Thermomechanical Behavior of Bulk Ni/MWNT Composites Produced via Powder Metallurgy**

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The thermal expansion behavior of Ni matrix composites reinforced with multiwalled carbon nanotubes (MWNT) fabricated by pressureless sintering and hot uniaxial pressing was studied in the range between 50 and 1050 °C and compared to that of pure Ni. The results show an active interaction between the MWNT and the Ni matrix by reducing the coefficient of thermal expansion (CTE) of pure Ni up to 76% between 50 and 400 °C. This reduction is due to the strong interfacial interaction between the matrix and the reinforcement and the low intrinsic CTE of the nanotubes. This outstanding behavior may be very useful in applications were low CTE is required as for example structural materials.

In the past years, carbon nanotubes (CNTs) have attracted great amount of scientific and technological interest due to their unique properties. Because of their low dimensionality and high aspect ratio, the physical behavior of these materials is outstanding, showing for instance: very high thermal conductivity,[1,2] high tensile strength[3] and very low or even negative intrinsic thermal expansion,[4,5] making them the ultimate reinforcement fibers for a wide range of composites. In this direction, a great amount of research was devoted to the study of different polymer-CNT[6] and ceramic-CNT systems,[7] somehow relegating the metal-CNT systems to a second row. Regarding the low thermal expansion of the CNTs, the question would be how this property could be fully utilized in different materials. Our hypothesis is that once an optimal dispersion of the CNT bundles and a proper integration into the matrix is achieved, the mechanical properties of the material would be improved by increasing the matrix – reinforcement adhesion. Therefore the CNTs would act as an anchorage, preventing the expansion of the

composite. The aim of this work was to design a sequence of steps in order to achieve a bulk metal matrix composite possessing remarkable thermal expansion behavior produced by powder metallurgy routes with a good dispersion of the CNTs in the matrix. The samples were densified by pressureless sintering and hot uniaxial pressing (HUP) both under vacuum. Thermomechanical (dilatometry) measurements were carried out on the samples under an inert gas atmosphere. Moreover, a microstructural characterization was made using x-ray diffraction (XRD) and focused ion beam/scanning electron microscopy (FIB/SEM).

1. Experimental

Multiwalled CNTs (MWNT) commercially available as Baytubes C150P (purity: >95%, outer diameter distribution: 5–20 nm, agglomerate size: 0.1–1 mm) and Ni dendritic powder (Alfa Aesar, average particle size: 44 μm) were used as starting materials. A colloidal mixing process was developed for the production of the precursor blends, which consists in the merging of the dispersion of the CNTs in an ultrasound bath with *N,N*-dimethylformamide (DMF) and the subsequent addition of Ni powder to the same dispersion in a Ni/CNT weight ratio 99:1 (Ni/CNT 1.0 wt%). The CNT concentration ratio to DMF was fixed at $0.023\,mg \cdot mL^{-1}$ as studied by Coleman and co-workers.[8] After 10 min in the ultrasound bath, the resulting solution was stirred to homogenize the mixture and afterwards was dried inside a ventilated furnace. Once the mixture was dried, the blend was milled in an agate mortar for a better integration of the CNTs to the Ni particles. In order to consolidate the powders into green pellets the sample was axially pressed in steel circular dies of 8 mm in diameter with an axial pressure of 990 MPa. Finally, the samples were sintered using two different powder metallurgy routes, namely: pressureless sintering (CPS) and

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HUP. The first technique was carried out in a vacuum (2×10^{-5} mbar) tube furnace at 950 °C for 2.5 h. The other group of samples were sintered in a hot uniaxial press in vacuum (2×10^{-6} mbar) at 750 °C for 2.5 h with an axial pressure of 264 MPa using alumina pistons inside graphite dies. Both sample stacks were measured by the Archimedes' method in order to provide a first evaluation of the densification. Afterwards, XRD measurements were performed using a CuKα radiation ($\lambda = 1.5406$ Å) in an X'Pert Pro MRD™ diffractometer (PANalytical B.V.) to verify the structural integrity of the CNTs. The microstructural characterization was carried out by cross-section images obtained with FIB/SEM using the Helios NanoLab™ 600 dual beam microscope (FEI Company) Finally, the thermal expansion data were collected in a Dilatronics II differential and vertical Theta Inc. apparatus at a constant heating rate of 5 °C · min^{-1} under Ar flow (4.6 grade). The runs were calibrated with silica glasses of the same thicknesses.

2. Results and Discussion

2.1. X-Ray Diffraction

In the past years, there have been contradictory affirmations about the reaction of the Ni–C system. Some researchers reported, based on thermodynamical calculations, that the formation of nickel carbide (Ni_3C) is unlikely to happen.[9] On the other hand, several groups have studied the formation and stability of Ni_3C in Ni–C systems.[10] In general, the CNTs surface shows very low reactivity but, when defects or open ends are present (as in the case of ultrasonic dispersion of CNTs), these sites become reaction prone sites.[9] The analysis of the XRD patterns delivers a qualitative assessment about the structural integrity of the CNTs after the densification process. Figure 1a shows the XRD patterns for both types of samples (CPS and HUP). Both samples showed the Ni (111), (200), (220), (311), and (222) planes. Since the diffraction intensity of Ni is significantly higher than of C and the added volume fraction of CNTs is relatively low (about 6.5%), the C peaks are probably covered by the background noise. From

these measurements we can confirm that no nickel carbide is observed thus suggesting that the CNTs structural and chemical integrity would not have been modified.

2.2. Thermal Expansion

The thermo-mechanical measurements showed very interesting results regarding the thermal expansion, particularly in the low temperature (50–400 °C) regime. The tested samples presented expansions and densifications, which could be attributed to residual matrix – reinforcement stresses.[12] It is noteworthy that up to about 450 °C the lowest thermal expansion was observed for the CPS composites. This could be attributed to a much lower breakage owing to the low consolidating pressure and the absence of pressure during sintering. The on-set densification temperature was observed at about 600 °C. Figure 1b shows the relative expansion (dL/L_o) of sintered specimens having 1.0 wt% of CNTs, and it may be noted at about 840 °C the Ni/CNT 1.0 wt% HUP specimen exhibits a clear densification bend. During the expansion a break point in the slope at roughly 450 °C is observed. The densification on-set might be directly related to the initial state in the solid state sintering (SSS).[13,14] Also, another change in the densification rate at around 930 °C is detected. These thermal effects will be thermo-kinetically analyzed in a further work. The maxima in the densification rates are around 1050 °C or lower, which is about 400 °C below the melting point of Ni. The high densification rates and the low temperatures at which densification takes place suggests a highly pure and active Ni powder having clean grain surfaces.

We have determined an expansion coefficient of thermal expansion (CTE) of 9.1×10^{-6} and 3.9×10^{-6} °C^{-1} for HUP and CPS samples respectively in the 50–400 °C range, a value considerably lower than that for pure Ni, of about 16.3×10^{-6} °C^{-1}. The lower expansion may be explained by a good fiber-matrix bonding at the high temperature sintering stage. In such an eventual condition the lower expansion of the CNTs may set up the matrix under tensile stress at room temperature.[12]
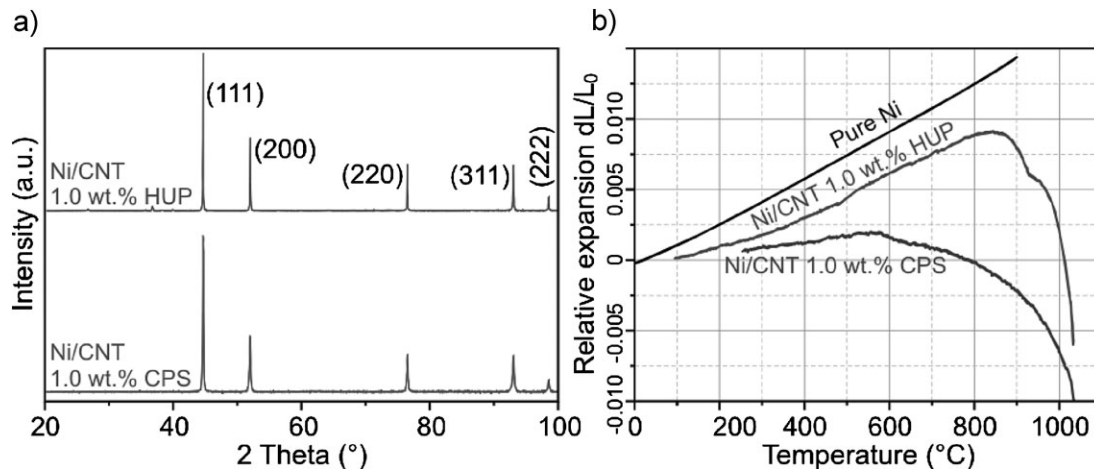

Fig. 1. a) XRD patterns of CPS and HUP samples. b) Thermal expansion curves of the samples. As a reference, pure Ni expansion was plotted from ref.[11]
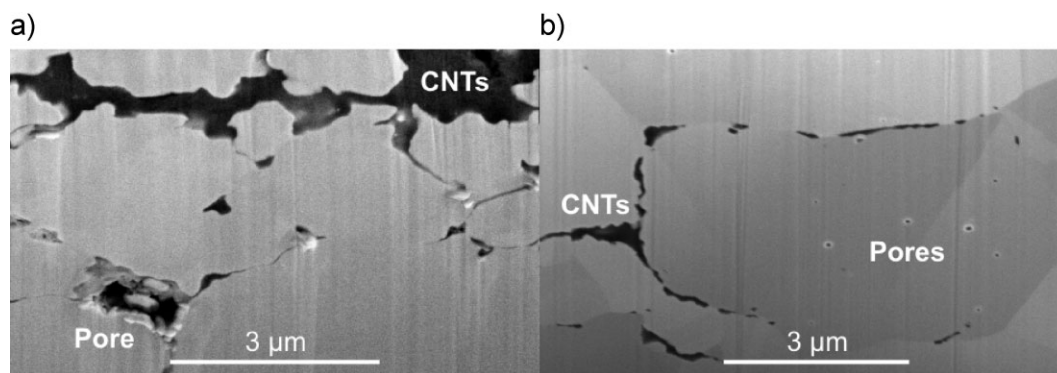
a)   b)

Fig. 2. SEM micrographs from FIB cross-sections of (A) CPS and (B) HUP composites.

2.3. Microstructural Characterization

Figure 2A shows the FIB cross-section of the Ni/CNT 1.0 wt% CPS sample, which presents a good densification despite the observed porosity. This sample was about 6% less dense than the pure Ni, as presented in Table 1. The porosity situated in the near region of the CNT clusters confirms that the cohesion between Ni and CNT clusters is very low or even in some cases non-existent. This reagglomeration might be generated in the pressureless sintering stage of the process where the heating ramp is low and the sintering neck formation is delayed, leaving the CNTs a pathway for their bundling. In this type of free densification process, the absence of external dimensional constrains at the time of the treatment permits the existence of voids where the CNTs reagglomerate. This is not the only effect due to the lack of dimensional restriction, but also the reaching of the theoretical density is complex because the material is free to expand in all directions. Moreover, it can be noticed that the pore size is in the submicron region.

However, for the case of the Ni/CNT 1.0 wt% HUP samples (Figure 2B) the pore size is drastically reduced to tens of nanometer size. In this case, the clusters size is smaller compared to the CPS sample, and most of them are located at grain borders. This particularity was already depicted for other types of composites and might be the responsible for the grain size regulation generated by stagnation due to a pinning effect produced by the CNTs.[15] This type of distribution is helpful for the load transfer from the matrix to the reinforcements. Contrary to the CPS process, in HUP there is a dimensional restriction of the sample due to the die allowing only the possibility to the material to self-diffuse towards the

inside. Based on our observations, we claim that the apparent intergranular CNT clustering could be actually a grain interface distribution that was just overlapped by the matrix and could not be differentiated by the FIB cross sections.

3. Conclusions

Ni matrix composites reinforced with 1.0 wt% of MWNTs were successfully manufactured with two different powder metallurgy routes. A colloidal mixing process was developed so as to achieve a proper distribution and interfacial bond between the MWNTs and the matrix. This integration was confirmed by the reduction in the thermal expansion coefficient from pure Ni up to 76% in certain cases. This reduction is directly related to the anchorage given by the MWNTs to the matrix preventing larger thermal expansions. Moreover, no carbide formation was observed by analyzing the phases present after the densification process. Further work will be carried out in order to comprehensively analyze the densification points observed in the thermal expansion curves. These composites may be promising in applications were low CTE and structural stability is required.

Table 1. Density Values of the Produced Samples and Their Thermal Expansion Coefficient (CTE).

Sample	Rel. density (%)	CTE ($\times 10^{-6}$ °C^{-1})	CTE Red. (%)
Pure Ni	100	16.3 ± 0.08	–
1.0 wt% HUP	95.5	9.1 ± 0.04	44.2
1.0 wt% CPS	93.7	3.9 ± 0.06	76.1

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