1 General Introduction

Since their observation by Iijima [1], due to their remarkable geometry and outstanding properties such as high mechanical stiffness and high thermal and electrical conductivities, carbon nanotubes (CNT) have received considerable attention as reinforcements in composite materials. Theoretical as well as experimental approaches reported a Young’s modulus as high as 1 TPa for highly crystalline CNT, generally produced by laser ablation or electric arc processes [2-4]. By contrast, the most commonly used multi-walled carbon nanotubes (MWNT) synthesized by chemical vapour deposition (CVD) techniques exhibit high defect density and Young’s modulus ranging from 10 to 200 GPa [3,5,6]. This smaller Young’s modulus has been explained by misalignment of the graphitic planes with the tubes axis and confirmed the influence of the synthesis method of CNT on their stiffness. By contrast, tensile strength of CNT seems not to be influenced by the regularity of their atomic structure and is in the range 30 to 150 GPa, for both nanotubes synthesized by arc discharge or CVD processes [4,7,8].

Since CNT can be chemically functionalised [9], they have been actively investigated as reinforcements in polymers [10,11]. Carbon nanotubes have also been used in order to reinforce ceramics [12]. However, very limited research has been done in the field of CNT-reinforced metal matrix composites (MMC) and the results reported so far are quite controversial. Before 2005, no real enhancement of mechanical properties of CNT-MMC was reported [13], mostly because of the difficulty to disperse CNT homogeneously in a metal matrix and potential reactions between CNT and matrix [14]. Powder metallurgy (PM) seems to be the most appropriated processing technique to bypass these challenges [15]. PM is usually achieved at low temperatures, avoiding the formation of Al4C3 carbides at the CNT/Aluminium interface [16]. In recent years, improvements of the mechanical properties of CNT-MMC prepared by PM have been reported, especially with pure aluminium matrices [17,18]. However, aluminium is not adapted for applications due to its weak mechanical properties. The particularity of this study is the reinforcement of an AA5XXX aluminium alloy, which is a high-performance alloy used in the aerospace industry. Here, we demonstrate that homogeneous dispersion of nanotubes in the matrix by repeatable and optimized PM process can lead to enhancement of the mechanical properties of high-performance alloys.

2 Materials and Methods

Multi-walled carbon nanotubes used for this study were synthesized by CVD techniques by Bayer MaterialScience AG. These CNT are delivered as dense agglomerates which makes their dispersion very difficult. They present an external diameter of 13-16 nm, a length ranging from 1 to 10 µm, a chemical purity over 98.0 wt.-% and contain 0.60 wt.-% cobalt as a residual catalyst. The atomic structure of these MWNT has been characterised using Raman spectroscopy. The Raman spectrum of CNT excited with the 514.5 nm line of an argon laser is presented in Fig. 1. The band around
1590 cm$^{-1}$ is called the G band and corresponds to carbon-carbon stretching [19]. The so-called D band observed around 1370 cm$^{-1}$ corresponds to zone edge phonons and is activated through a mechanism of double resonance involving elastic scattering of the electrons by structural defects [19]. Therefore, the I_D/I_G intensity ratio is widely used to study the defect density in carboneous structures [19]. The coherence length of MWNT, corresponding to the distance separating two structural defects on CNT atomic structure can be estimated to be as small as 10 nm, typical of a very defective structure [20].

The matrix was an aluminium alloy powder from the AA5XXX series (AlMg - N2 atomized) with an average particle size of about 25 µm (Fig. 2). This non age-hardenable Al-alloy exhibits particularly good specific mechanical characteristics. Typical pictures of scanning electron microscopy (SEM) of the MWNT and AA5XXX powder are presented in Fig. 3 and 4.

The morphology of the powders and the homogeneity of the mixtures were investigated using a JEOL-JSM-6320F SEM with an accelerating voltage of 15 kV. The backscattered electron mode was used in order to reveal the CNT-agglomerates in the mixtures.

CNT/AA5XXX composite was prepared following the usual powder metallurgy process steps (Fig. 5). CNT were firstly dispersed in the matrix material using planetary ball-milling. 2.0 wt.-% CNT were mixed with 100 grams of the matrix powder in a 250 ml jar using 50 milling balls (10 mm diameter). This processing step was achieved by high milling kinetics in order to untangle CNT-agglomerates and disperse CNT homogeneously. The milled powder mixture was degassed under vacuum down to a pressure of 10^{-2} mbar at a temperature between 300°C and 400°C in a stainless steel capsule to avoid humidity and oxidation. After this step, the mixed powders were hot isostatic pressed under high pressure at 350°C before being extruded through a 6 mm diameter die. Finally, tensile specimens were machined from the extruded rods in order to investigate the mechanical properties of the composite. Experiments were achieved on a 50 kN Zwick 1466 testing instrument at a crosshead speed of 1 mm/min. The Young’s modulus of the material produced was determined using a “Mess- und Feinwerkechnik Mini MFA” extensometer with a gauge length of 10 mm.

3 Results and Discussion

Homogeneous 2.0 wt.-% CNT-AA5XXX powder mixture has been obtained after ball-milling as presented in Fig. 6. Metallic particles have been radically reshaped through plastic deformation and cold welding mechanisms (Fig. 6). Indeed, metallic particles with originally a 25 µm diameter, show a diameter up to 100 µm after milling. During this milling/welding process, CNT agglomerates have been dispersed and CNT have been trapped into matrix particles; that is why nanotubes are hardly observable on the SEM pictures, even at high magnification (Fig. 7). Mechanical properties of the composite are reported in Fig. 8 and are compared with that of the unreinforced aluminium alloy. The produced composite material shows a ductile behaviour. The enhancement of the mechanical properties due to the reinforcement with CNT can be observed in Fig. 8: Young’s modulus, yield strength and tensile strength have been increased by 5%, 9% and 15%, respectively, with respect to pure aluminium alloy prepared in the same conditions. These increases are attributed to CNT/matrix load transfer and also to the generation of additional dislocations. This strengthening is associated with a significant decrease of the elongation at fracture. However, the elongation at fracture measured on the specimen as well as its relative density over 99% makes the material eligible for static aerospace applications.

4 Conclusion

Dense CNT-reinforced high-performance aluminium alloy composites were prepared by a repeatable powder metallurgical process. Homogeneous dispersion of CNT in metallic matrix has been achieved and optimized. The corresponding composite material containing 2.0 wt.-% CNT shows Young’s modulus, yield strength and tensile strength increased by 5%, 9% and 15%, respectively, with respect to pure aluminium alloy processed in the same conditions.
HIGH-PERFORMANCE METAL MATRIX COMPOSITES
REINFORCED BY CARBON NANOTUBES

Fig. 1. Raman spectrum of as-received MWNT.

Fig. 2. Particles size distribution of AA5XXX powder.

Fig. 3. SEM pictures of as-received MWNT.

Fig. 4. SEM pictures of as-received AA5XXX powder.

Fig. 5. Powder metallurgy process steps.

Dispersion of CNT in metal matrix by ball-milling

Degassing of powder mixture (10^-2 mbar)

Hot isostatic pressing (High pressure, 350°C)

Extrusion and tensile specimens machining

Fig. 6. SEM observations (backscattering electrons) of CNT-AA5XXX powder mixture after high milling kinetics.
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References


