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Hardness of Multi Wall Carbon Nanotubes reinforced aluminium matrix composites

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ABSTRACT

The macro hardness (HV_{20}) was measured for aluminium and 1–9 wt% Multi Wall Carbon Nanotubes (MW-CNTs) composites that were milled and hot compressed. The hardness increased with increasing fraction of MW-CNTs up to 6 wt% (HV_{20} = 151) and then remained constant. The content of MW-CNTs was significantly higher than reported for similar materials and measurements. The composites were analysed by Raman, TEM and XRD. The Raman and TEM showed MW-CNTs were still present after milling and hot pressing. The XRD was used to determine the Al crystallite size which was used to determine Hall–Petch contribution to the composite hardness.

1. Introduction

The need to pursue new materials which are lighter and stronger is still ever present. This is evident in fields such as Aerospace, Renewable Energy, Electronics, Architectural Structure and Alternative Transport where Metal Matrix Composites (MMC) materials have found increasing use [1]. Since the unique properties of Carbon Nanotubes (CNTs) were reported by Iijima in 1991 [2], they have been increasingly used as a reinforcement material in polymers [3], ceramics [4] and metals [5] because of their low density and very high theoretical strength [6]. At present, for applications where high strength is needed, the CNTs are combined with a matrix to utilise these unique properties. The light metals, such as Mg and Al, are ideal matrices because there is a large scope for increasing the strength, while not increasing the weight [1]. In this study, pure Al was chosen because of its simple chemistry, material properties and structure.

The use of CNTs in matrices other than organic matrices (i.e. polymer) has been less developed. The initial research involving CNTs and Metal Matrix Composites (MMC) has been slower to develop from the initial work of Doome et al. and Kuzumaki et al. in 1998 [7,8]. A number of publications have appeared recently regarding the fabrication of CNT–MMC in different metals matrices, such as Al, Cu, Mg, Ti, Fe, Fe_3Al, Ni, Sb, Ag, Co and Metallic Glass which has been recently reviewed [5,9]. These publications have used a variety of techniques, such as Spray Methods, Electrochemical Techniques and Chemical Methods [5,9] to form consolidated metallic materials.

Initial methods using Powder Metallurgy only used a short milling times (5–10 min) because of the fear of destroying the CNTs [10,11]. An alternative method used rubber assisted dispersion of CNTs in an Al matrix [12] has been one method to address this issue. Perez-Bustamante et al. showed that with longer milling time (2 h) there was a doubling of material properties with 0.75 wt% Multi Wall CNTs (MW-CNTs) [13]. More recently, work has been conducted with higher content of CNTs and showed similar improvements in mechanical properties [14–21]. It has been observed that during the milling process with Al powder, the CNTs can be damaged to some extent [17]. The grain structure of the metal matrix has not been extensively investigated previously. It has only been more recently that suitable Al samples have been prepared with a grain size below 100 nm where the Hall–Petch effect contributes significantly to the mechanical properties [20,22,23]. Choi et al. [23] and Poirier et al. [17] have shortly discussed the Hall–Petch contribution to the mechanical properties. More recently Choi et al. [20] have investigated this further. This will be explored in more details in this paper.

This work is to explore the application of MW-CNTs as reinforcing materials to increase the strength of MMC materials of Aluminium by powder metallurgy routes; planetary ball milling and hot compaction. A study is performed on the chemical composition and structure of the composites to evaluate the strengthening

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mechanisms that lead to improved hardness properties for Al/MW-CNT composites.

2. Experimental

The Al powder used in all experiments was supplied by Ecka Granules (AS 011 purity ⩾99.5%) with a particle size of less than 65 μm and the MW-CNTs were from Bayer (Baytubes® C150P, purity >99.5%). A detailed analysis of the MW-CNTs has previously been conducted by Tessonnier et al. [24]. Samples of MW-CNT Al MMC were produced with varying amount of MW-CNTs, 1 wt%, 3 wt%, 6 wt% and 9 wt% added to the Al matrix. The MW-CNT and Al were mixed by a laboratory planetary ball mill (PM400, Retsch GmbH) under an inert atmosphere of Argon. Milling was conducted using 10 mm steel balls with a Ball to Powder Ration (BPR) of 10:1 at a speed of 360 rpm. 20 wt% Heptane was added as a Process Control Agent (PCA). Milling was conducted for a total milling time of 20 h with a repeated sequence of 20 min milling, followed by a 10 min pause interval. Further details regarding the milling process can be found elsewhere [25]. After milling, the milling balls showed negligible wear. The milled powders were consolidated by hot pressing to form bulk samples of 30 mm in diameter and with a 3 mm thickness. The powders were placed into a die made of high temperature steel, heated in an oven up to a temperature of 350 °C for 60 min and rapidly transported to the uniaxial press (less than 5 s). Compaction was done by applying a pressure of 570 MPa for 10 s. For the extruded samples, the blend was put into an extrusion mould, heated to 500 °C for 1.5 h and then transported rapidly to the press. The extrusion was performed with an extrusion ration of 14:1, a ram speed of 1 mm s^{-1} for the sample with a diameter of 8 mm. The length was typically around 15–20 cm allowing the preparation of two tensile specimens per extrusion.

The density of all samples was measured by Archimedes' method according to ISO 3369:1975 and all had a theoretical density between 96% and 99%. The macro Vickers Hardness (HV_{20}) was measured according to EN ISO 6507-1 with a load of 20 kg for 15 s (220, GNEHM Härteprüfer AG). Raman spectra were measured on a Renishaw 2000 spectrometer equipped with holographic notch filters for elastic scattering and a CCD array detector. The samples were excited with the helium–neon laser (632.8 nm). The laser was focused onto the sample using the 50× objective that is mounted to the microscope. Each sample was measured in twelve different places and each spectrum was corrected for the baseline. The instrument was calibrated with Si single crystal. The electron microscope images were taken with a Jeol JEM-2200FS high resolution transmission electron microscope. The fracture surface of the extruded samples was observed after tensile tests under a high resolution scanning electron microscope (Hitachi S-4800). The XRD was measured with X'Pert Pro diffractometer (PANAlytical) with a Cu Kα (λ = 1.5148 Å, 35 kV and 40 mA) in the 2θ range 25–140° using a linear detector (X'Celerator). A step size of 0.0167° and a scan rate of 0.021°/s was used. The instrumental line broadening was determined with an annealed sample of Y_2O_3 (Alfa Aesar, purity 99.999%). The Rietveld refinement was done using a program called Maud developed by Prof. Lutterotti at the University of Torento [26].

Extruded samples were machined to achieve a standard tensile test specimen with a gauge diameter of 4 mm according to DIN 50125. The tensile tests were performed on a UTS machine according to EN ISO 6852-1:2009.

3. Results and discussion

Initially the Al/MW-CNT samples were investigated by TEM. An example of these subsequent images is presented in Fig. 1 for the composition containing 9 wt% of CNTs. The identification of the CNTs is indeed easier for larger amounts. A typical milled Al/MW-CNT particle is given in Fig. 1A and B. The TEM images clearly show a MW-CNT on the surface of the aluminium particle. The MW-CNT can be seen lengthwise and looking down the axis. During the milling process the MW-CNTs have become shorter however they are still present. Fig. 1C and D shows a TEM image of the Al–9 wt% MW-CNT hot pressed sample. Fig. 1C shows the nanograined aluminium and also some Al_4C_3 while a high-resolution image of Fig. 1D looks down the axis of a MW-CNT. The TEM images show that MW-CNTs are still present after milling and hot pressing. The MW-CNTs have been shortened by the milling processes but are still present and no cracks are seen at the interface with the matrix. Moreover, no large agglomerates of nanotubes could be found neither with TEM nor with high resolution

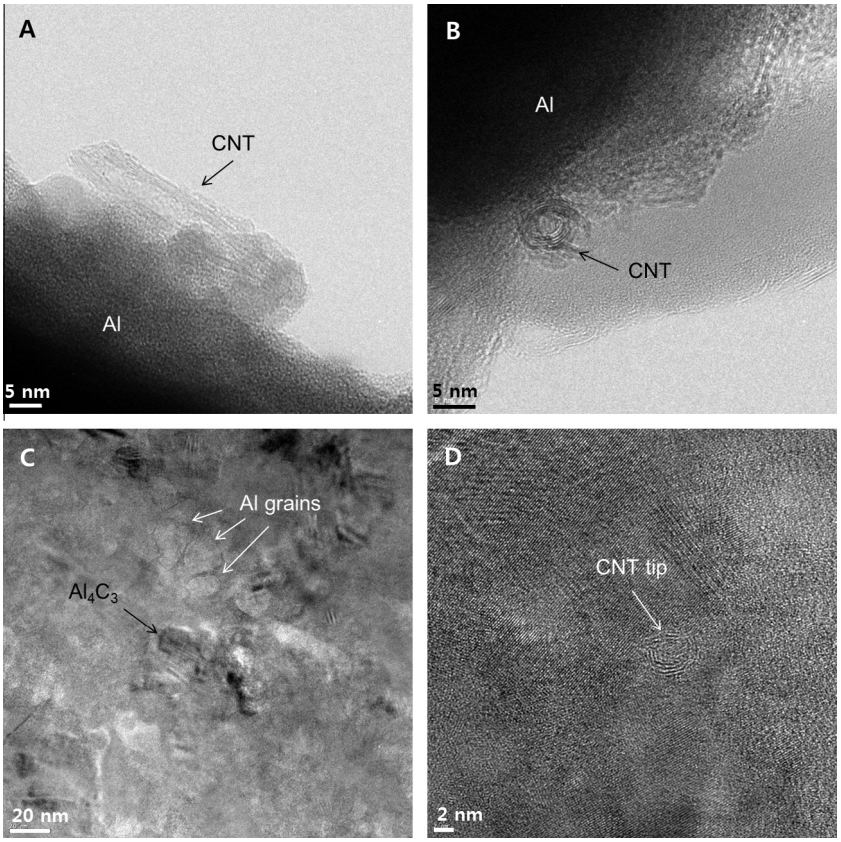

Fig. 1. TEM images of the Al/MW-CNT composite. Image A and B show the presence of MW-CNTs on the surface of the milled Al particles. Image C shows the presence of nanosized Al grains in the matrix (highlighted by white arrows) and the formations of some Al_4C_3 during the milling and hot pressing. Image D shows that MW-CNTs are present in the milled and hot pressed Al matrix.