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Mechanical Behaviour with Temperatures of Aluminum Matrix Composites with CNTs

Danilo Marini*, Virgilio Genova , Francesco Marra, Giovanni Pulci, Marco Valente

Dept. of Chemical Engineering, Materials, Environment, Sapienza University of Rome – INSTM Reference Laboratory for Engineering of Surface Treatment, Rome Italy
danilo.marini@uniroma1.it

Aluminum is a very useful structural metal employed in different industrial sectors, in particular it is used in large quantities in automotive, aeronautic and nautical industries. The main reasons of its wide use are: a very good oxidation resistance, excellent ductility, low melting temperature (660 °C) and low density (2.71 g/cm^3). However, in order to reduce the emissions and fuel consumption is necessary to reduce the overall weight of vehicles by increasing mechanical properties of the structural material. The improvement of mechanical properties is normally achieved through use of reinforcement in materials, used like matrix, in order to improve some specific characteristics.
In this work composites of carbon nanotubes (CNTs) dispersed in aluminum were made. The most difficulties in the preparation of this type of composite are represented by the low wettability between metallic matrix and fillers and the possibility of the oxidation of metal during melting with consequent decreasing of mechanical proprieties. The composite was obtained by three consecutive step: the first one is the functionalization of fillers surface to improve the fillers dispersion, the second one is the dispersion of fillers in the matrix by powder mixing and the third one is the melting and casting of the mix prepared.
In particular, fillers used are multi walled carbon nanotubes (MWCNTs) with functionalized surface by treatment with a solfonitric solution. Melting and casting are carried out with the aid of an induction furnace with a controlled atmosphere system and centrifugal casting. Argon is the inert gas used to prevent the oxidation of aluminium during fusion. Young’s modulus was evaluated at different temperature and correlated with the different CNTs percentage. The dispersion rate of fillers and the microstructure of the sample were evaluated by FESEM micrograph.

1. Introduction

Metal matrix composite materials (MMC) represent a good solution for environmental problems caused by the emissions of vehicles, thanks to the possibility to reduce their overall weight by increasing specific mechanical properties of structural materials. In the last years, aluminum is one of the most studied structural materials to produce MMC due to its large use in different industrial sectors like: aeronautical, nautical and automotive in witch the low weight of vehicles is very important (Alam and Kumar, 2016).
However, the demand for aluminum and its alloys having some much higher technological properties is increasing and an answer at this demand could be given by a good production process of Al-composites.
Different type of reinforcements can be used to produce Al-composites that can be different in chemical composition, structure and size. Nanotechnology is a rapidly expanding field which is developing in different sector, due to the high reactivity of materials in nanoscale, for example a number of studies on nanotechnology applications in environmental pollution can be found in the literature. (Bavasso *et al.*,2016; Muradova *et al.*, 2016; Vilardi and Di Palma, 2016; Vilardi, Verdone and Palma, 2017).
In particular, carbon is one of the mostly used reinforcement, that now a day, is available in different structure and size, like microfibers (CMFs), nanoplatelets (CNPs) and nanotubes (CNTs) (Bartolucci *et al., 2011*).
Since its discovery, CNTs have received significant attention by researchers and the reasons are represented by their excellent mechanical (1 TPa of Young’s modulus), electrical (10^{-6} – 10^{-4} Ωcm at 300K) and thermal properties (3000 W/mK at room temperature) (Genova et al. 2015; Di Pascasio et al., 2016).

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There are different types of CNTs and they can be classified in single walled carbon nanotubes (SWCNT), double walled carbon nanotube (DWCNT) and multi walled carbon nanotube (MWCNT). The SWCNT consist of a single plane of graphene wrapper to create a cylindrical structure with a diameter of 1-2 nm. The DWCNT and the MWCNT consist of two or more SWCNT to form a coaxial cylindrical structure.
In this work composites of multi wall carbon nanotubes dispersed in aluminum were made (Al-MWCNT).
The most difficulties in the preparation of this type of composite are represented by the low wettability between metallic matrix and fillers and the possibility of the oxidation of metal during melting with consequent decreasing of mechanical proprieties.
Researchers have observed various results in production of Al-CNT composites, some have obtained significant increase of strength (Mokdat *et al.*, 2016), other ones have observed irrilevant increase or decrease of some properties of composite (Simões *et al.*, 2015). Many of these different results depends on the quality of fillers dispersion, composite fabrication process and interfacial interaction between matrix and fillers. Fillers dispersion is another one crucial problem in preparation of Al-CNT composites, due to the tendencies of CNT to form agglomeration due to the Van der Waals interaction.
In this work, the MMC were obtained by the aid of an induction furnace with centrifugal casting and atmosphere control system to avoid the metal oxidation. It was demonstrated that the induction melting allows to obtain a good dispersion of fillers in the melting matrix (Mansoor and Shahid, 2016). Furthermore, to prevent the agglomeration problem, the nanotubes were functionalized by superficial treatment in order to decrease the interaction forces.

2. Experimental

2.1 Materials

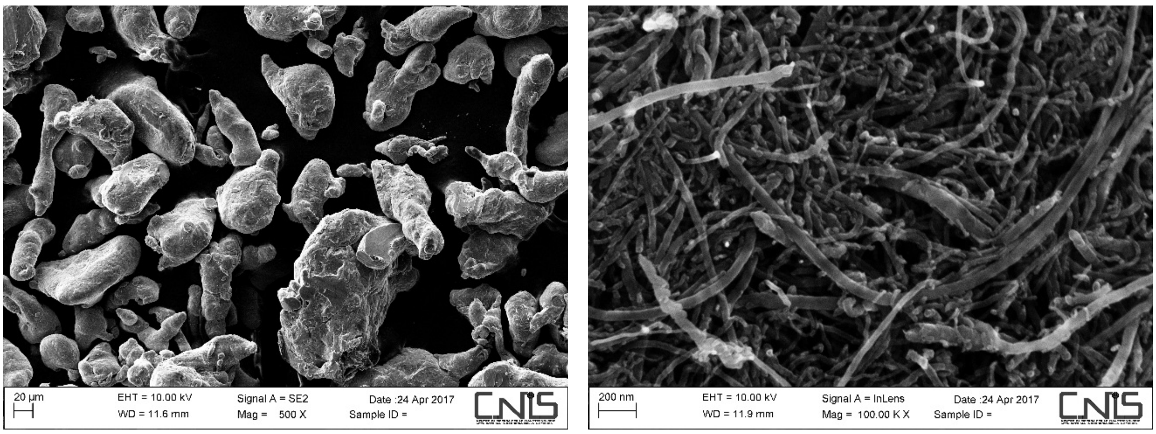
Aluminum powders (particles size ≈ 30 µm), provided by COMETOX (Italy), where used without further purifications (Figure. 1A).
Multi walled carbon nanotubes (MWCNTs, >95 %, o.d. 50-80 nm, specific surface area 60 m^2 g^{-1}) were purchased from Cheap Tubes Inc., USA (Figure. 1B). The average density given by manufacturer is ≈ 2.1 g cm^{-3}.

2.2 Functionalization of MWCNTs

Functionalization of MWCNTs was performed by treatment with a solfonitric solution. It has been established that with acid treatment is possible to insert carboxyl groups on the surface of MWCNTs improving their solubility in polar solvent (K. Hun *et al.*, 2008), this treatment allows to obtain a better dispersion of MWCNTs.
In this work, the follow method was adopted: a weighed quantitative of MWCNTs was placed in suspension in a mixture of concentrated H_2SO_4 and HNO_3 (3:1, vol/vol) refluxed at 60° C for 24 hours.
Ultrasonic bath was used to allow a more homogeneous surface modification.

2.3 Preparation of Al-MWCNT composites

The samples were prepared by powders metallurgy way. Aluminum powders (Figure 1A) were mixed with several quantities of functionalized MWCNTs (Figure 1B) in acetone to facilitate the dispersion of fillers in the metal powder.



A B

Figure 1: SEM micrographies of aluminum powder as received (A) and MWCNT after functionalization (B).

After mixing and complete evaporation at room temperature of acetone, the resultant powder mix was compacted in pellets with 30 mm of diameter and 5 mm of thickness.
The pellets were obtained by hot pressure in Hitech Europe pneumatic mounting press (Tecmet 2000 s.r.l. Italy). at 200 °C and 6 bar for 10 minutes.
This procedure was adopted to prepare Al samples and Al-MWCNT composites samples with four different percentage of fillers (0.5 wt%-1.0 wt%-1.5 wt%-2.0 wt%).
The pellets obtained was processed with a Neutor Digital induction furnace and cast in graphitic dies. (F.lli Manfredi Italy). Centrifugal force was used as fillers dispersive.
The melting pot C12 (F.lli Manfredi Italy) was used and the samples, obtained after casting, were in rods form (10 x 12 x 50 mm).

2.4 Characterization

SEM micrographies were acquired by using a FE-SEM HR Zeiss Auriga 405. The samples for SEM analysis were obtained by cutting the rods perpendicularly to the casting axis in several positions in order to investigate the fillers segregation.
Four point flexural tests were performed with Zwick/Roell Z2.5 that is equipped with a MAYTEC extensimeter and a furnace which allows to run tests at temperatures up to 1500 °C (Pulci *et al.*, 2011; Di Girolamo *et al.*, 2015). The samples were prepared by cutting and polishing the as casted specimens in smaller rods (4 x 3 x 45 mm). All of the tests were carried out by a four-point bending test fixture device, designed and built expressly for these tests. The device is characterized by two supporting rollers with 5 mm of diameter and spaced by 40 mm. Two upper rollers for load application, with same diameter but spaced of 20 mm between them and 10 mm with the lower support rollers are directly connected at strain-gage load cell. For 25 °C tests, a steel device was used, while for tests at temperature a SiC device with same measure was used (Baiamonte *et al*., 2015). Load was measured with a 1kN strain-gage load cell directly mounted on the testing machine cross head. The bending tests were performed in stroke control at a constant rate of 0.5 mm/min in order to obtain a quasi-static loading condition according to the ASTM C-12111. A pre-load of 4 N was applied with constant rate of 1 mm/min.
In the case of bending tests at 200 °C and 400 °C the system was brought at set point temperature at 10 °C/min and was kept at this temperature for 30 min before loading the test. After test the system was cooled at RT at 15 °C/min. The density of samples was performed by using a Mettler Toledo AL 54 (Italy) analytical balance equipped with the accessory for the density measurements of solids by the Archimede Method.

3. Results and discussion

The density for the pure Al was found similar to the bulk value. This can confirm that there is no defectiveness formation (such as void or crack) during the melting and casting process. However, the fillers addition modifies the density of the resulting composites (Table 1) with a decrease of about 15% for the 2 wt% sample. This is probably due to the formation of void because of the low interaction between the molten matrix and the CNTs surface.

Table 1: Measured densities of the Al-MWCNT composites (Theorical density, d_{th}, was assumed equal to the density of pure aluminium bulk).

Samples	Fillers [wt%]	d_s [g/cm^3]	d_s/d_{th} [%]
Al-bulk	0	2.697	100
Al_0	0	2.674±0.013	99.16
Al_0.5	0.5	2.494±0.059	92.46
Al_1	1.0	2.454±0.011	91.00
Al_1.5	1.5	2.358±0.020	87.44
Al_2	2.0	2.312±0.027	85.72

Four bending flexural tests at 25 °C (Figure 2A) shows a decrease in Young's modulus (E mod) after 1.5 wt% of fillers. This confirms the results obtained by density measurement (Table 1) and the variation of E mod can be assigned to the defectiveness of the samples. However, before 1.5 wt% the addition of nanofillers doesn't afflict the modulus even for a significant change of density (for Al_1 the density is almost 10% less than the bulk values). On the contrary, the contribution for the sample at 2 wt% in CNTs is negative. This could be explained by considering the density of the composites: variation in the range of 9 to 15 % (respectively from 1 wt% of CNTs to 2 wt% of CNTs) are the obvious proof of porosity due to the lack of interaction between the carbon and the molten metal. Despite on this, the results given by the trend of E mod relative to 2 %wt of CNTs at 400 °C show the direct influence of CNTs in the matrix: in fact, as consequence of an important decrease in E modulus for pure Al, higher is the temperature, higher is the effect of the reinforcement influence in the composite property. Density measurement of the samples after high temperature tests have shown no significant modification.

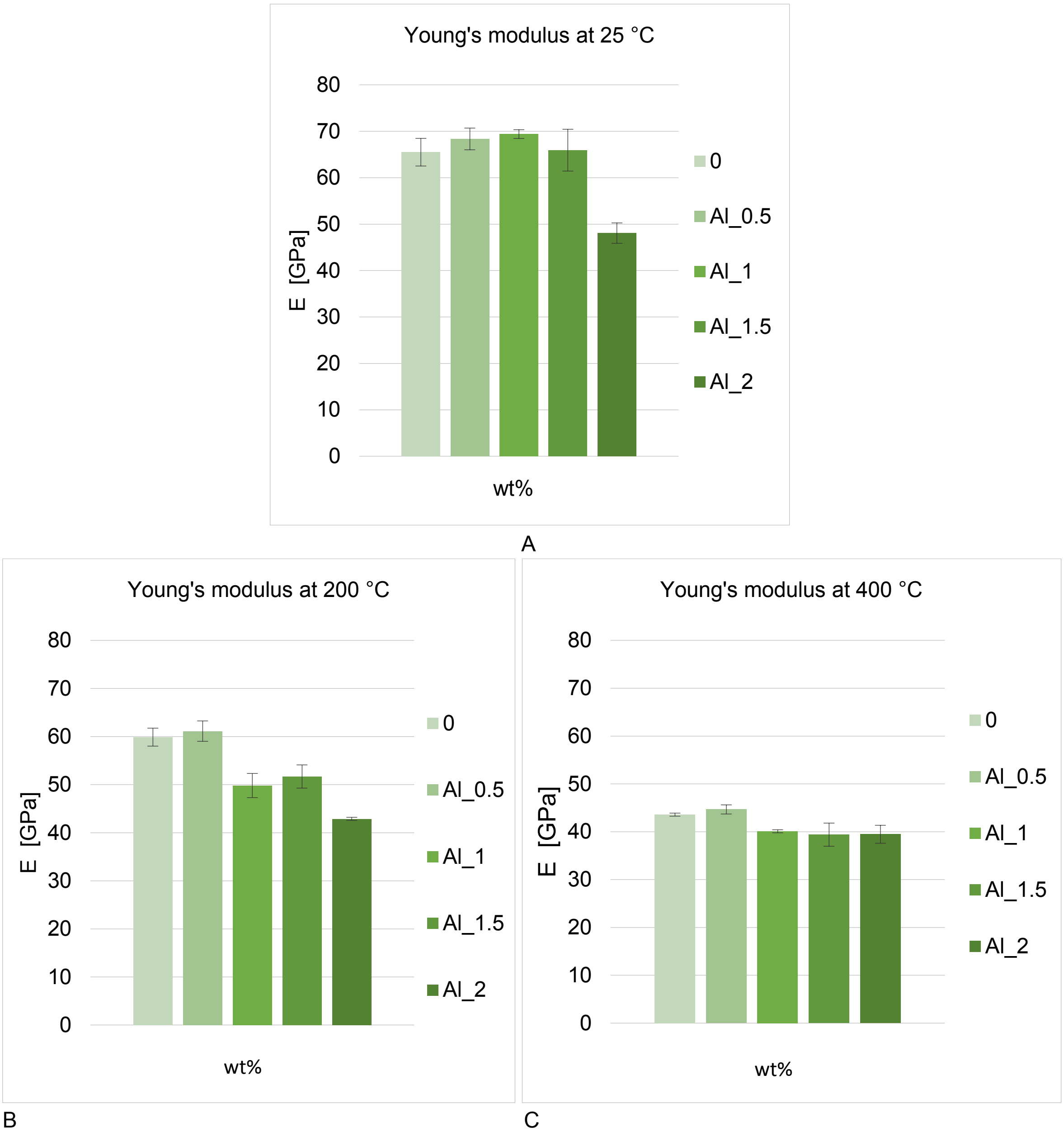


Figure 2: Young's modulus trend of Al-MWCNT composites, with different percentage of fillers, at 25 °C (A), 200 °C (B), 400 °C (C).

SEM analysis was conducted in order to investigate the dispersion of the fillers and their surface interaction with the metal matrix. Unfortunately, it was not so easy to observe CNTs after cutting and polishing procedure because of the malleability of the Al. In Figure 3 it is shown an aggregation of CNTs inside the matrix. This image confirms that the wettability and dispersibility of the fillers are not optimized and the composite fabrication procedure needs some implementation. Surface modification in order to increase the wettability of the fillers in the matrix are now studied. Furthermore, the possibility to coating the CNTs with metal thin film can increase their density with an improvement in dispersion and orientation of the CNTs inside the matrix.

Table 2: Young's modulus trend of Al-MWCNT at different temperatures and percentage of fillers.

Temperature [°C]	Fillers [wt%]	E mod [GPa]
25	0	65.5±2.9
	0.5	68.3±2.3
	1	69.4±0.9
	1.5	65.9±4.5
	2	48.1±2.1
200	0	59.9±1.9
	0.5	61.1±2.1
	1	49.8±2.5
	1.5	51.7±2.4
	2	42.9±0.3
400	0	42.9±0.3
	0.5	43.6±1.8
	1	44.7±0.9
	1.5	39.4±4.5
	2	39.5±2.1

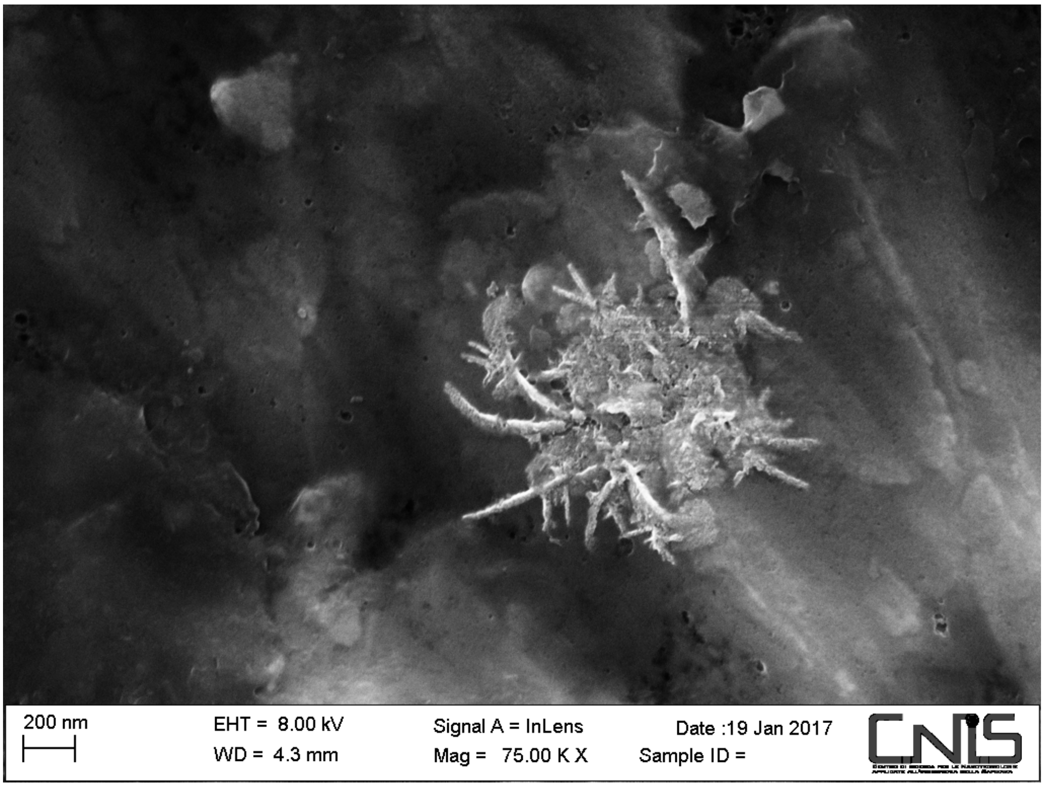


Figure 3: SEM micrographies of MWCNT agglomerated inside the Al matrix. Sample Al_2 after cutting.

4. Conclusion

Aluminum-CNTs composites with several wt% of fillers were produced with a new orientation technique (centrifugal casting). The powder metallurgy way was selected to allow a dispersion of the CNTs inside the matrix. The centrifugal casting way was selected to obtain a good orientation without losing the bulk properties (by using, for example, a sintering way). Four bending flexural tests was conducted for all the samples, at different temperatures (25, 200 and 400 °C). E modulus variations have shown that, at high temperature, it is possible to observe the direct influence of the reinforcement in composites properties. Despite the rate of dispersion and orientation has not yet been optimized, the results at high temperature has shown that the procedure selected is promising.

Reference

Alam, S. N. and Kumar, L. (2016) 'Mechanical properties of aluminium based metal matrix composites reinforced with graphite nanoplatelets', *Materials Science and Engineering A*. Elsevier, 667, pp. 16–32. doi: 10.1016/j.msea.2016.04.054.

Baiamonte, L., Marra, F., Pulci, G., Tirillò, J., Sarasini, F., Bartuli, C. and Valente, T. (2015) 'High temperature mechanical characterization of plasma-sprayed zirconia-yttria from conventional and nanostructured powders', *Surface and Coatings Technology*. Elsevier B.V., 277, pp. 289–298. doi: 10.1016/j.surfcoat.2015.07.071.

Bartolucci, S. F., Paras, J., Rafiee, M. A., Rafiee, J., Lee, S., Kapoor, D. and Koratkar, N. (2011) 'Graphene-aluminum nanocomposites', *Materials Science and Engineering A*. doi: 10.1016/j.msea.2011.07.043.

Bavasso, I., Vilardi, G., Stoller, M., Chianese, A. and Palma, L. Di (2016) 'Perspectives in Nanotechnology Based Innovative Applications For The Environment', *Chemical Engineering Transactions*, 47, pp. 55–60. doi: 10.3303/CET1647010.

Chen, X., Xia, J., Peng, J., Li, W. and Xie, S. (2000) 'Carbon-nanotube metal-matrix composites prepared by electroless plating', *Composites Science and Technology*, 60(2), pp. 301–306.

Di Girolamo, G., Marra, F., Schioppa, M., Blasi, C., Pulci, G. and Valente, T. (2015) 'Evolution of microstructural and mechanical properties of lanthanum zirconate thermal barrier coatings at high temperature', Surface and Coatings Technology. Elsevier B.V., 268, pp. 298–302. doi: 10.1016/j.surfcoat.2014.07.067.

Di Pascasio, F., Genova, V., Gozzi, D., Latini, A. and Lazzarini, L. (2016) 'High temperatures gas-solid reactivity of aluminum-carbon nanotubes composites', *Thermochimica Acta*. Elsevier B.V., 640, pp. 8–18. doi: 10.1016/j.tca.2016.07.015.

Genova, V., Gozzi, D. and Latini, A. (2015) 'High-temperature resistivity of aluminum carbon nanotube composites', *Journal of Materials Science*. Springer US, 50(21), pp. 7087–7096. doi: 10.1007/s10853-015-9263-y.

George, R., Kashyap, K. T., Rahul, R. and Yamdagni, S. (2005) 'Strengthening in carbon nanotube/aluminium (CNT/Al) composites', *Scripta Materialia*, 53(10), pp. 1159–1163. doi: 10.1016/j.scriptamat.2005.07.022.

Laurent, C., Flahaut, E. and Peigney, A. (2010) 'The weight and density of carbon nanotubes versus the number of walls and diameter', *Carbon*. Elsevier Ltd, 48(10), pp. 2994–2996. doi: 10.1016/j.carbon.2010.04.010.

Mansoor, M. and Shahid, M. (2016) 'Carbon nanotube-reinforced aluminum composite produced by induction melting', *Journal of Applied Research and Technology*. doi: 10.1016/j.jart.2016.05.002.

Mokdad, F., Chen, D. L., Liu, Z. Y., Xiao, B. L., Ni, D. R. and Ma, Z. Y. (2016) 'Deformation and strengthening mechanisms of a carbon nanotube reinforced aluminum composite', *Carbon*, 104, pp. 64–77. doi: 10.1016/j.carbon.2016.03.038.

Muradova, G. G., Gadjieva, S. R., Di, L. and Vilardi, G. (2016) 'Nitrates Removal by Bimetallic Nanoparticles in Water', *Chemical Engineering Transactions*, 47, pp. 205–210. doi: 10.3303/CET1647035.

Pulci, G., Tului, M., Tirillò, J., Marra, F., Lionetti, S. and Valente, T. (2011) 'High temperature mechanical behavior of UHTC coatings for thermal protection of re-entry vehicles', Journal of Thermal Spray Technology, 20(1–2), pp. 139–144. doi: 10.1007/s11666-010-9578-9.

Simões, S., Viana, F., Reis, M. A. L. and Vieira, M. F. (2015) 'Influence of dispersion/mixture time on mechanical properties of Al-CNTs nanocomposites', *Composite Structures*, 126, pp. 114–122. doi: 10.1016/j.compstruct.2015.02.062.

Vilardi, G. and Di Palma, L. (2016) 'Kinetic Study of Nitrate Removal from Aqueous Solutions Using Copper-Coated Iron Nanoparticles', Bulletin of Environmental Contamination and Toxicology. Springer US, 98(3), pp. 1–7. doi: 10.1007/s00128-016-1865-9.

Vilardi, G., Verdone, N. and Palma, L. Di (2017) 'The influence of nitrate on the reduction of hexavalent chromium by zero-valent iron nanoparticles in polluted wastewater', 20710(July 2016), p. 20710. doi: 10.5004/dwt.2017.20710.

Zhong, R., Cong, H. and Hou, P. (2003) 'Fabrication of nano-Al based composites reinforced by single-walled carbon nanotubes', *Carbon*, 41, pp. 2001–2004. doi: 10.1016/S0008-6223(02)00427-X.

Zhu, X., Zhao, Y. G., Wu, M., Wang, H. Y. and Jiang, Q. C. (2016) 'Fabrication of 2014 aluminum matrix composites reinforced with untreated and carboxyl-functionalized carbon nanotubes', *Journal of Alloys and Compounds*. Elsevier B.V, 674, pp. 145–152. doi: 10.1016/j.jallcom.2016.03.036.