



High temperatures gas–solid reactivity of aluminum–carbon nanotubes composites



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ABSTRACT

The gas–solid reactivity of metal–carbon matrix composites such as aluminum–carbon nanotubes (Al–CNT) sintered samples was studied at temperatures below and above the melting point of Al in O₂, synthetic air, CO₂, H₂–Ar (5% v/v) and Ar. Small cylindrical samples of different composition with “single-walled” CNTs (SWCNTs) or “multi-walled” (MWCNTs) were sintered in Ar at 625 °C and the resulting materials showed densities ranging from 92.2 to 99.0% of the theoretical density of bulk Al. Thermogravimetric analysis (TG) with simultaneous differential thermal analysis (DTA) up to 1200 °C shows that the Al–CNT composites do not behave as a two independent phases system. This is mainly demonstrated by the following phenomena: *i*. The lowering of the melting point of Al, the magnitude of which cannot be explained by the expected very low solubility of C in Al at this temperature; *ii*. The amount of α-Al₂O₃ grown in oxidizing atmospheres and at the highest temperatures depends from the CNT content in the composite; *iii*. The formation of Al₄C₃ occurs only in presence of molten Al as shown by environmental X-ray diffraction “XRD”. Field emission scanning electron microscope “FESEM” and high-resolution analytical transmission electron microscopy “HRTEM” investigations confirm that at the sintering temperature no detectable chemical interaction exists between Al and CNT.

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1. Introduction

In the field of the composite materials the dominant role is played by carbon reinforced polymers, CRP, where carbon is present as a graphitic form with different morphologies: fibres and nanostructures such as nanotubes (CNTs), fullerenes, nano-onions, graphene, etc. Many papers [1–4] and several technological applications of CRP based materials are present in our everyday life.

There is not a similarly abundant literature for the carbon reinforced metals, CRM, and this is partially due to the difficulties in dispersing any form of carbon in a metal matrix, MM, with respect to polymers. The higher physical stability of metals or alloys (high melting point, mp), no viscous state before mp, poor mutual wettability, low amount of interfacial bonds and unbridgeable differences in thermal expansion coefficients are serious limitations that generally do not allow an easy carbon dispersion. In the melted state of the MM, the dispersion of carbon is usually impracticable because the metal carbide formation is even more favoured.

The mechanical behaviour of CRMs is the most studied property and some papers can be found about this topic [5–8]. As far as the authors’ knowledge, no data are reported on the chemical reactivity of CRM in towards common gaseous phases especially at high temperatures.

At high temperatures, neutral atmospheres or high vacuum do not affect CRMs whereas CRPs pyrolyse. In oxidizing atmospheres, CRPs tend to burn out; CRMs reduce the carbon content while a formation of metal oxides may occur. Both CRPs and CRMs can reduce their carbon content in hydrogen atmospheres through the formation of light hydrocarbons. Depending on the chemical nature of the polymer, hydrogenation can occur on CRPs whereas metal hydrides formation in CRMs depends on the metal.

Looking at the increasing interest for light CRM composites not only as structural materials but also as functional materials for hydrogen production [9] and as electrical conductors, we focused our experiments on Al–CNT composites for determining their electrical properties [10] and, in the present work, for studying the reactivity of such materials towards different atmospheres. The interfacial reaction in Al–CNT films was already studied [11] under high vacuum between 400 and 950 °C. Though the use of Al–CNT composites is expected well below the Al melting point, their

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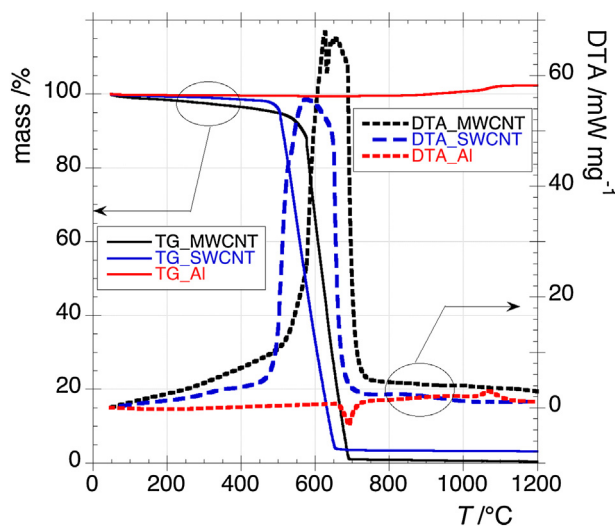


Fig. 1. Thermogravimetric (TG), left scale – solid curves, and differential thermal analysis (DTA), right scale – outlined curves, of the pure species constituting the composites under study, i.e., MWCNTs (24.278 mg), SWCNTs (27.628 mg) and Al sintered pellet (77.220 mg). Measurements carried out in pure O₂ at heating rate of 20 °C min⁻¹.

behaviour at higher temperatures can give useful information to understand phenomena occurring at lower temperatures but usually undetectable in such conditions. In planning our experiments, a great deal of attention was paid for an efficient dispersion of CNTs in the metal powder without making use of both ball milling, that produces large damages on CNTs, and dispersion in melted Al to avoid the carbide formation.

The scope of this work is to study the solid-gas reactivity at high temperatures and in different atmospheres of Al-CNT sintered composites with both single (SW) and multi walled (MW) CNTs.

2. Experimental details

2.1. Starting materials and preparation of Al-CNT composites

2.2.1. Carbon nanotubes and aluminum powder

Multi-walled carbon nanotubes (MWCNT, >95%, o.d. 50–80 nm) and single-walled carbon nanotubes (SWCNT, >90%, o.d. 1–2 nm) were purchased from Cheap Tubes Inc., USA. The average true density as given by the manufacturer is $\approx 2.1 \text{ g cm}^{-3}$.

The ash content as determined by TG in O₂ (solid curves in Fig. 1) was 3.18 wt.% and 0.43 wt.% for SWCNTs and MWCNTs, respectively. The DTA peak shape (outlined black curve in Fig. 1) of MWCNTs around 600 °C is a fingerprint of two kinds of MWCNTs at least with different number of walls [12]. Further characterizations of CNTs by Raman spectroscopy, SEM and HR-TEM were reported elsewhere [12]. Aluminum powder (purity 99.97%, ~ 325 mesh) was purchased from Alfa Aesar.

2.2.2. Functionalization of MWCNTs

Oxidative functionalization of MWCNTs was performed by auto-clavation in alkaline aqueous solution of potassium peroxydisulfate according to the procedure reported in literature [13].

2.2.3. Preparation and sintering of Al-CNT composites

Considering the low content of CNT in the composites, 1:1 wt./wt. Al-CNT mixtures were prepared and appropriate amounts of Al were added in order to obtain the desired contents. The mixtures were ultrasonicated in ethanol for at least 1 h then filtered. The resulting powders were then carefully mixed in an agate mortar with the addition of some acetone to facilitate the process.

Table 1

Measured densities of sintered Al-CNT composites. Theoretical density, d_{th} , was assumed equal to the density of pure Al bulk (2.697 g cm^{-3}).

w% CNT	$d_s/\text{g cm}^{-3}$	$d_s/d_{th}/\%$
Al_sint	2.669 ± 0.005	98.96
Al_bulk	2.697	100
Al-SWCNT		
0.80 ± 0.04	2.661 ± 0.004	98.67
2.0 ± 0.1	2.511 ± 0.008	93.10
2.7 ± 0.1	2.598 ± 0.005	96.33
2.8 ± 0.1	2.487 ± 0.004	92.21
3.2 ± 0.2	2.533 ± 0.007	93.92
4.2 ± 0.2	2.527 ± 0.006	93.70
Al-MWCNT		
0.26 ± 0.01	2.665 ± 0.005	98.81
0.30 ± 0.01	2.517 ± 0.005	93.33
0.60 ± 0.03	2.591 ± 0.006	96.07
2.4 ± 0.1	2.623 ± 0.008	97.26
2.7 ± 0.1	2.583 ± 0.007	95.77
3.9 ± 0.2	2.567 ± 0.008	95.18
4.2 ± 0.2	2.527 ± 0.006	93.70

The samples in form of cylindrical pellets were prepared by compression of the powders at 0.3 GPa (3 kbar) by using a hydraulic mounting press of a weighted amount of mixture in a 6 mm diameter stainless steel mould. The force was applied for 5 min, then relaxed for a few seconds and then applied again repeating this procedure at least three times. The pellets were sintered in a tubular furnace at 625 °C for 3 h under a flow of 99.999% pure argon ($60 \text{ cm}^3 \text{ min}^{-1}$ @STP). Longer sintering times do not change appreciably the density. The final average size of the cylindrical shape of the samples was $\sim 6 \text{ mm dia.} \times \sim 3 \text{ mm height}$.

3. Measurements

3.1. Density measurements

A Gibertini Crystal 300 (Italy) analytical balance equipped with the accessory for the density measurements of solids was utilized for determining the density of the sintered samples. The density values of the samples studied are listed in Table 1.

3.2. Thermogravimetric (TG) and differential thermal analyses (DTA)

By using a Netzsch STA 409 PC Luxx (resolution 2 μg , RT to 1500 °C operating range) the simultaneous TG-DTA analyses were performed. The DTA was calibrated against the melting points of In, Sn, Zn, Al, Ag, Au and Ni. The measurements were performed under controlled atmospheres of Ar, Ar-H₂ 5% vol/vol, O₂, CO₂ and synthetic air (N₂/O₂ 80/20 vol/vol). The Netzsch gas control box controlled the gas flows. Throughout this work, the heating rate was kept at 20 °C min⁻¹. Pelleted sintered samples of Al/CNT composites were used for TG and DTA measurements. This was done to obtain more realistic information for each sintered composite.

3.3. Environmental X-ray diffraction (XRD)

A Panalytical X'Pert Pro powder diffractometer (Bragg-Brentano geometry, Cu K α radiation, $\lambda = 0.154184 \text{ nm}$) was used for the temperature-controlled powder X-ray diffraction experiments. The diffractometer is equipped with an Anton Paar XRK 900 environmental chamber capable of operating under inert, reducing and oxidizing atmospheres up to 900 °C. The measurements were carried out under inert gas (argon) flow. The diffractometer is equipped with an ultrafast RTMS X'Celerator detector. The powder samples were placed in a Macor glass-ceramic sample holder.

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