PAPER REF: 4058

CNT AGGLOMERATES SIZE AND DISTRIBUTION INFLUENCE ON ALUMINUM COMPOSITES STRENGTH

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ABSTRACT

Carbon nanotubes (CNT's) incorporation in metal matrix composites (MMC's) is hampered by the development of attractive van der Waals forces, which lead to the formation of CNT agglomerates. Most of the existing processes used to fabricate these MMC lead to the formation of these agglomerates. Therefore, a detailed characterization of CNT agglomerates size and dispersion can enlighten their influence in the composite strength. This work presents a comprehensive statistical study, quantifying agglomerates by size, for different CNT contents in the composite, in order to relate these factors with the obtained tensile strength of the composite.

Keywords: Carbon nanotube (CNT), metal matrix composite, aluminium alloys, powder metallurgy, tensile strength.

INTRODUCTION

Aluminum-based composites are one of the most promising materials, once they gather advantageous properties like low density and high specific stiffness (Esawi A., Morsi K., 2007), suitable for a great variety of applications, especially where these properties are vital, such as automotive and transportation industry. Aluminum-based metal matrix composites are being developed by the use of new reinforcements and also by developing and/or optimizing production processes, in order to achieve better mechanical properties.
Carbon nanotubes exceptional mechanical properties (Pérez-Bustamante R. et. al, 2008)
, extremely low thermal expansion (Tang Y. et. al., 2004), and high thermal conductivity (Tang Y. et. al., 2004), are leading to the development of new CNT reinforced composites, using polymeric (Thostenson E. T. et. al., 2005; Thostenson E. T. et. al., 2001), metal (Lim D. S. et. al., 2005) or ceramic (Peigney A. et. al., 2000) matrices. Concerning metal matrices, both single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT), are being used as reinforcements, mainly in aluminum alloys (Lim D. S. et. al., 2005; George R. et. al., 2005; Deng C. F. et. al., 2007; Zhong R. et. al., 2003; Morsi K. et. al., 2007), but also in titanium(Kuzumaki T. et. al., 2000), copper (Carreño-Morelli E., 2006; Dong S. R. et. al., 2001; Tu J. P. et. al., 2001; Kim K. T. et. al., 2006; Li H. et. al., 2009) and magnesium alloys (Carreño-Morelli E. et. al., 2003).
Some processing techniques have demonstrated to be able to take a significant advantage of CNTs by substantially increasing composite properties. C. N. He et al., (He C. et. al., 2007) obtained a 184% improvement in ultimate tensile strength, when compared with base material, with an addition of 5 wt. % CNT's. These authors produced a composite by using the chemical vapor deposition (CVD) technique, with CNT's being produced in situ, in aluminum powder, achieving, this way, a good dispersion. In order to compare these results with those obtained by a traditional route of mixing aluminum powders with CNTs, the same

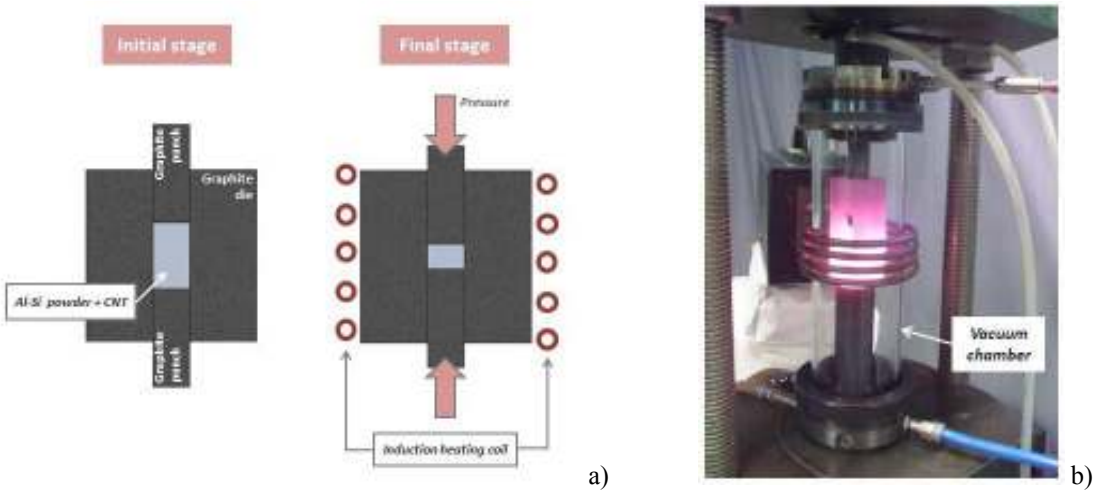
authors also produced specimens by ball-milling CNT's in the aluminum alloy powder. They verified that the improvement in ultimate tensile strength was 52% (He C. et. al., 2007). C. N. He et al., in another work (He C. N. et. al., 2009) and using the same CVD process to produce aluminum CNT's composites, tried different amounts of carbon nanotubes (1.5; 3.5; 5 and 6.5 wt. %) and verified that the 5 wt. % samples presented the best mechanical properties (tensile strength and young modulus).
However, although effective at laboratory level, the CVD processing technique (He C. et. al., 2007; He C. N. et. al., 2009) does not seem suitable for large-scale production of the composite. The most promising techniques for large-scale industrial implementation are still based on mechanical mixture of CNT's to metal powders following the processing route already used in powder metallurgy (PM) industries. Hence efforts should be allocated in optimization of this procedure to optimize CNT's proper distribution.
One of the biggest problems concerning the incorporation of carbon nanotubes as reinforcement in metal matrix composites is still the difficulty to disaggregate nanotube agglomerates, due to developed attractive van der Waals forces (He C. et. al., 2007). Agglomerates are responsible for the reduction of the expected composite enhancement of mechanical properties (He C. et. al., 2007). Further, as the matrix metal powder average size is usually much larger than that of CNT's, it is difficult to achieve their homogeneous distribution in the composite (Deng C. F. et. al., 2007). Therefore, achieving a uniform dispersion of CNT's in MMC's is a not fully accomplished challenge in PM, for the most widely used CNT's mixing technique, namely the ball milling technique (Esawi A., Morsi K., 2007; Pérez-Bustamante R. et. al, 2008; George R. et. al., 2005; Deng C. F. et. al., 2007; Carreño-Morelli E., 2006). In this technique, metal powders and carbon nanotubes are placed in stainless steel jars containing stainless steel spheres. Normally the jars are filled with argon to avoid the oxidation of metal powders and then agitated with a certain rotation speed, using a mechanic system (Esawi A., Morsi K., 2007; Morsi K. et. al., 2007). The ball milling and sintering or hot consolidation of powdered mixture can be preceded by different mixture techniques like blending ultrasonically metal powders with CNTs in an organic solvent (e.g., alcohol) followed by solvent evaporation (Tang Y. et. al., 2004; Zhong R. et. al., 2003).
Although it is known that CNT's agglomerates are responsible for properties reduction (Esawi A. M. K. et. al., 2008; Esawi A. M. K. et. al., 2010) and although several studies focus on the production of MMC using CNT ball milling technique, to date no investigation has been performed concerning the characterization and influence of CNT agglomerates in the composite tensile properties. In this sense this study presents a comprehensive statistical study, quantifying agglomerates by size and amount, for different CNT composite contents, presenting a new methodology to assess the existence of CNT's agglomerates and to characterize them.

EXPERIMENTAL PROCEDURE

Fabrication of CNT-reinforced Al-Si composites

Aluminum Silicon powder (Al-Si 88-12 wt. %, 99% pure - 325 mesh) purchased from AlfaAesar - Germany, and Multi-Wall Carbon Nanotubes (MWCNT) Nickel coated, grown by CCVD, from *CheapTubes.com* - USA, were used to produce Al-Si based nanocomposites. The Al-Si powder had a measured average particle diameter of 8 μm, while the MWCNT possess a length between 0.5 and 2.0 μm and a diameter higher than 50 nm (information given by the supplier).

Powder metallurgy technique was used to obtain three types of composites, with different MWCNT additions: 2, 4 and 6 wt. %. Unreinforced samples (Al-Si 88-12 wt. %) were also produced by the same PM technique, for comparison purposes.
Al-Si powders and MWCNTs mixture was made inside a closed stainless steel jar, together with 12 steel milling balls with 10 mm diameter, presenting a ball-to-powder weight ratio of 10:1. The jar was placed in a rotation device and the mixing was made with a constant rotation speed of 40 rpm, during 6 days (low-energy ball milling).
Afterwards the Al-Si/MWCNT mixture was introduced in a rectangular profile graphite die (fig. 1(a)) and slightly compacted. The die was then placed in a vacuum chamber (fig. 1(b)), where it was heated till 550ºC.



a) b)

Fig.1 Hot pressing (a) schematic representation and (b) vacuum chamber detail.

The samples were produced applying uniaxial load pressure of 35 MPa and a temperature of 550 ºC during 10 minutes (hot pressing). The obtained samples had average dimensions of 44 x 3.4 x 6 mm.

Characterization techniques and image analysis

The produced composites were characterized regarding the distribution of MWCNT in the matrix, especially concerning the presence of agglomerates, by means of Scanning Electron Microscopy (SEM), in backscattered view. Fig. 2 presents a SEM image in backscattered view of an Al-Si/2%CNT composite sample, showing the presence of agglomerates due to the fact that the CNT's are nickel coated and easily observed in backscattered view (CNT's white color comes from the nickel coating).

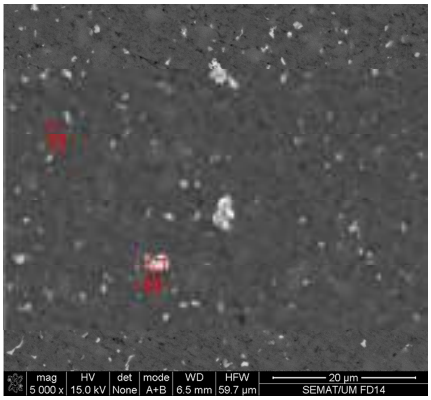


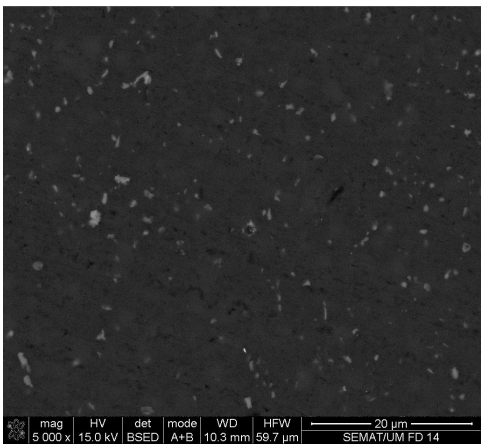
Fig.2 SEM image in backscattered view of an Al-Si/2%CNT composite sample.

Table 1 presents the chemical composition of the areas observed in fig. 2, showing that the white areas are CNT's. This fact allows an easy agglomerates size observation and quantification. Without the nickel coating, CNTs observation with these lower amplifications was not possible. From Table 1 it is possible to conclude that no delamination of the CNT's nickel coating occurred, since nickel was not found in the matrix (Z1 zone chemical composition).

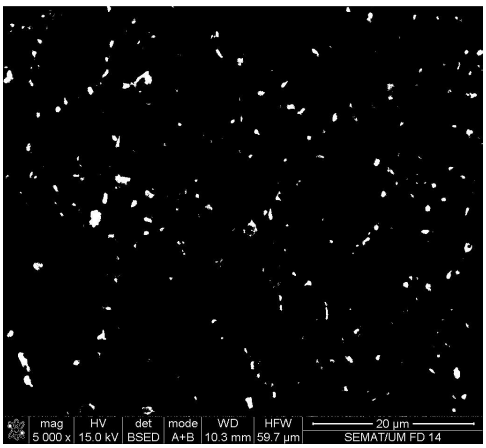
Table 1 Chemical composition of zones Z1 and Z2 presented in figure 2.

Element	*Concentration (wt. %)*	
	Z1	*Z2*
Al	89.0	60.8
Si	11.0	3.6
Ni	-	**30.0**
C	-	5.6

The obtained images were then processed, applying a threshold filter in order to further highlight the agglomerates (fig. 3a and 3b) and be able to count and measure them, discriminating the area of the agglomerates and their distribution considering area, as described in fig. 4.



a)



b)

Fig.3 SEM image in backscattered view: (a) Al-Si/CNT composite with 2 wt. % MWCNT and (b) same SEM image, with threshold filter, enhancing the carbon nanotubes distribution and presence of agglomerates.

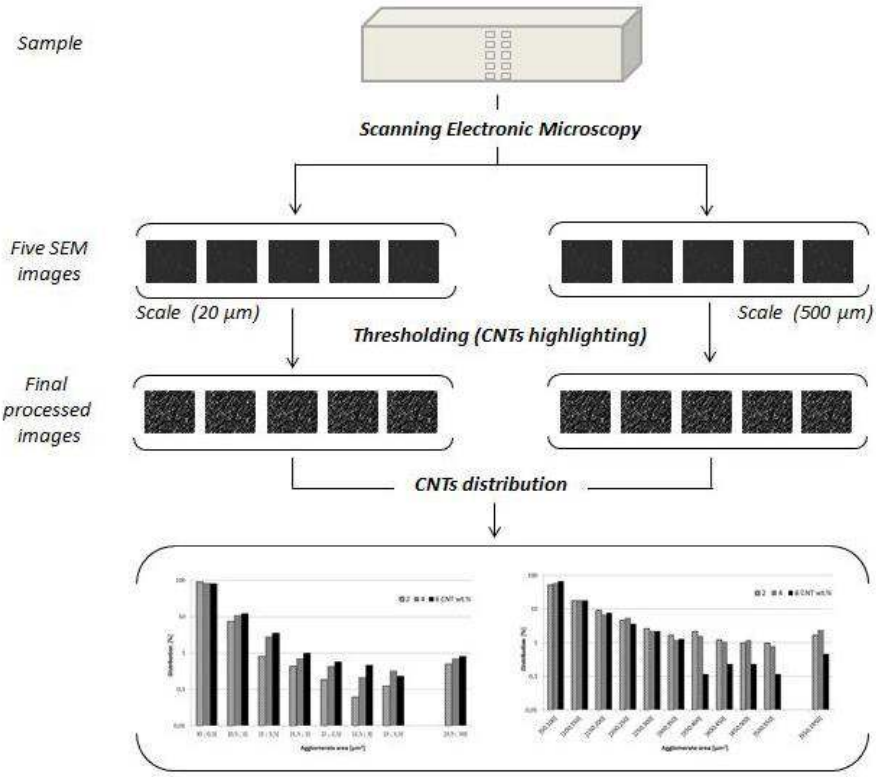


Fig.4 Implemented procedure for SEM images analysis, for CNT agglomerates quantification.

Mechanical testing

Dog-bone shaped tensile test specimens were machined from the produced samples, in order to perform tensile tests, in a servohydraulic universal tensile testing machine (Instron 8874), equipped with a 25 kN capacity load cell. Tests were performed at room temperature (~23 ºC), with a crosshead speed of 0.05 $mm.s^{-1}$.

RESULTS AND DISCUSSION

Results of tensile strength as well as CNTs distribution as a function of the CNT's content in the matrix, for 2, 4, and 6% of CNTs in the matrix, will be subsequently presented.

Tensile Strength

Fig. 5 shows the experimental results of tensile strength for the Al-Si/CNT composites produced in this work, as a function of CNT's content. It can be seen that there is an increase of about 25% in tensile strength with incorporation of CNT's (2% CNT's) but for CNT's weight content higher than 2% the properties suffer a decrease.

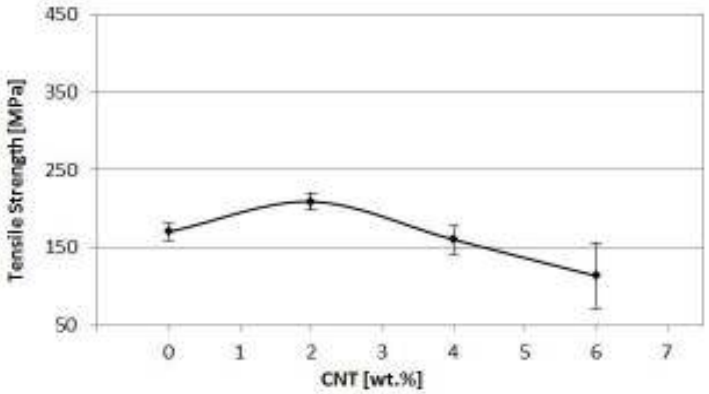


Fig.5 Tensile strength for different Al-Si/CNT composites, with 0; 2; 4 and 6 wt. % CNT, produced and tested in the present work.

In fig. 6 are presented the results achieved by C.N. He et. al. (He C. N. et. al., 2009), for Al/CNT composites produced using in situ chemical vapor deposition. It can be seen that properties increase till an amount of about 5% of CNT's and tensile strength increases in about 185% as compared to the matrix properties. In C.N. He et. al. work it is assumed that CNT's are ideally distributed in the matrix (with no agglomerates) and these results will be used in this study for comparison purposes.

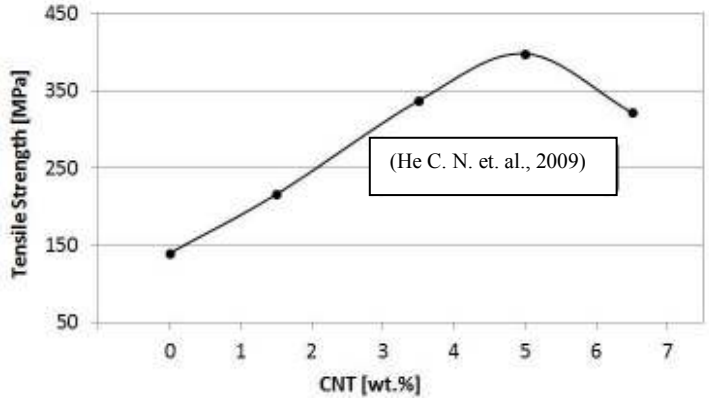


Fig.6 Tensile strength of different Al/CNT composites, with 0; 1.5; 3.5; 5 and 6.5 wt. % CNT, produced and tested by C. N. He et al. (He C. N. et. al., 2009)

C. N. He et. al. produced the CNT-reinforced aluminum composites by synthesizing CNTs into the aluminum powders in situ by a chemical vapor deposition (CVD) process. Post-processing analysis allowed concluding that the formed CNTs have a diameter between 5 and 25 nm, and a length between 1 and 3 μm. These as-grown CNTs are well-graphitized multiwalled nanotubes, with the presence of Ni. According to the authors, a homogenous distribution is obtained, and no agglomerates are formed. Concerning the mechanical properties, assessed by means of tensile tests, the authors concluded that a strong interfacial bonding was obtained between CNTs and the matrix; once most CNTs are ruptured in the fracture surface, and few are pulled out.

The present work uses Nickel coated Multi-Wall Carbon Nanotubes (MWCNTs), with length between 0.5 and 2.0 μm and a diameter of approximately 50 nm, while the matrix alloy is an Al12Si alloy in powder form.

Although there exists some differences between both studies, namely on the matrix material (Al in C. N. He et. al. work and Al-Si in this work) and on the processing route that in the present study was by mixture of the CNTs and the matrix alloy by low-energy ball milling,

followed by hot pressing, there are strong similarities between studies, allowing to make, on the opinion of the authors of this work, to some extent, a comparison between them in terms of the effect of the agglomerates in the composite tensile strength, since in both works, MWCNTs, with similar dimensions, are used in the composites. Thus, C. N. He et. al. work can be used as a reference, setting the influence of CNTs in aluminum composites in an ideal scenario - when agglomerates are not formed and a good dispersion is obtained, and the present work will allow taking conclusions about the influence of agglomerates in these composites.

While in the present work (fig. 5) the highest tensile strength value is achieved with a CNT content of 2 wt. %., in C.N. He et. al. work, the highest value is obtained for 5 wt. % CNT (fig. 6). Moreover the improvement in mechanical properties is of about 25% in the present work and of about 185% in ref. 20. The decrease in tensile strength improvement (25% as compared to 185%) as well as the CNT content for which it is obtained (2% as compared to 5%) will be considered a cause of the CNT's agglomerates formation, commonly accepted as the main detrimental effect on CNTs reinforced aluminum based composites (Esawi A. M. K. et. al., 2008; Esawi A. M. K. et. al., 2010).

CNTs distribution

In order to clarify the influence of CNTs agglomerates in the composite mechanical properties (namely on tensile strength), an agglomerates distribution study, by size, in the produced Al-Si/CNT composites was performed. The obtained results allow a quantification of CNT's dispersion as a function of CNT's content in the produced composites. Results are shown in fig. 7 to 10.

Fig. 7 relates to measurements of agglomerates with areas up to 50 μm^2, representing well dispersed CNTs, as well as agglomerates of one to few CNTs (amplifications of 5000 times were used in used pictures). These results show a similar pattern in agglomerates distribution, for all the produced Al-Si/CNT composites (with 2, 4 and 6 wt. % CNTs). In all of them it is verified that more than 93% of the agglomerates are less than 1 μm^2 in area (fig. 8). Considering the representativeness of these small agglomerates ([0, 1] μm^2) in all of the produced composites, they will be, hereafter, named as Type A agglomerates (fig. 8).

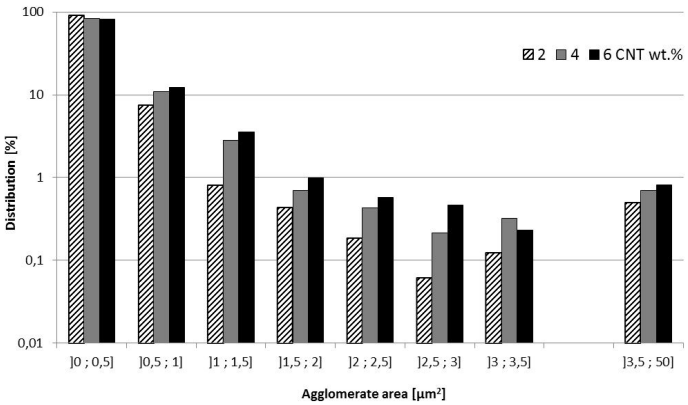


Fig.7 CNTs agglomerates distribution, determined in pictures with 5000 times magnification - percentage of agglomerates by size classes (y-axis with logarithmic scale).

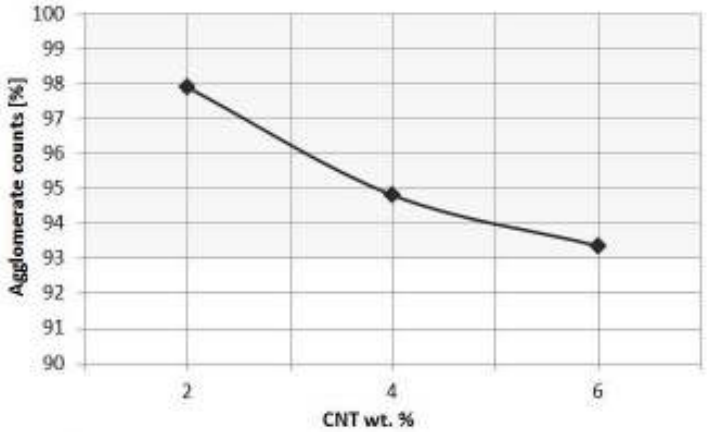


Fig.8 Type A agglomerates ([0, 1] μm^2) counts for Al-Si/CNT composites with 2, 4 and 6 wt.% CNT.

Fig. 9 presents measurements of agglomerates with areas up to 1950 μm^2. All Al-Si/CNT composites, with 2, 4 and 6 wt. % CNT, show a similar pattern in agglomerates distribution, however, agglomerates with area above 350 μm^2 are less represented in the composite with 6 wt. % CNT (amplifications of 123x were used in these pictures).

In all of the produced composites, more than 93% of the agglomerates have area above 50 μm^2 and less than or equal to 550 μm^2 (fig. 10). Considering the representativeness of these agglomerates in all of the produced composites, agglomerates with area within the range]50, 550] μm^2 are named hereafter as Type B agglomerates (fig. 10).

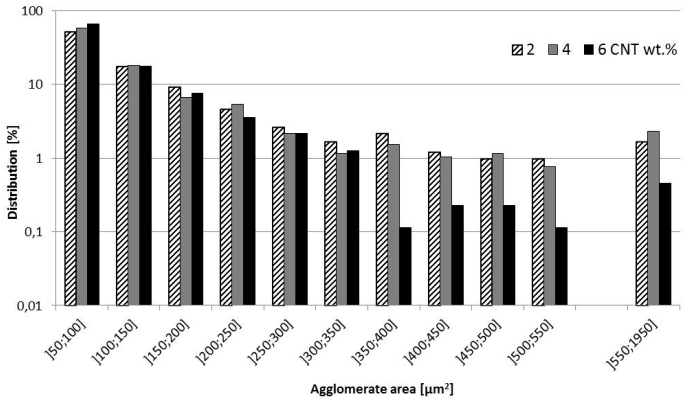


Fig.9 CNTs agglomerates distribution, determined in pictures with 123 times magnification - percentage of agglomerates by size classes (y-axis with logarithmic scale).

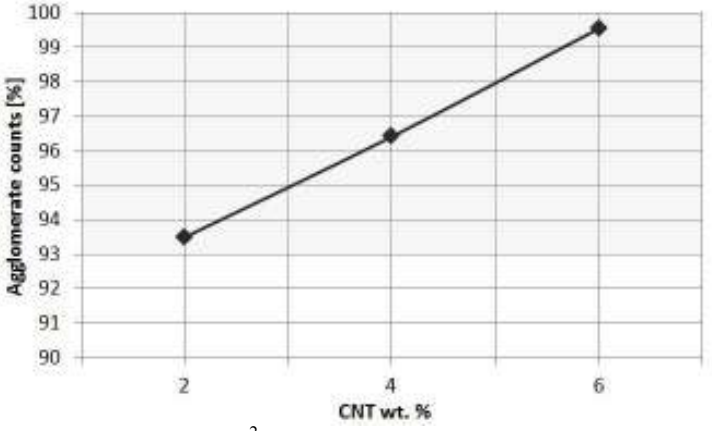


Fig.10 Type B agglomerates ( ]50, 550] μm^2) counts for Al-Si/CNT composites with 2, 4 and 6 wt.% CNT.

It is worth to mention that different magnifications were used for the different measurements. Type A agglomerates were measured in pictures with 5000x magnification and type B agglomerates were measured with 123x magnification. In the type A pictures it was not possible to properly quantify big agglomerates due to higher amplification and in type B pictures it was not possible to properly observe the very small agglomerates due to the lower amplification.
Fig. 8 shows that Type A agglomerates are more represented in Al-Si/2%CNT composite, decreasing for greater CNTs contents. On the other hand, Type B agglomerates are more represented in Al-Si/6%CNT composite (fig. 10).
The first main observation from the previous results is that as the volume fraction of CNT's increases in the composites (from 2 to 6 wt. %), the ability to disperse the CNTs decrease. There are less small agglomerates (fig. 8) and more big agglomerates (fig. 10) with increasing CNTs volume fraction in the composite. These results confirm what was expected but never before verified experimentally and never quantified.
In order to quantify the influence of the agglomerates in the produced composites, the area occupied (as measured in photographs) by the agglomerates was measured and divided by the photograph area. The results are presented as the area fraction of the agglomerates in the whole material. Fig. 11 shows the results for the different CNT contents and type of agglomerate.

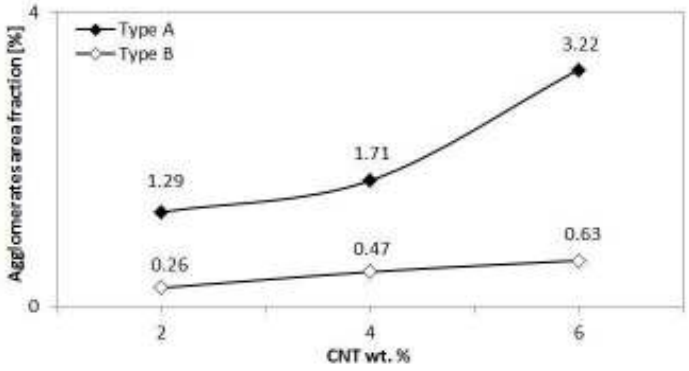


Fig.11 Type A and type B agglomerates area fraction (in percentage) for Al-Si/CNT composites with 2, 4 and 6 wt.% CNT.

It can be seen in fig. 11 that both type A and type B agglomerates area fraction increase with CNT's content in the composite. An interesting conclusion is that with increasing CNT's content, the type A agglomerates area fraction increases, while the measured counts of these agglomerates decrease (fig. 8). This trend is explained by the fact that with increasing CNT content, the agglomerates area tend to approximate the upper limit (1 μm^2), indicating a tendency to agglomerate with higher CNT content.

CONCLUSIONS

The main conclusions that can be drawn from this work are the following:

- It is possible to quantify the CNT's dispersion in the matrix by using Ni coated CNT's and image analysis;
- A new methodology to assess the existence of CNT's agglomerates and to characterize them is possible to be established;
- The ability to disperse CNT's in the matrix depends on CNT's content in the composite;

- The higher the CNT content in the matrix the higher the amount of agglomerates with area between 50 and 550 μm^2;
- Tensile strength decreases as the amount of CNT's agglomerates with area between 50 and 550 μm^2 increases.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the funding by Ministério da Ciência, Tecnologia e Ensino Superior, FCT, Portugal, under grant SFRH/BD/44077/2008.

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