Tester, Materials Tester Company, Xuanhua, Hebei Province, China) under dry sliding conditions at room temperature. The dimensions of the pins were Φ6 mm × 12 mm, and the sliding disk (GCr15, hardness of 60 HRC) with 70 mm in diameter was used as counter-body. The applied load was 100 N. A fixed rotating speed of 400 rpm was used and each test was performed for 10, 20, 30 and 60 min, respectively. The surface of wear test samples was ground and polished with 2000 # grit paper. According to the ASTM G99-95a standard, the volume loss was calculated from the pin height change under wear testing, and the replicate wear experiments were performed more than three times.

3. Results and discussion

3.1. Microstructure of the coatings

Surface SEM observation of twice laser irradiated spheroidal graphite cast iron is shown in Fig. 1. Columnar dendrites appear in the laser irradiated areas (Fig. 1(a). Interestingly, they are spirally assembled in some local regions around big particles (Fig. 1(b–d)). High magnification SEM observation reveals that, they are thin plate-like products (Fig. 1(e) and (f)), indicating the transformation of iron base to martensite plates.

A Fe-based coating of 400–500 μm thickness is achieved after twice laser irradiation, with no cracks, porosities and other defects which existed, as demonstrated by the cross-sectional SEM observation of laser irradiated spheroidal graphite cast iron (Fig. 2(a–b)). Stress field is created in the thick coatings and cracks are usually found in these coatings. In our experiment, the stress which resulted from laser irradiation may be reduced by the relatively soft graphite phase of the spheroidal graphite cast iron.

Gradient microstructure is formed after laser irradiation. From spheroidal graphite cast iron substrate to laser irradiated area, more and more martensite is created, with less and less graphite found. In addition, from cast iron substrate to laser irradiated area, the size of graphite is becoming smaller and smaller, indicating the exfoliation of graphite (Fig. 2(c–e)). Small particles and black strips around graphite is found (Fig. 2(f–h)), suggesting the exfoliation of graphite to carbonaceous nanostructures. In addition, a white "ring" is formed by spirally assembled nanoparticles around the graphite particle (Fig. 2(f)), indicating the formation of iron carbide between graphite and iron base of cast iron.

A cross-sectional XRD pattern of the laser irradiated spheroidal graphite cast iron is shown in Fig. 3. It is demonstrated that, body centered cubic (BCC) iron is the predominant phase (JCPDS card, 87-0722), suggesting the formation of martensite in spheroidal graphite cast iron. Carbonaceous materials (JCPDS card, 75-1621) are also found. The strong peak at 26.5° can be indexed as the (002) plane of graphite carbon, with a strong peak at 43.9° corresponding to the (101) plane of hexagonal carbon, suggesting the exfoliation of graphite to graphene. Additionally, Fe_3C (JCPDS card, 89-2722) is also formed after laser irradiation.

TEM observation reveals that, the dendrite microstructures are fine martensite plates (Fig. 4(a–b)), with twin being the main substructure (Fig. 4(c–d)). In addition, carbide is formed in the laser irradiated coating (Fig. 4(e–f)). Nanometer scale ribbons are found, as shown by

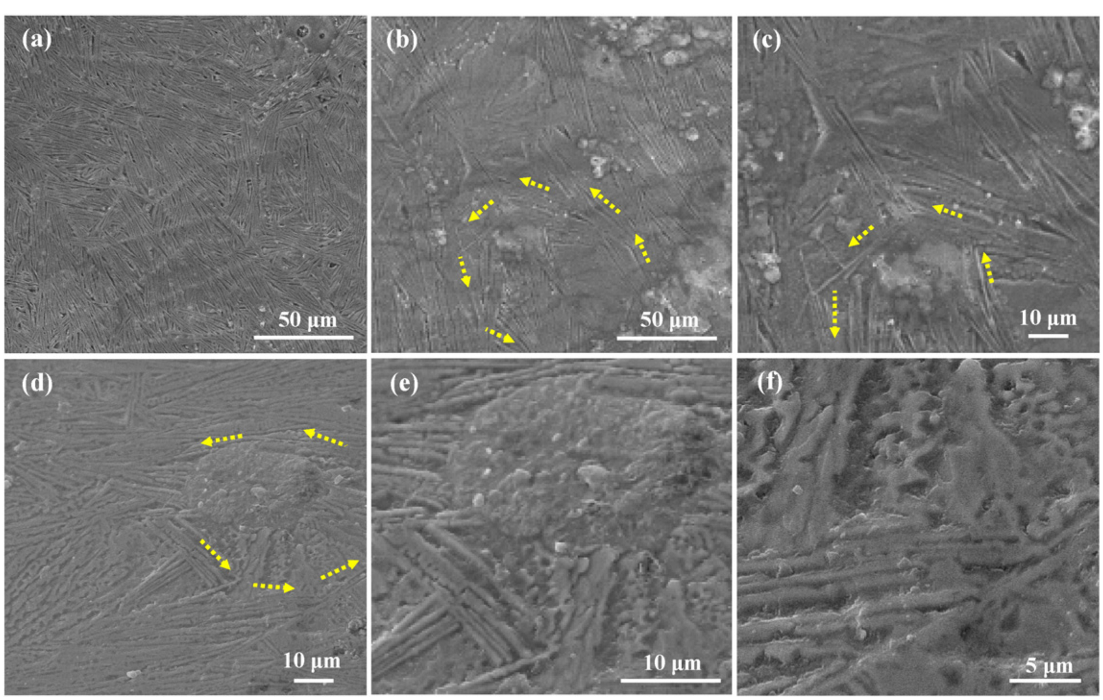

Fig. 1. Surface SEM morphologies of laser irradiated coating.