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Alain Peigney, Emmanuel Flahaut, Christophe Laurent, Françoise Chastel, Abel Rousset. Aligned carbon nanotubes in ceramic-matrix nanocomposites prepared by high-temperature extrusion. *Chemical Physics Letters*, 2002, vol. 352, pp. 20-25. 10.1016/S0009-2614(01)01441-5 . hal-00990974

HAL Id: hal-00990974

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Submitted on 14 May 2014

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To link to this article : DOI:10.1016/S0009-2614(01)01441-5
URL: [http://dx.doi.org/10.1016/S0009-2614\(01\)01441-5](http://dx.doi.org/10.1016/S0009-2614(01)01441-5)

To cite this version:

Peigney, Alain and Flahaut, Emmanuel and Laurent, Christophe and Chastel, Françoise and Rousset, Abel *Aligned carbon nanotubes in ceramic-matrix nanocomposites prepared by high-temperature extrusion.* (2002) Chemical Physics Letters, vol. 352 (n° 1-2). pp. 20-25. ISSN 0009-2614

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Aligned carbon nanotubes in ceramic-matrix nanocomposites prepared by high-temperature extrusion

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Abstract

Carbon nanotube (CNT)–metal-oxide nanocomposites are extruded at high temperatures. The superplastic forming is made easier by the CNTs. It is possible to align the CNTs in ceramic-matrix nanocomposites, which are bulk materials rather than fibers or thin films. The CNTs withstand the extreme shear stresses occurring during the extrusion. In addition to electron microscopy revealing the alignment, the materials show an anisotropy of the electrical conductivity, which could be adjusted by controlling the amount of CNTs.

1. Introduction

Theoretical and experimental studies on carbon nanotubes (CNTs) have brought to the fore their exceptional mechanical properties and interesting electrical characteristics such as a metallic or semi-conducting behavior. Another important feature of CNTs is their very high aspect ratio (5000–50 000). It has thus been proposed that CNTs could advantageously substitute carbon fibers as reinforcing elements in composites. Moreover, they could confer electrical conductivity to otherwise insulating materials, without altering their other properties since very low volume fractions could be sufficient to assure the percolation of the CNTs network. To avoid the electrostatic charging

of an insulating matrix, an electrical conductivity above 10^{-4} S/cm is needed. Some electrical conductivity is required to provide electrostatic discharge and also as electromagnetic radio-frequency interference protection.

Most of the research on CNTs-containing composites has so far dealt with polymer-matrix materials. In particular, the possibility of aligning the CNTs in a thermoplastic matrix has been demonstrated [1–4]. Ceramic-matrix composites have been much less investigated. CNT–SiC composites have been prepared [5] by mixing large multiwall CNTs (MWNTs – 30–40 nm in diameter) with SiC powder and hot-pressing the mixture. An improvement of about 10% over monolithic SiC both in bending strength and fracture toughness was reported, but the microstructure of the dense materials was not fully investigated. The present laboratory has reported the preparation of dense CNT–Fe–Al₂O₃, CNT–Co–MgO and CNT–Fe/

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Co–MgAl₂O₄ nanocomposites by hot-pressing and has investigated their mechanical and electrical characteristics [6–8]. In these materials, the CNTs are mainly single- or double-walled and form small bundles very homogeneously dispersed between the metal-oxide grains. Hot-pressing at high temperatures (1500–1600 °C) damages some CNTs, producing disordered graphene layers which gather at matrix grain junctions. Probably because of a too low relative density (87–93%), the fracture strength and the fracture toughness of the CNT-containing composites are generally lower than those of the corresponding carbon-free metal-oxide composites and only marginally higher than those of the ceramics. Electron microscopy observations reveal that some CNTs are trapped inside the matrix grains or at grain boundaries. Most of these CNTs are cut near the fracture surface after some pullout and could contribute to a mechanical reinforcement. However, this was not demonstrated at a macroscopic scale. One of the most interesting results [8] was that, whereas the ceramics and metal-oxide nanocomposites are insulators, the CNT–metal-oxide composites are electrical conductors with an electrical conductivity in the range 0.2–4.0 S/cm. This was attributed to the percolation of the CNTs. The values of the electrical conductivity are fairly well correlated to the relative quantity of CNTs, the specimens becoming insulators if the CNTs are destroyed since the so-produced disordered graphene layers do not percolate anymore.

It has been shown that, when their grains are maintained at sufficiently low sizes (less than 1 μm), many polycrystalline ceramics become superplastic in both compression and tension [9]. Superplasticity allows the use of thermomechanical processing for the forming of these materials. On the one hand, high-temperature extrusion has been successfully applied to superplastic ceramics [10]. On the other hand, Nauer et al. [11] have shown that the high-temperature extrusion of SiC whisker–zirconia composites led to the orientation of the whiskers in the extrusion direction, thus resulting in a mechanical reinforcement.

In the present Letter, it is shown for the first time that it is possible to align CNTs in bulk ceramic-matrix nanocomposites, using the high-

temperature extrusion technique, and that the resulting materials show an anisotropy of the electrical conductivity.

2. Experimental

The CNT–Co–MgO, CNT–Fe–Al₂O₃ and CNT–Fe/Co–MgAl₂O₄ composites were prepared in several steps. Firstly, the appropriate monophased oxide solid solutions (α -Al_{1.84}Fe_{0.16}O₃, Mg_{0.8}Fe_{0.1}Co_{0.1}Al₂O₄ and Mg_{0.9}Co_{0.1}O) were prepared by chemical routes. Each powder was composed of primary grains smaller than 100 nm. In Al₂O₃- and MgAl₂O₄-based powders, the as-produced primary grains were strongly aggregated and required attrition-milling using ZrO₂ balls in order to reduce aggregate size to less than 1 μm. This however produced a mild contamination of these powders by ZrO₂ particles about 1 μm in size. In a second step, the oxide powders were reduced in a H₂–CH₄ atmosphere (18 mol% CH₄, maximum temperature 1050 °C). Transition metal particles (Fe, Co or Fe/Co alloy) a few nanometers in diameter were produced, both inside and at the surface of each grain of the powder. The surface metal particles catalyze the in situ formation of single-walled CNTs (SWNTs) and MWNTs (mostly double-walled), which gathered in extensively branched bundles and were extremely well dispersed as a web-like network between the matrix agglomerates, as described in previous papers [12–14]. The carbon content in the powders was determined by flash combustion.

Dense composites were prepared by high-temperature extrusion in a graphite die, under primary vacuum. The die profile was manufactured from the design proposed by Kellett et al. [10] for the extrusion of ZrO₂-based ceramics. The large (14 mm diameter) and small (6.7 mm) cylinders are joined by a conical part with a cone angle of 26°. Lubrication was obtained by covering all the internal surface of the die with graphite paper. Firstly, the composites were partially densified under a mild load (8.6 MPa) and the materials were then extruded under a 43 MPa load (Fig. 1). Al₂O₃ and MgAl₂O₄-matrix materials were extruded at 1500 °C but the extrusion of MgO-matrix materials were required to increase the

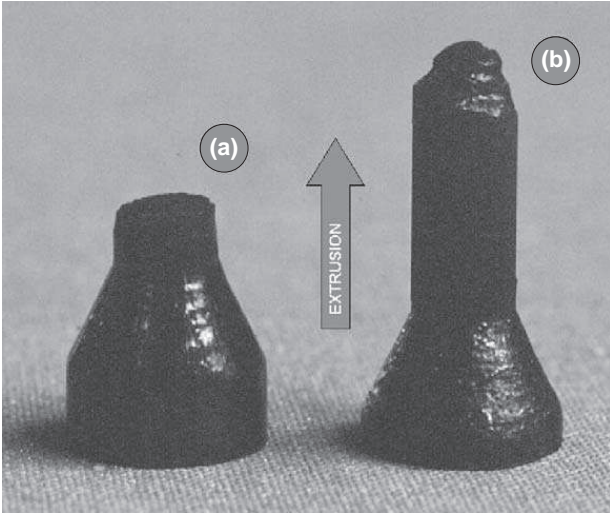


Fig. 1. Photograph of materials: at the beginning of the extrusion process (a) and when the extrusion is completed (b).

temperature up to 1730 °C. Cylindrical extruded rods, 6.7 mm in diameter and 20 mm in length were obtained.

The powders and the extruded materials were studied by X-Ray diffraction (XRD). Parallelepipedic specimens were machined from the composites with a diamond blade and ground with diamond suspensions. Relative densities were calculated from measurements obtained by the Archimedes method, using for CNTs the density of graphite ($d_{\text{graphite}} = 2.25 \text{ g/cm}^3$), in a first approximation. Polished-etched surfaces and fracture profiles were observed by scanning electron microscopy (SEM). High-resolution electron microscopy (HREM) observations were performed on two samples of the CNT-Fe/Co-MgAl₂O₄ material, cut either parallel or perpendicularly to the extrusion direction and then thinned by ion-milling. The electrical conductivity (σ) of the dense specimens was measured at room temperature with DC currents on parallelepipedic specimens ($1.6 \times 1.6 \times 8 \text{ mm}^3$), both in the direction of extrusion and in the transverse direction. The current densities used were lower than 160 mA/cm^2 .

3. Results and discussion

The densification of the extruded materials is of the order of 90%, which is similar or slightly higher

than what was obtained for similar hot-pressed specimens [8]. XRD pattern analysis revealed no other phases than those present in the starting composite powders. The carbon content is however relatively low (in the range 2.2–6.1 wt% for the different starting powders), and thus the presence of carbon cannot be determined quantitatively from the XRD patterns of the extruded materials. SEM observations of the extruded composites seem to show that they contain less CNTs than the corresponding powders. It has been determined that the average extrusion speed is higher for the CNT-Fe/Co-MgAl₂O₄ composite (ca. 200 $\mu\text{m}/\text{min}$) than for the corresponding Fe/Co-MgAl₂O₄ and MgAl₂O₄ oxide materials (ca. 100 and 10 $\mu\text{m}/\text{min}$, respectively) also prepared for the sake of comparison. This may reveal a lubricating role of the CNTs. The trend is that the extrusion speed decreases progressively for Al₂O₃- and MgAl₂O₄-matrix materials but rapidly for MgO-matrix materials. SEM observations show that, for CNT-Fe-Al₂O₃ and CNT-Fe/Co-MgAl₂O₄, the average grain size is lower than 1 μm (respectively, about 0.5 and 0.8 μm), in contrast to CNT-Co-MgO for which the grain size is ten times larger, about 10 μm . Thus, the grain growth is moderate for the first two materials, and it is very pronounced for the third one. Grain-boundary sliding which is known to be the predominant mechanism of the superplastic deformation in fine-grained ceramics [9] is inhibited by the concurrent grain growth, particularly for the CNT-Co-MgO sample. By comparison, the grain sizes were higher in samples nor containing any CNT, which confirms that the CNTs act as grain growing inhibitors [8]. As a consequence, the higher extrusion speed of CNTs-containing materials can also be explained by grain-growth inhibition.

In the MgO-matrix composite, SEM observation of fracture profiles showed only rare traces of CNTs, most of them having been destroyed. As noted earlier [8], this points towards a thermal instability of CNTs in the primary vacuum at very high temperatures (1730 °C). The destruction of the CNTs in CNT-Co-MgO samples explains both the exaggerated grain growth and the very rapid decrease of extrusion speed for these materials. However, in spite of grains becoming rapidly

larger than 1 μm , the extrusion proceeds at a reduced speed (4–8 $\mu\text{m}/\text{min}$), as a consequence of the intrinsic superplasticity of MgO grains themselves. By contrast, CNTs bundles with no apparent damage could be observed in the CNT–Fe–Al₂O₃ and CNT–Fe/Co–MgAl₂O₄ nanocomposites. This shows that the exceptional mechanical characteristics of the CNTs allow them to withstand the extreme stresses, notably shear stresses, that occur during the extrusion. Interestingly, the CNTs (or CNTs bundles) appear to be aligned (Fig. 2). It was however noticed that the alignment is more or less pronounced in different areas, as expected according to the location and the distance covered by the CNTs within the die during the extrusion. The alignment is not a consequence of the fracture, as evidenced by the observation that the extremi-

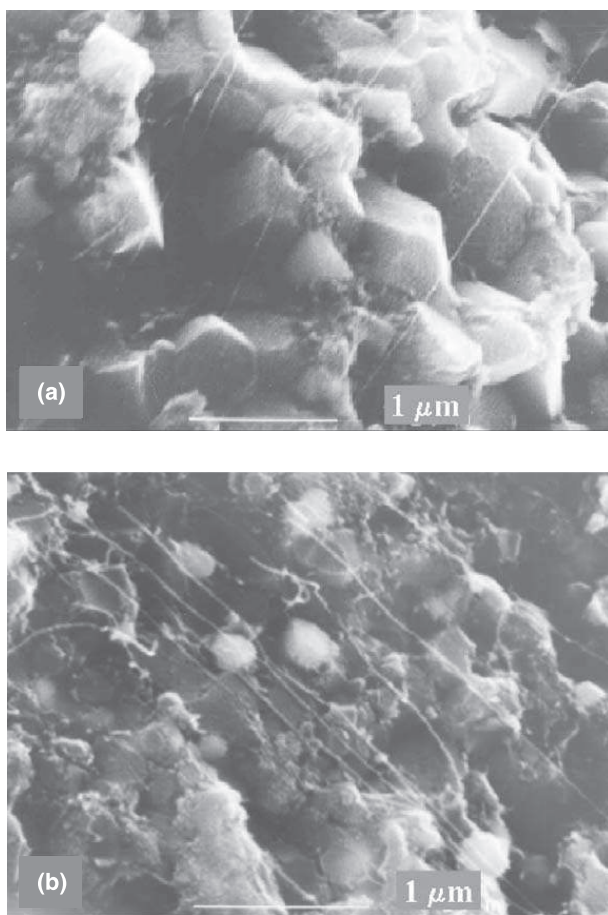


Fig. 2. SEM images of fracture profiles of the CNT–Fe–Al₂O₃ (a) and CNT–Fe/Co–MgAl₂O₄ (b) composites prepared by extrusion at 1500 °C. Note the alignment of the CNTs.

ties of the CNTs bundles are entrapped in the ceramic-matrix, being thus well tightened between these points. Moreover, the attack by hot H₃PO₄ of non-fractured CNT–Fe/Co–MgAl₂O₄ dense composites has led to the same kind of images, when no mechanical stress was involved during the sample preparation, thus confirming that the CNTs show a preferential orientation along the extrusion direction. HREM observations revealed linear and circular fringes due to the walls of CNTs which are either located inside pores or superimposed with matrix grains, thus showing that some CNTs seem to be undamaged by ion-milling. Disordered fringes were also observed, showing that some CNTs have been damaged, probably during the hot-extrusion. In the sample cut perpendicularly to the extrusion axis, most fringes were circular whereas most were linear in the sample cut parallel to the extrusion axis. These observations confirm the relative alignment of CNTs previously revealed by SEM observations.

The results of the measurement of the electrical conductivity (σ) of the CNT–metal-oxide composites are schematically shown in Fig. 3. The very low values measured for CNT–Co–MgO (Fig. 3a) reflect the almost total destruction of the CNTs, in both the non-extruded (upper) and extruded (lower) parts of the material. For the CNT–Fe–Al₂O₃ and CNT–Fe/Co–MgAl₂O₄ composites (Figs. 3b and c, respectively), the values measured in the non-extruded part are similar to those measured on hot-pressed specimens [8]. By contrast, the values measured at the bottom of the extruded part are significantly lower, which confirms that a fraction of the CNTs has been damaged or destroyed by the extrusion. Note that no measurable value of σ can be obtained on the corresponding oxides and metal-oxides composites prepared by hot-extrusion for the sake of comparison, which confirms that they are insulating materials when they do not contain CNTs. Two opposing phenomena are taking place simultaneously during the extrusion: on the one hand, some of the CNTs are obviously damaged or destroyed by the extrusion process, leading to a decrease of the electrical conductivity. On the other hand, we believe that the alignment of the remaining CNTs must lead to an increase of the

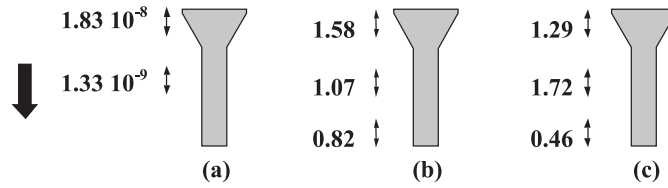


Fig. 3. Electrical conductivity (S/cm) measured on various parts of the extruded composites: (a) CNT–Co–MgO; (b) CNT–Fe–Al₂O₃; (c) CNT–Fe/Co–MgAl₂O₄. The bold arrow indicates the extrusion direction. The measures were done on test specimens sampled in different parts of the composites.

electrical conductivity along the extrusion direction. The *balance* between these two phenomena leads to the final result. According to our experimental results, the degradation of the CNTs is more important in the case of the MgO oxide matrix. Comparing the Al₂O₃ and MgAl₂O₄ oxide matrices, it seems that the aligning effect is more obviously brought to light in the latter case, as evidenced by the increase of the electrical conductivity along the extrusion direction when the extrusion is long enough to have started the aligning of the CNTs, but not enough to have damaged them too much (which is what explains the decrease of the electrical conductivity when we go further down along the sample).

Another CNT–Fe/Co–MgAl₂O₄ dense composite containing twice as much CNTs as the one described above was prepared by hot-extrusion. The CNTs quantity was evaluated using a method based on specific surface area measurements as described elsewhere [12–14]. The values measured for σ in the non-extruded part, along the extrusion direction and in the transverse direction (Fig. 4), are similar to each other (ca. 2.5 S/cm) and only slightly higher than those obtained for the previous composite. Interestingly, in the extruded part, there is a strong increase of the electrical conductivity measured along the extrusion direction ($\sigma_{//} = 20$ S/cm) whereas much lower values are measured in the transverse direction ($\sigma_{\perp} = 0.6$ S/cm). This anisotropy of the electrical conductivity, of the order of a factor 30, evidences the alignment of the CNTs, at the macroscopical scale, thus supporting the conclusions of the SEM and HREM observations. The need of enough remaining CNTs for the alignment to have an effect on the electrical conductivity is also well illustrated by the comparison of

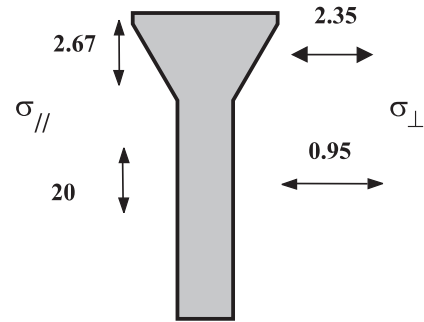


Fig. 4. Electrical conductivity (S/cm) measured on various parts of an extruded CNT–Fe/Co–MgAl₂O₄ composite containing twice more CNTs than the one described in Fig. 3c. The measures were done on test specimens sampled in different parts of the composite.

the two CNT–Fe/Co–MgAl₂O₄ dense composites: in the second material prepared, the electrical conductivity is already twice as much in the upper part of the sample, compared to the first one. The increase of the electrical conductivity (along the extrusion direction) in the middle of the sample – that is to say at half way along the extrusion direction – already noted in the first experiment, is even more important in the second one. This can be explained by the higher amount of remaining (and aligned) CNTs in the dense material obtained in the second case, because the starting composite powder was containing twice as much CNTs, both extrusions having been completed in exactly the same experimental conditions. We consider this result to be an additional evidence of the alignment of the CNTs within the bulk material. Preliminary thermogravimetric analysis tests revealed that the CNTs–metal-oxide composites could retain their electrical conductivity even at a work temperature of ca. 400 °C in air.

4. Conclusions

CNT–metal-oxide composites have been extruded at high temperatures. For temperatures up to 1500 °C, some of the CNTs remain undamaged neither by the high temperature nor by the extreme shear stresses. Moreover, the superplastic forming is made easier by the CNTs, which inhibit the matrix grain growth and also acts as a lubricating agent. It is shown for the first time that it is possible to align CNTs in ceramic-matrix nanocomposites. In addition to electron microscopy revealing the alignment, the materials exhibit an anisotropy of the electrical conductivity. The electrical conductivity value could be adjusted by controlling the amount of CNTs.

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