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A high temperature X-ray diffraction study of the influence of MWCNTs on the thermal expansion of MWCNT/Ni composites

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ABSTRACT

The inclusion of multiwall carbon nanotubes (MWCNTs) into metallic matrices is expected to improve their electrical and mechanical performance. This work analyses the lattice thermal expansion behavior of MWCNT-reinforced Ni composites in order to understand the influence of CNTs on their thermomechanical properties. The lattice thermal expansion coefficient (CTE) of the composites was estimated from X-ray diffraction measurements as a function of the temperature. The MWCNT-reinforced composites show higher lattice CTE (up to 12%) compared to pure Ni. This behavior is mainly produced by the expansion mismatch between the matrix and the reinforcements. We suggest three main mechanisms that explain the behavior of the CTE of metallic matrices in presence of MWCNT. These mechanisms correlate to the anchoring effect observed in previous macroscopic measurements of thermal expansion carried out on the same system.

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1. Introduction

Metal matrix composites are widely used in different fields of applications in materials science. Due to their electric and magnetic properties, Ni composites are used in commercial rechargeable batteries electrodes [1,2], reactor electromagnets in [3] and as a constituent in electrical contact materials [4], among others. The latter composites usually contain either ceramic elements that are intrinsically electrically insulating or semiconductive at best, thereby reducing the global thermal and electrical conductance; or a high amount of noble metals. We propose an alternative that circumvents both drawbacks: the use of conductive, high performance reinforcements. Since their discovery [5–7], carbon nanotubes (CNTs) have shown outstanding physical properties and are a benchmark for thermally conductive materials to date [8,9], presenting tailored semiconductor behavior [10] as well. Multiwall carbon nanotubes (MWCNTs)

have the particularity of always being metallic (zero band gap conductors) due to the fact that they possess at least one metallic layer [11].

The understanding of the lattice thermal expansion behavior of Ni composite systems is fundamental to the design of functional materials, especially for those subjected to thermal cycling. As it has been reported, CNTs can actually have negative coefficient of thermal expansion (CTE) with a minimum at 800 K [12]. These negative expansion modes are due to a gain in structural and vibrational entropy, translating into a dimensional decrease [12]. Thus the inclusion of MWCNTs into metallic matrices is expected to increase the span of application fields by improving their thermomechanical performance. Several authors [13–15] have developed studies on the thermal expansion behavior of certain alloys and materials, yet no attention has been paid to MWCNT/Ni composites.

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This work analyzes the lattice thermal expansion behavior of the Ni lattice in MWCNT/Ni composites in order to understand the influence of CNTs on their thermomechanical properties. As reported in a previous work [16], several systems were fabricated by mixing Ni dendritic powder with 1.0, 3.0 and 5.0 wt.% of MWCNTs by a colloidal mixing process and then consolidated by cold pressing at 990 MPa. The lattice parameters were measured by X-ray diffraction (XRD) in a high-temperature (HT) chamber under medium vacuum conditions. Our novel results highlight the influence of the CNT distribution throughout the Ni matrix on the thermomechanical properties of the composites, as well as the CNT/lattice interaction under a thermal input. The obtained knowledge constitutes a basis for a further understanding of the mechanisms acting in the composites under thermal load.

2. Experimental

The MWCNT/Ni bulk composites were manufactured by cold pressing at 150 bar and sintered at 950 °C for 2.5 h in vacuum. The starting materials were Ni dendritic powder (Alfa Aesar, 325 mesh) and MWCNT Baytubes C150P (Bayer Materials Science). The composites were made with 1.0, 3.0 and 5.0 wt.% of the filler. In order to compare their behavior and the influence of the CNT content, pure Ni samples were also manufactured with the as-received powder. The

microstructure of the samples was analyzed in a dual-beam focused ion beam/scanning electron microscopy (FIB/SEM) workstation (FEI Helios NanoLab 600).

The HT-XRD measurements were carried out in an Anton Paar HTK1200 HT-chamber at $\sim 10^{-6}$ mbar and mounted in a PANalytical X'Pert MPD X-ray diffractometer. The diffractograms were obtained using a parallel θ – θ geometry configuration and a $\text{CuK}\alpha_1$ radiation ($\lambda = 0.15406$ nm). The incident and diffracted optical geometries were parallel and the irradiated area ranged from 11.7 mm² for the (220) reflection to 19.2 mm² for the (111) reflection. The diffraction angle was varied from 20° to 90° with a step size of 0.0131° and a 0.5 s/step rate. The applied voltage and current were 40 kV and 40 mA, respectively. In order to avoid systematic errors from misalignments and thermal expansions of the sample holder, the 2θ scan data were corrected using the Nelson–Riley (NR) approximation [17].

The Nelson–Riley method is an extrapolation procedure where the systematic error introduced by the eccentricity of the sample with respect to the rotation axis in the diffractometer is corrected. This eccentricity has been found to be proportional to $\cos^2(\theta)$. For the correction, the calculated lattice parameter “a” from the raw data is plotted against $\cos^2(\theta)/\sin(\theta)$, which is a widely used function for cubic systems. The obtained points are later linearly fitted and the intersection with the y-axis provides the corrected lattice parameter.

For the HT-XRD measurements, the samples were heated from 50 to 950 °C at 10 °C/min and the diffractograms were

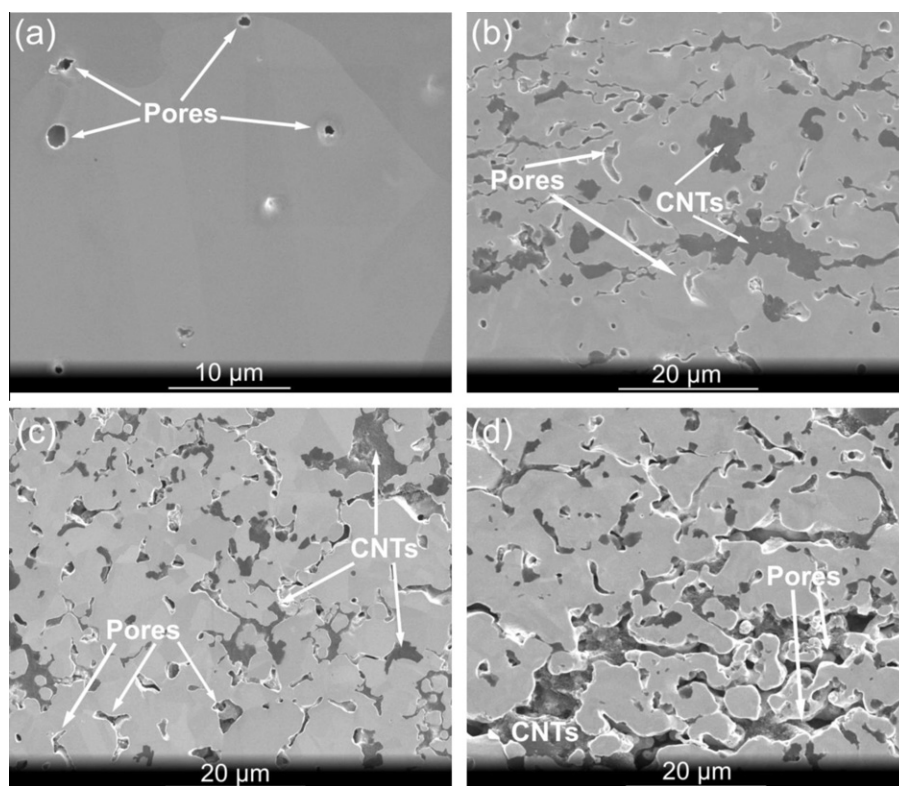


Fig. 1 – SEM micrographs of (a) pure Ni, and a Ni matrix with (b) 1.0%, (c) 3.0% and (d) 5.0% MWCNTs in weight. The dark grey areas inside the free volumes correspond to CNTs. The grey zones observed in the Ni matrix with different refinements correspond to different grains.

obtained every 100 °C after a 15 min stabilization. The temperature distribution in the sample was thus homogenized and errors due to temperature gradients were reduced.

3. Results and discussion

The SEM micrographs in Fig. 1 reveal the integration of the MWCNTs in the Ni matrix. In the pure Ni samples, a small number of pores and grain boundaries can be seen. This amount of porosity is normal and is mainly due to the samples manufacturing technique. The final densities of the studied composites are around 95–96%. Other sintering

techniques such as spark plasma sintering (SPS) might indeed be a solution for the improvement in the densification of the composites; however it has been reported in the literature [18] that, under the processing conditions of the mentioned technique, the structural integrity of the fillers is compromised either due to decomposition or reaction with the matrix material. The composite samples present a higher free volume and MWCNTs at the grain boundaries. Particularly, in the 3.0 and 5.0 wt.% samples, certain pores reveal poor cohesion between the reinforcements and the matrix. This is due to a higher degree of agglomeration of the MWCNTs, which further translates into a low adherence between the clusters

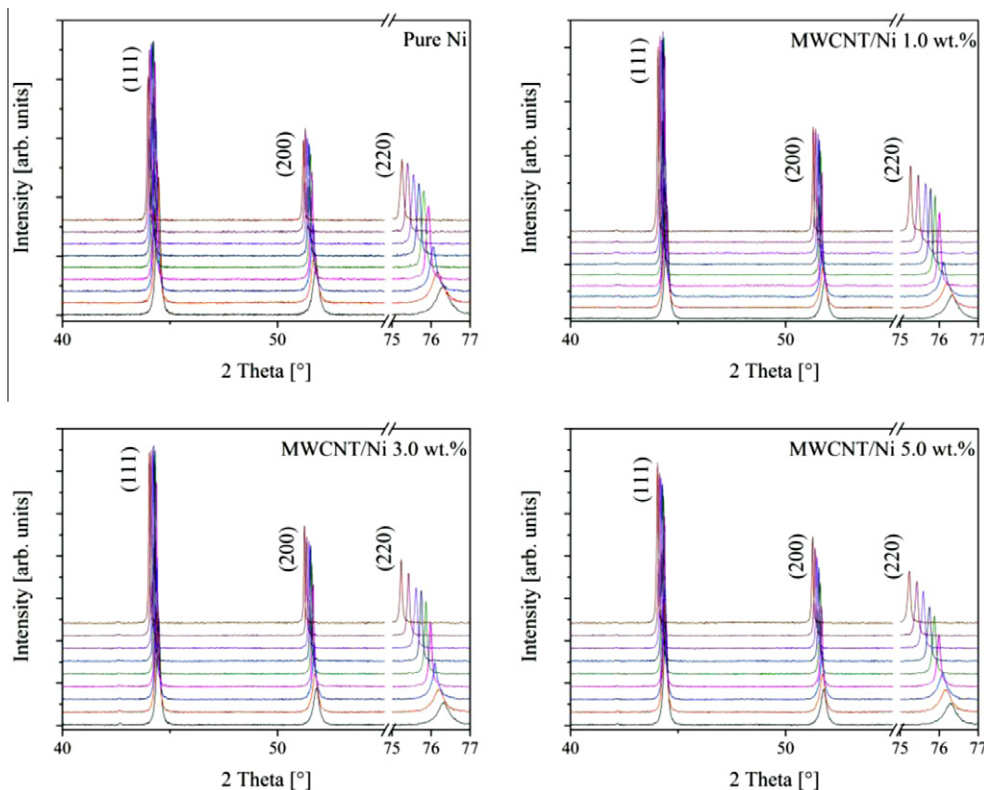


Fig. 2 – Diffractograms of the tested samples as a function of the temperature (in °C). The lower curve corresponds to 50 °C and the last to 850 °C. The shift of the (111), (200) and (220) Bragg peaks towards lower 2θ angles are due to the expansion of the d-spacing between the corresponding planes.

Table 1 – Ni lattice parameters measured in all MWCNT/Ni samples by HT-XRD and estimated by the NR method.

Temperature (°C)	$a_{\text{corrected}}$ (nm)			
	0 wt.%	1.0 wt.%	3.0 wt.%	5.0 wt.%
50	0.3526(1)	0.3526(1)	0.35261(8)	0.3526(1)
150	0.35328(9)	0.3532(1)	0.35321(6)	0.35321(8)
250	0.35376(7)	0.35376(4)	0.35378(2)	0.35381(3)
350	0.354361(5)	0.35437(1)	0.35439(1)	0.35440(2)
450	0.35492(3)	0.35494(3)	0.35497(3)	0.35499(2)
550	0.35551(1)	0.3555(6)	0.35555(3)	0.35561(3)
650	0.35612(1)	0.356(1)	0.35621(4)	0.35634(3)
750	0.35674(2)	0.357(1)	0.35706(4)	0.35711(4)
850	0.35739(2)	0.358(1)	0.35792(5)	0.35796(4)

and the matrix. However, the 1.0 wt.% sample displays a better dispersion and distribution within the matrix. The reduced amount and size of the clusters improves the adhesion of the MWCNTs to the matrix.

As showed in Fig. 2, the Bragg reflections (111), (200) and (220); were observed in all the samples throughout the complete temperature range. In the diffractogram measured at 50 °C they were located at 44.51°, 51.84° and 76.37°; respectively. After heating, these peaks shifted towards lower 2θ angles due to the expansion of the d-spacing between the corresponding planes. The MWCNT/Ni samples presented similar behavior and no other Bragg reflections were observed with the inclusion of the MWCNT into the matrix. The estimated values of the face-centered cubic lattice parameter of Ni as a function of temperature are summarized in Table 1. It is worth noting that the Bragg reflections become narrower as the temperature increases mainly due to the growth and/or coalescence of the grains and to stress relaxation processes.

The lattice thermal expansion corresponds to a temperature-gradient-induced reversible variation of the lattice parameter of a crystal. In the general case, the relation between the lattice parameter and the temperature can be modeled by polynomial dependence [19]. The first-order temperature term describes a harmonic behavior, valid for small amplitudes of atomic vibration (<1%). The second-order term corresponds to the asymmetry of the mutual Coulomb repulsion between atoms. The third-order term corresponds

to large amplitudes of atomic vibration that lead to energy dissipation. Non-harmonic behaviors are usually significant at temperatures close to absolute zero or melting points. Since the melting point of Ni is higher than 1400 °C [20], we have thus assumed harmonic first-order behavior of the lattice expansion.

The lattice parameter estimated by NR was fitted with a linear regression [17]. As presented in Fig. 3, the curves show a similar behavior, but differ in their slopes. The CTE is defined as the fractional variation in length per unit temperature change $\alpha = (1/L_0) \cdot \partial L / \partial T$. The calculated CTE of the pure Ni samples was $1.66(2) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, which agrees with the standard powder value [16,21]. The values for the MWCNT/Ni composites were $1.86(7) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ (1 wt.%), $1.83(5) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ (3 wt.%) and $1.86(5) \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ (5 wt.%). The composites showed a higher lattice CTE than that of pure Ni by around 12% for the 1 wt.% samples, while the increment in MWCNTs did not significantly affect the thermal expansion of the composites.

Our present results disagree with the behavior of the thermal expansion coefficient reported in bulk metal matrix composites containing CNTs and measured by differential dilatometry [16]. Regarding this, Roy et al. [22] mention that usually in materials with a very low CTE, the bulk thermal expansion is not necessarily identical to that of a single crystal from which it is fabricated. Indeed, this anomaly is produced mainly by a compensation effect resulting in an

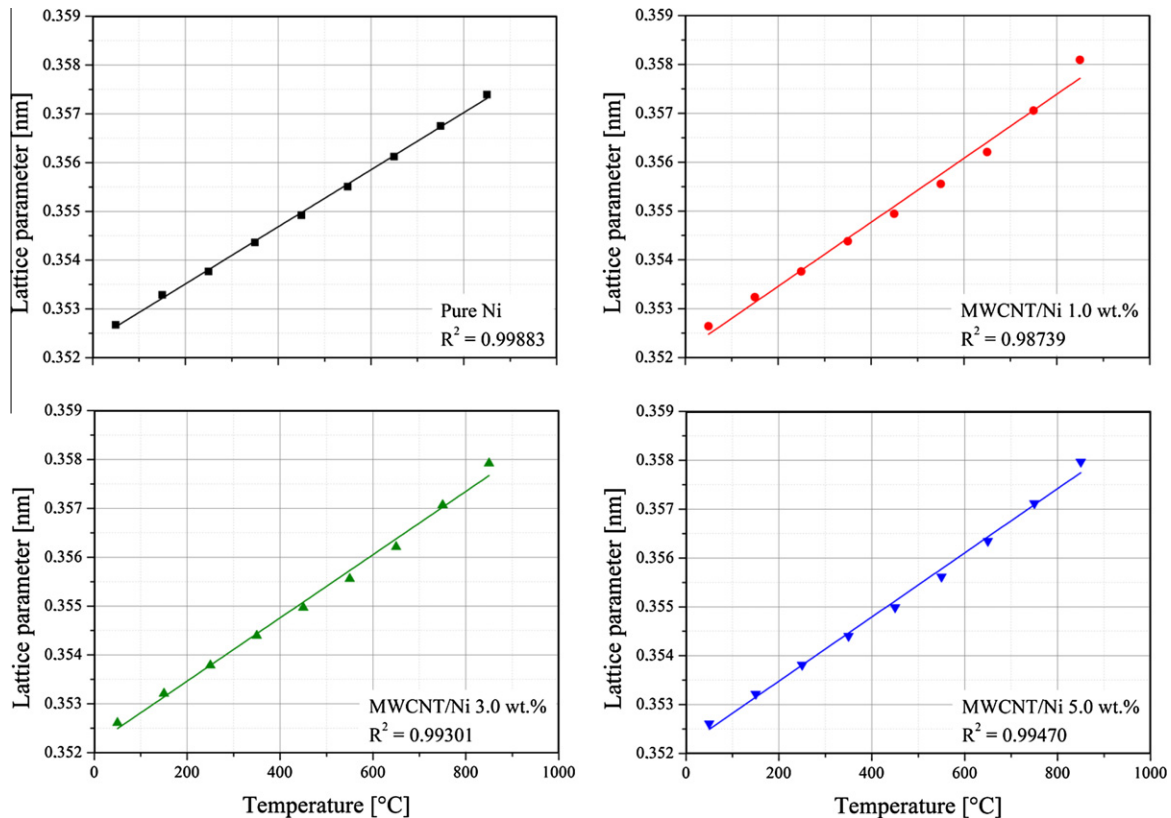


Fig. 3 – Lattice parameter of the MWCNT/Ni composites estimated from the data shown in Fig. 2 using the Nelson–Riley method. Linear regression fitting was performed in order to estimate the thermal coefficient of expansion of the composites as a function of the percentage of MWCNTs added to the Ni matrix. The statistical error of the measurements is lower than the size of the data symbols.

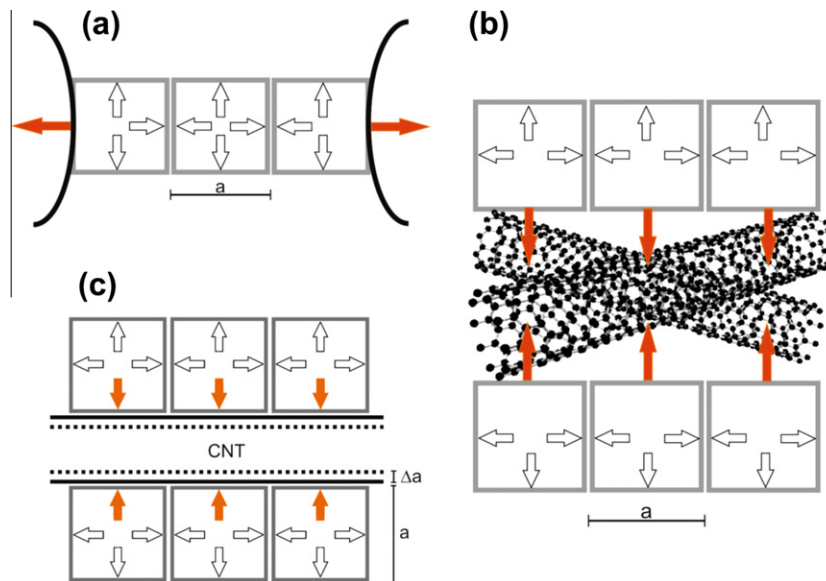


Fig. 4 – Scheme of possible thermal expansion mechanisms of the Ni unit cells in presence of CNTs (not to scale). Lattice expansion between (a) porosities, (b) CNT clusters and (c) grain boundaries delimited by a single CNT. The lattice parameter of Ni is represented by “a”.

average CTE value. By analyzing the available research on this topic, we found that the fundamentals of the interaction between the CNTs and the metallic matrix were to some extent not deeply discussed and described. Uddin et al. observed [23] that the addition of MWCNT to Cu and Al reduces the CTE up to 20% compared to that of the pure metals. The explanation given is based on the uniform dispersion and proper embedding of the MWCNT in the metallic matrix, restraining the grains, bridging and pulling the matrix together during the thermal cycling. Another work carried out in this direction [24] reports a reduction of about 65% in the CTE of an SWCNT/Al composite. This decrease is explained by powerful constraints provided by the SWCNT, grasping the matrix material.

In order to explain the observed behavior of the CTEs, we suggest three main probable lattice expansion mechanisms that could be acting in the composites during the thermal input. Since the expansion is measured in the Ni matrix, the lattice unit cells that are adjacent to pores or clusters present more free volume to expand without restraint (Fig. 4a and b). When a single CNT is in a grain border (Fig. 4c), the adjacent unit cells also expand more than the ones inside the grain since CNTs have zero or negative thermal expansion under thermal inputs [12]. All the described mechanisms produce a relaxation of the micro-stresses, which are measurable by XRD within the information volume range ($0.53\text{--}0.62\text{ mm}^3$). By analyzing the variation of the lattice parameter with the temperature for all the samples (with and without embedded CNTs), a shift in the values in the $10^{-2}\text{--}10^{-3}\text{ \AA}$ range is observed. This variation represents the absolute dimensional change in the lattice. When compared to the lattice parameter at room temperature and the CNT diameters, it is about 3–4 orders of magnitude lower. Despite this difference and considering the CTE close to zero for the CNTs [12], it can be assumed that the anchoring provided by the CNTs to the

matrix could actually be enhanced by the absorption of lateral displacement by the CNTs. When studying the behavior at a lower scale, this effect is observed as a partially-free expansion of the lattice within the composite. However, when measured macroscopically, it produces a reduction in the coefficient of thermal expansion. This difference might be due to unmeasured lattice defects originated by the addition of CNTs into the manufacturing process. The presence of second-phase particles introduces deviations from the expected behavior based on previous studies carried out with the same technique. For example, in the case of Ni-based alloys [13,14], the results are in accordance with commercial values. The influence of second phases on the behavior must be carefully determined using complementary techniques in order to state a definitive conclusion regarding the thermomechanical behavior of composites. In this regard, further experiments are required in order to either confirm or dismiss the presented hypotheses.

4. Conclusions

Composites consisting of Ni matrices reinforced with MWCNTs were successfully fabricated and characterized by SEM and HT-XRD. The lattice parameters of the Ni composites were determined as a function of the temperature by XRD using the Nelson–Riley method, thus avoiding systematic errors from the thermal expansion of the sample holder. We observe that the addition of MWCNTs as fillers increases their lattice coefficient of thermal expansion mainly due to the presence of free volume between the grains in the matrix produced by the agglomeration of nanotubes and porosity. Also, no significant variation of the coefficient was observed after increasing the percentage of carbon nanotubes probably due to the small size of the information volume obtained by XRD. Furthermore, we propose three different mechanisms

that may be acting in the composite, which explain the macroscopic response in the bulk material. The difference with the bulk CTE measured in previous works can be explained by the presence of dislocations, defects and voids. Moreover, anchoring provided by the CNTs to the matrix could actually be enhanced by the absorption of lateral displacement by the CNTs. The results presented in this paper highlight the importance to state the limitations of different techniques that measure similar physical properties. Other complementary techniques should be accordingly compared in order to state a definitive conclusion regarding the thermomechanical behavior of Ni matrices filled with CNTs.

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