

FULL PAPER – MAGNESIUM COMPOSITES REINFORCED BY METAL COATED CARBON NANOTUBES

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ABSTRACT

The interest to use carbon nanotubes (CNTs) to reinforce light metals has increased in recent years due to their potential application as lightweight high performance materials. One challenge in producing CNT composites is to achieve a homogenous dispersion of CNTs in the metal matrix. In order to effectively disperse CNTs in the Mg melt, we for the first time introduced the idea of using metal coated CNTs to promote the integration into Mg matrix. In this paper, Pt was selected to coat the CNT surface. TEM and EDX confirm that atomic Pt has been successfully deposited onto CNTs. The dispersion and stability of metal coated CNTs in solution have been investigated and compared to CNTs without metal coating. The Pt coated CNT reinforced Mg composites were also produced via a melt stirring process. The mechanical properties of such composites also showed a clear upward tendency, which we attribute to the Pt coating to help the dispersion of CNTs.

1 INTRODUCTION

In spite of a strong drive to introduce CNTs into metallic matrices due to their extraordinary mechanical, thermal and electrical properties, the homogeneous dispersion of CNTs in such matrix remains one of the biggest challenges. Due to the high specific surface area, the nano-scaled particles have a large tendency to form agglomerates [1]. One way of breaking up the bundles of CNTs is the sonification process. The active principle is the cavitations in which the CNTs are separated by formation and collapsing of steam bubbles through pressure fluctuations on the surface. Due to the high applied pressure (up to 100.000 bars) from the sonification, the CNTs are mechanically separated. But ultrasonification can cause damage to the structure of the CNTs [2]. Another problem of this method is the re-agglomeration after the sonification because of the high specific surface area of CNTs. The functionalization of the CNT surface has attracted more and more attention and can be quite efficient to disperse CNTs in solvents and polymer matrix. Different organic groups have been tried to be functionalized on the surface of CNTs [3]. However, the organic functionalization group cannot work properly in metal matrix because they are not stable at the high process temperatures of producing the metals. All organic groups decompose at temperatures higher than about 400°C.

The most common way to deagglomerate the CNT bundles to produce metal composites is ball milling which is a part of the common powder metallurgy route [4-6]. But this method causes heavy damage of the CNTs because of the high shear forces which act on the CNTs [7].

Recently chemists have managed to coat metal atoms directly on the CNTs surface [8]. One promising way is to create an electrical charge on the surface of the CNTs by using different polyelectrolytes and then deposit the metal on the CNT surface. Coatings of CNTs with different metals give us the idea that it could help the dispersion of the CNTs in the metal matrix because the high specific surface energy can be reduced by the coated metals. Also an improved wettability of the metal coated CNTs in a metal matrix could be obtained through the metal coating, which may lead to a better interfacial bonding. Another advantage is that the metal coating can survive through the high process temperature of producing metal composites. The variety of metal coatings is big, for example copper, iron and nickel [9], platinum, palladium and tin [10], different metal complexes contained Pt, Mo and Pd [11] have all been tried. Simulations have been done to check the binding affinities and the interfacial structures of metal particles onto CNTs in a gold matrix [12]. One experimental example for such a MMC is a Sn-Ag-Cu solder with nickel-coated CNTs as reinforcements from Han [13].

In our previous research, we have successfully produced CNT reinforced AZ91 composites by a two step process including a pre-dispersion and melt stirring [14-16]. In this work, we will coat CNTs with metal and produce their AZ91 composites. The metal coating and the composites will be characterized by various methods.

2 EXPERIMENTAL

30 mg of CNTs were added to a beaker with aqueous solution of sodium chloride and then sonicated for one hour. Afterwards 400 mg of a PDDA solution was weighted in and stirred with 100 rpm for half an hour to make sure that the separated CNTs were covered with the positive electrolyte PDDA. The excess PDDA was removed by centrifugation cycles. The centrifuge was operated with a speed of 11000 rpm and a duration time of 8 min. The collected CNTs were redispersed in distilled water and 80 mg of the polyelectrolyte PSS. The solution was stirred at 100 rpm for another 30 min. The excess PSS was extracted by centrifugation with the same parameters like the PDDA before. Then the centrifuged CNTs were redispersed and another 400 mg PDDA was added, stirred again and washed by centrifugation afterwards using exactly the same parameters which were mentioned above. Now the CNTs have been coated by three polyelectrolyte layers on the surface and the outer polyelectrolyte has a positive charge on the CNTs outside wall. For the metal coating, the CNTs were diluted in 120 ml water. 85.9 mg H₂PtCl₆ and 240 mg of trisodium citrate dehydrate were added and sonicated for 30 min. Afterwards sodium sulfite aqueous solution with a concentration of 0.05 Mol/l was added drop by drop under mild sonification. As the last step the solution was centrifuged by 6 cycles to get rid of the residual such as the non-reacted metal-salt. After the last washing step the solution was dried by a heater at 80°C to get the resulted metal coated CNTs.

The Pt-coated MWCNT/AZ91 composite was produced by the same two-step process [14]. Using the same process other samples such as non-coated MWCNT/AZ91 composite and pure AZ91 alloy were produced for comparison. A FEI Titan3 80-300 transmission electron microscope (TEM) equipped with an image aberration corrector was employed for analyzing the coating status of Pt on the surface of MWCNTs. Mechanical properties of the composites were measured by compression test.

3 RESULTS AND DISCUSSION

Initially to verify the metal or metal compound on the surface of CNTs, high resolution images were recorded by HRTEM and the corresponding metal element was checked by EDX. Figure 1a shows

the metal coating on the surface of a CNT. The black dots indicate the presence of platinum clusters which can be confirmed by EDX (Figure 1b).

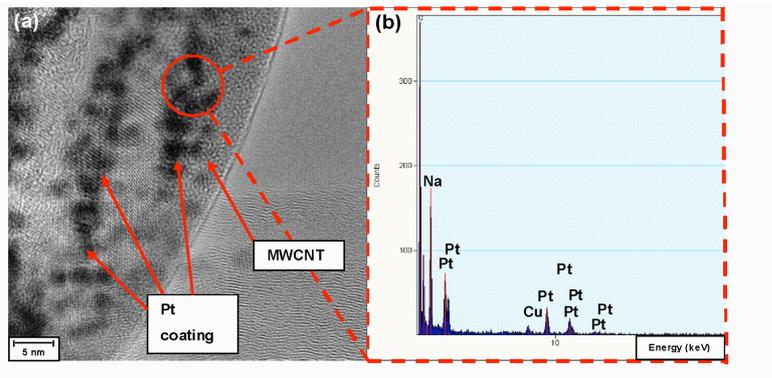


Figure 1 (a) TEM image of Pt coating on the surface of individual MWCNTs; (c) EDX acquire at selected area on surface on Pt-coated MWCNTs.

Different from coating continuous metal layers on CNTs as described in [3], surface decoration of CNT with metals as achieved as in Figure 1a may provide further benefits. If, instead of a continuous coating layer, isolated metal nanoparticles as in Figure 1a are deposited on the CNT surface then these nanoparticles may serve a dual purpose that goes well beyond what can be achieved by a continuous coating. Firstly, discrete metal nanoclusters on the CNT surface can help to prevent agglomeration by the simple means of acting as geometrical 'spacers'. This effect is well known in the context of graphene where decoration of exfoliated graphene sheets with Pt nanoclusters was shown to prevent face-to-face aggregation of the sheets [4]. Secondly, attaching metal nanoclusters rather than continuous metal coatings to CNT may have additional benefits. If a metal such as Pt or Ni bonds well to sp² carbon and the interfaces between the nanoclusters and the CNT are strong, then such nanoclusters may act as 'nano-rivets' enhancing interfacial shear stress transfer if the decorated CNT is embedded in a metal matrix.

The mechanical properties of Pt coated CNT reinforced Mg composites were measured and showed improved properties compared to pure AZ91 and to AZ91/CNT composites based on uncoated CNTs as shown in Figure 2.

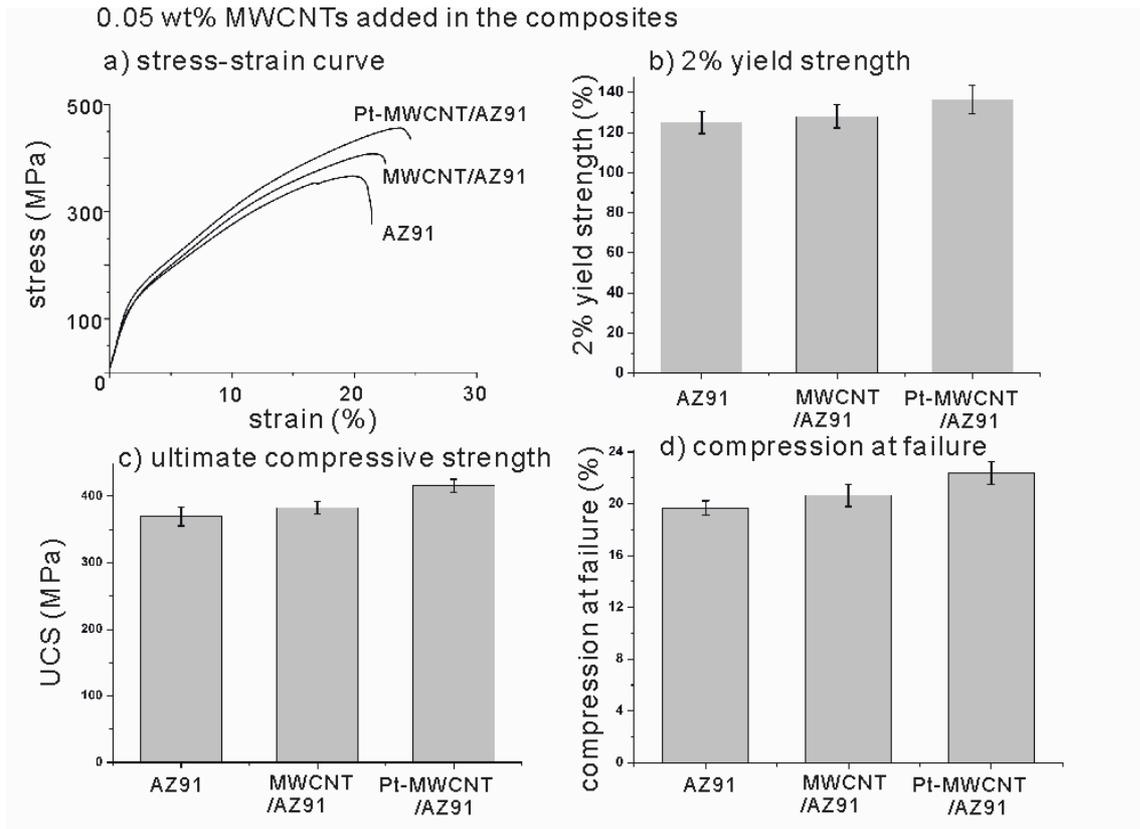


Figure 2 (a) Typical stress-strain curves of pure AZ91, 0.05 wt% raw MWCNT/AZ91 composite and 0.05 wt% Pt-MWCNT/AZ91 composite. Comparison of (b) 2 % yield strength, (c) ultimate compressive strength (UCS) and (d) compression at failure of 36 samples.

However the change is relatively small compared to the usual scatter of experimental results. The reason for affinity of the average values is that the real amount of metal coated CNTs in the AZ91 composites is less than real 0.05 wt% due to the big amount of waste during the metal coating process. At the calculation of the amounts of metal coated CNTs for the composites, we assumed that there is no loss of metal coated CNTs. The weight of the CNTs after the metal coating also differs a lot because of the non-uniform coating with platinum. Nevertheless, an upwards tendency of the mechanical properties can still be found by using metal coated CNTs to produce CNT/ AZ91 composites. This can be attributed to an improved dispersing of CNTs, as well as a possible wettability. More experiments are required.

4 CONCLUSIONS

Pt has been deposited on the surface of multiwall carbon nanotubes. By adding small amounts of Pt coated MWCNTs, an upward trend in the mechanical properties of Mg AZ91 composites could be observed when compared to adding raw MWCNTs. Our explanation for this tendency is that a better dispersion of metal coated CNTs in AZ91 melt can be achieved as metal coating weakens the Van der Waals force between CNTs. On the other hand it is apparent that the improvement in mechanical properties is relatively small, hardly beyond the usual scatter band of results. This leads us to the conclusion that further improvements to the deposition process are required.

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