Journal of Alloys and Compounds 601 (2014) 146–153

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Fabrication of carbon nanotube reinforced iron based magnetic alloy composites by spark plasma sintering

Mahesh Kumar Mani [a,*], Giuseppe Viola [b,c], Mike J. Reece [b,c], Jeremy P. Hall [a], Sam L. Evans [d]

[a] Wolfson Centre for Magnetics, Cardiff School of Engineering, Cardiff University, UK
[b] School of Engineering and Materials Science, Queen Mary University of London, UK
[c] Nanoforce Technology Ltd., London, UK
[d] Institute of Mechanical and Manufacturing Engineering, Cardiff School of Engineering, Cardiff University, UK

ARTICLE INFO

Article history:
Received 25 December 2013
Received in revised form 17 February 2014
Accepted 26 February 2014
Available online 6 March 2014

Keywords:
Intermetallics
Metal matrix composites
Sintering
Mechanical properties
Order-disorder effects
Magnetic measurements

ABSTRACT

Near equiatomic Fe–Co composites containing up to 10 vol% of carbon nanotubes (CNTs) were prepared by spark plasma sintering at 900 °C by applying a uniaxial pressure of 80 MPa for 2 min. The powder mixtures were blended by two methods: (a) ultrasonication in dimethylformamide, drying and dry ball milling; (b) dry ball milling. It is the first attempt to fabricate bulk CNT reinforced Fe based alloy composites by a sintering route. The CNTs helped to increase the volume fraction of the long range ordered structures in the matrix alloy. The former dispersion route helped to produce composites with better magnetic and mechanical properties than the latter one. Composites containing less than 1.5 vol% of CNTs showed an increase in saturation induction, mean bending strength, hardness in relation to the monolithic material due to the better densification produced by the addition of CNTs. A significant reduction in the coercivity was observed in all the composites with lower vol% of CNTs (<2%) due to the increase in the compact density and the formation of nanocrystalline ordered crystallites with reduced dimensions, with respect to that of the monolithic material. Spark plasma sintering helped to retain the structural integrity of CNTs in all the Fe based composites fabricated.

1. Introduction

Modern power generation systems and actuators, magnetic bearings used in transport systems and energy storage systems such as flywheels demand soft magnetic materials with good mechanical properties [1–4]. The magnetic material selected for the aforementioned applications should possess high saturation magnetisation to minimize the weight of material used and good mechanical properties to improve the lifetime, reliability and efficiency of the power systems. Fe–(30–50 at%) Co alloys are the known commercial soft magnetic materials that exhibit the highest saturation magnetisation (2.3–2.45 T) [3]. Fe–50 Co in the alloy range exhibits additional advantageous characteristics such as higher permeability and zero magnetocrystalline anisotropy [5]. Unfortunately, the brittle nature of the intermetallic Fe–50Co alloy poses problems during fabrication and service [6]. The ductility of the alloy has been improved by ternary additions that promote precipitate formation such as vanadium and niobium [7,8]. The toughened Fe–50Co–X (where X is a ternary element) alloys are deformed and heat treated to tune their mechanical and magnetic properties depending on the requirements [5]. However, all the mechanical property improvements were accomplished at the expense of magnetic properties. Powder metallurgy (PM), which is widely used to shape brittle materials into useful shapes, and short fibre composite strengthening, which offers unique advantages such as toughness enhancement and flexibility of tuning the final properties by varying the type and amount of reinforcements, have been jointly attempted only once in these stoichiometric alloys using SiC whiskers [9].

Carbon nanotubes (CNTs) are considered to be a suitable short-fibre reinforcements because of their extremely small size, high aspect ratio, high tensile strength (~150 GPa) and elastic modulus (~1 TPa) [10,11]. The nanosized carbon based fillers have been employed in metal matrix composites to improve one or many of the following characteristics: mechanical strength; hardness; toughness; electrical conductivity; thermal conductivity; corrosion resistance; hydrogen storage capacity; and to reduce coefficient of friction and coefficient of thermal expansion [12,13]. The main challenges associated with the fabrication of any metal matrix CNT composites include: (a) dispersion of the fillers uniformly in the matrix; (b) minimisation of deleterious interfacial reaction;

* Corresponding author. Tel.: +44 07814656021; fax: +44 02920874716.
E-mail address: metlymahesh@gmail.com (M.K. Mani).

http://dx.doi.org/10.1016/j.jallcom.2014.02.169
0925-8388/

(c) maintaining the structural integrity of CNTs after processing; and (d) densification of the compacts. The former challenge can be met by employing colloidal processing [14] and high energy ball milling [15] at the marginal expense of the aspect ratio and quality of the CNTs and the latter three requirements can be met by using a rapid sintering technology.

Spark plasma sintering (SPS) is a relatively new and rapid powder consolidation process with unique characteristics in relation to conventional sintering methods including low sintering temperatures, very fast heating and cooling rates (>500 °C/min), short holding time, high pressure applied during sintering, high throughput with high current (>1000 A) and low voltage (<10 V), clean grain boundaries and flexible sintering environment [16,17]. Hence, without any prior cold pressing or additives, dense compacts of a wide variety of materials can be produced with minimal grain growth [18].

In this article, the effects of CNT addition on the structural, magnetic and mechanical characteristics of spark plasma sintered Fe–Co composites have been investigated.

2. Materials and methods

Oxygen functionalised multi-wall carbon nanotubes and gas atomised Fe–50Co powders with average particle size of 9.5–11 μm were obtained from Haydale Ltd., UK and Goodfellow Ltd., UK, respectively. The functional group (=O) was covalently attached on the surface of the nanotubes by a plasma treatment method. The functional group was believed to promote effective dispersion during the subsequent colloidal mixing process by minimizing the Van-der-Waals force of attraction between the nanotubes [19]. The number of walls, wall thickness and morphology of the as-received CNTs were characterised using a high resolution JEM-2100 LaB_6 Transmission Electron Microscope.

Two different methods were employed to mix the as-received CNTs with the matrix alloy powder. In the first method, different volume fractions (from 0.5 to 5 vol%) of CNTs were dispersed in dimethylformamide (DMF) under ultrasonic agitation for 90 min. DMF was selected for its ability to realise homogeneous and stable CNT dispersions [20]. About 20 g of Fe–50Co powder was added to each suspension and the slurry was sonicated for 30 min. The slurry was heated on a hot plate maintained at 150 °C to evaporate the DMF. The Fe–Co/CNT mixture was dry milled for 1 h in a ball pestle impact grinder with ball to powder ratio (BPR) of ~1:1. In the second method, 20 g of Fe–Co powder was blended with different volume fractions of CNTs (up to 10 vol%) in the ball mill with BPR 1:1 for 1 h without any prior colloidal processing. Hereafter, the former mixing method will be referred as U + B method and the latter method as B method. In order to differentiate the influence of ball milling from the CNT additions on the microstructure and magnetic and mechanical properties, samples were also prepared by ball milling the as-received Fe–50Co powder for 1 and 5 h.

The monolithic and composite powder mixtures were consolidated in a SPS furnace (HPD 25/1 FCT, Germany) using graphite die and punches under the conditions determined to be optimum in the previous work (T = 900 °C, t = 2 min, P = 80 MPa) [21]. The sintered compacts were ground with SiC abrasive paper to remove any carbide layer on the surface. The densities of the compacts were measured using the Archimedean method with water.

The cross-section of the sintered samples was ground, polished and etched with 10% Nital and examined using an optical microscope to reveal the grain morphologies. The crystallographic phases present in the materials were studied using an XRD (Philips PW1710 Automated Powder Diffractometer) equipped with Cu target X-ray tube operated at 35 kV and 40 mA. The scanning was carried out between 2 and 90 °2θ at a scan speed of 0.005 °2θ/s. X-ray diffraction studies were also performed using a Siemens D500 diffractometer with a slow scan rate of 0.02 °2θ min^{-1} using Co Kα radiations to investigate the characteristics of the long range ordered structures in the matrix alloy [22].

Vickers hardness testing was performed on the unreinforced and composite samples at five different locations under an applied load of 30 kg for 4 s. Samples with rectangular cross section (24 mm × 18 mm) were cut from 30 mm diameter circular samples by wire electric discharge machining (EDM) and their quasi DC magnetic response was measured using a custom built permeameter [23]. After magnetic testing, 5 strip samples of length 24 mm and cross sections varying between 3 and 4 mm were cut from each rectangular sample. Three point bending test were performed on the strip samples using a Zwick testing machine at a crosshead speed of 2 mm/min and the bending strength was calculated using the following equation,

$$M = 3Wl/2bd^2$$

where M = flexural strength; W = fracture load; l = test span (22 mm) distance between support points; b = width of specimen; and d = thickness of specimen. The fracture surfaces of two randomly selected samples from each set were examined using a scanning electron microscope (FEI Quanta 650 FEGSEM). In order to evaluate the structural quality of CNTs in the composites, the fractured surfaces of two randomly chosen samples of each CNT composite were characterised using a Renishaw inVia Raman microscope. The analysis was performed at seven different locations on each composite using a 514 nm argon laser with the power and spot size maintained at 12.5 mW and 5 μm, respectively.

3. Results and discussion

The TEM images of the as-received CNTs are shown in Fig. 1. The outer tube diameter and number of concentric graphite layers in the walls were not constant. They varied between 5–30 nm and 4–20, respectively. The dimensions of the inner tube followed the same trend as that of the outer tube diameter. The walls of some of the CNTs showed extensive imperfections as indicated by arrows in Fig. 1(a) and (b). The imperfections could have been: (a) present in the as-received tubes; and/or (b) introduced during the plasma treatment that was done to attach O_2 functional groups on the CNT walls.

To understand the effect of ball milling and CNT additions on the sintering behaviour, the displacement of the piston during sintering was examined for the monolithic powder and composite powder mixtures. The piston speed is plotted against SPS temperature in Fig. 2. Ball milling for 1 h in atmospheric conditions caused a significant change in the sintering behaviour of the Fe–Co powder. Most of the densification occurred in the initial stages of sintering (as shown by the sudden drop in the piston speed at about

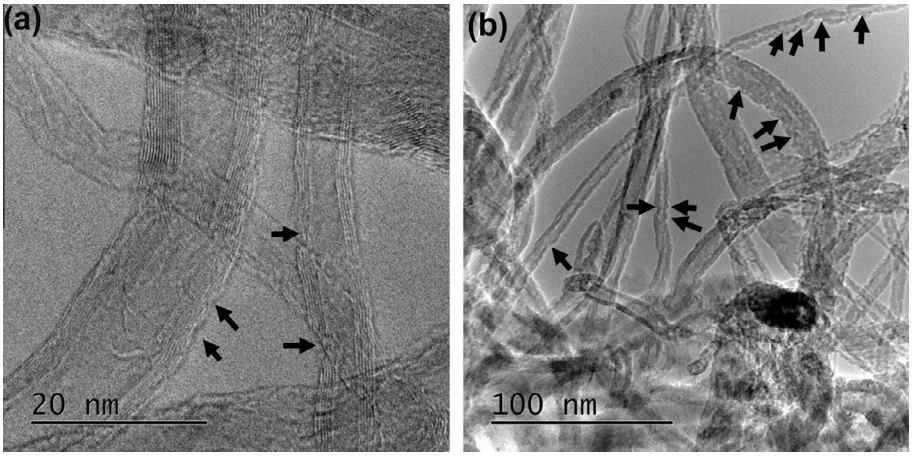

Fig. 1. Transmission electron micrographs of as-received CNT in the O_2 functionalised state; the arrows denote the defects on the CNT walls.