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Analysis of the acid, base and air oxidized carbon microspheres synthesized in a single step from waste engine oil

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ABSTRACT

Carbon microsphere (C-μS) ball bearings are prone to corrode after long exposure to oxidizing environments. ~4.2 μm diameter C-μSs synthesized from waste engine oil (at 600 and 900 °C) by dry autoclaving, were exposed to nitric acid (30 and 60 vol.%), piranha (H_2SO_4:H_2O_2 60:40 and 90:10), base (NH_4OH:H_2O_2 15:30 and 30:15) and air oxidation at 300 and 450 °C for 12–48 h. The oxidation processes were monitored by weight loss analyses, scanning electron microscopy, X-ray diffraction, Raman spectroscopy, chemical functionalization and electrical conductivity measurements. Crystallinity and higher graphitic content in the C-μSs results in better resistance to oxidation.

1. Introduction

Carbon microspheres (C-μSs) have tremendous potential as ball bearing lubricants to reduce friction and material wear in technologies such as internal combustion engines, turbines, hydraulics, vehicle gears and compressors, microelectromechanical systems and computer disk drives [1]. The microspheres of carbon [1] and silica [2] demonstrate better frictional performance and improved rolling behavior than the nanometric spherical particles such as bucky ball fullerene C_{60} [3,4] WS_2/MoS_2 nanoparticles [5–7], carbon nanotubes [8], nanopearls [9] and nano-onions [10,11]. Since the diameter of the microspheres is larger than the roughness of the shearing surfaces, they can easily roll over the surface. However, the small size of the nanoparticles traps them in surface asperities. In fact the ball bearing efficiency of C-μSs is evident from its reported tensile strength, greater than 8 GPa before fracture [12].

The ball bearings undergo failure, corrosion and reduced lifetime with increased time of usage which ultimately affect the efficiency and lifetime of the machinery [12]. The factors responsible for such corrosion include high oil temperatures, exposure to oxygen, fuel spillage, contamination from engine coolants, extended oil change intervals and unwanted emission of by-products such as formic acid, nitric acid, and carbon monoxide. from combustion of engine fuels. All these events essentially thicken the lubricant and cause deposits on the engine. The ball bearings made of C-μSs are prone to such corrosion in the presence of chemicals and at elevated temperatures. Carbon starts oxidizing to carbon monoxide (CO) and carbon dioxide (CO_2) from ~300 °C in air. Smaller the carbon particles and higher the amorphous content, greater is its tendency to get oxidized. If the corrosion extended to the C-μSs is monitored it will provide a database for the extreme environments in which the C-μS ball bearings can be used. In fact, the oxidation behavior has been utilized to chemically functionalize carbon nanotubes [13,14] and graphene [15] for targeted applications.

The solid C-μSs researched so far were synthesized by chemical vapor deposition [16], hydrothermal method [17] and chemical activation using acid-pretreated resin beads [18]. However, to meet the technological demands, there is a need to produce C-μSs in kilogram quantities from cheap and/or waste resources, by environmentally friendly processes. One such method is a high temperature high pressure reaction inside a closed cell. Waste plastics were successfully converted to C-μSs by this method [12,19], which is one-pot, solvent-free and does not allow the produced greenhouse gases to escape from the reactor. In the present work, the C-μSs were synthesized in large quantities by the same approach from waste engine oil at two different temperatures. The degree of corrosion/oxidation of the C-μSs was systematically monitored by treating with two different concentrations each of nitric acid, piranha, ammonium hydroxide–hydrogen peroxide mixture and air heating. The electrical measurements demonstrate the changes in electrical conductivity due to oxidation.

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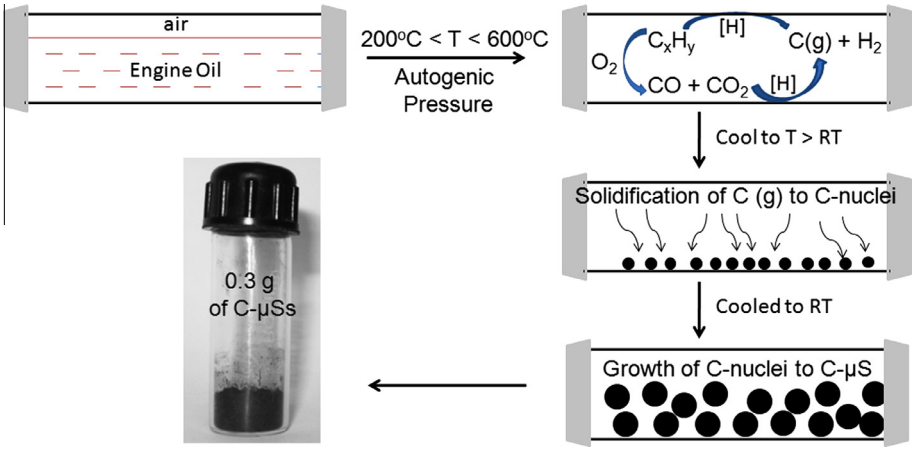

Fig. 1. Formation mechanism of C-μSs.

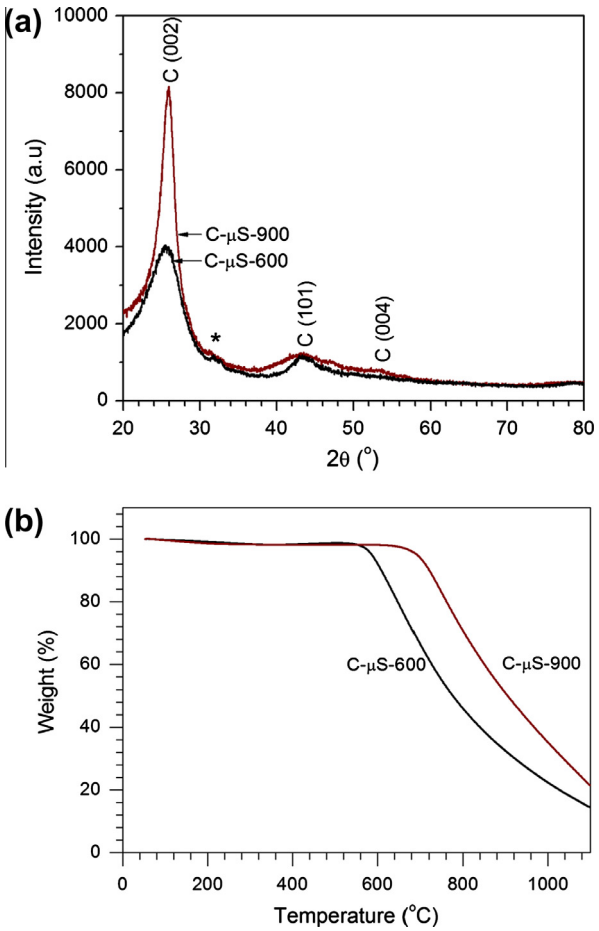

Fig. 2. (a) XRD patterns of C-μS-600 and C-μS-900. Asterisk denotes the weak (104) reflection from Cr_2O_3 impurity. (b) Corresponding TGA plots.

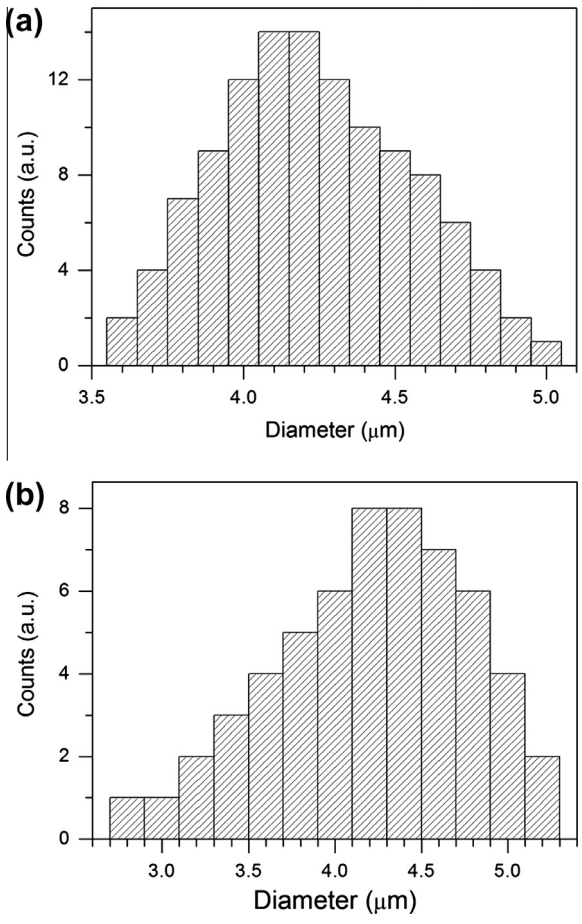

Fig. 3. Diameter histograms of (a) C-μS-600 and (b) C-μS-900.

2. Experimental section

2.1. Materials and characterization

The engine oil spill was collected from the car engine in the local servicing station. The engine oil used is Castrol GTX (India) with viscosity grade SAE-5W-50, where SAE stands for Society of Automotive Engineers (US), and 5W denotes that the oil can be used up to 5 °C in winter. The single grade engine oils as defined by SAE imply that a polymeric viscosity index improver additive was not used. Nitric acid (HNO_3, Merck 70 wt.%), sulphuric acid (H_2SO_4, Merck 96 wt.%), hydrogen peroxide (H_2O_2, Merck 30% (v/v)), ammonium hydroxide (NH_4OH, Sigma Aldrich 28–30%) were used without further purification. Ham-Let Union (SS316) 3/8″ stainless steel reactors were used for the synthesis of the carbon microspheres. The C-μS synthesis and their subsequent air oxidation was performed in a Carbolite wire-wound tube furnace – single