Metallization Development of Multi-Walled Carbon Nanotubes (MWCNTs) with Copper by an Electroless Plating

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Abstract: In this study, Multi Walled Carbon Nanotubes (MWCNTs) were coated with copper by an electroless plating process. The aim is to form a strong bond between the MWCNTs and the Aluminum matrix. Aluminum in liquid form has a high surface tension compared to the surface tension of MWCNTs, resulting in very poor wettability. The surface of MWCNTs coated with metal (copper) will increase the dispersion and wettability between MWCNTs and the Aluminum matrix. The research was conducted at the mechanical engineering laboratory, Bali State Polytechnic. Coating MWCNTs with copper is carried out in three steps, namely: activation, acceleration, and electroless. MWCNTs were activated using a Pd-Sn colloidal solution adapted from the Plating on Plastics (POP) industry. The ingredients used in the activation process were a mixture of 37.5 ml of Pd-Sn colloid solution, 37.5 ml of HCl (37%), and 175 ml of DI water. In the acceleration process, fluoride acid (HF 55%) is used as an accelerator. The last process is the electroless plating process, in which the surface of the MWCNTs that has been catalyzed is inserted into the Copper-Cobalt (Cu-Co) electrolyte solution. Copper-coated MWCNTs were characterized using scanning electron microscopy (SEM-EDX) analysis using (JEOL-JSM 6510 A) at the Mechanical Engineering Materials Laboratory, Udayana University. The results of the SEM-EDX test showed that the copper content was 84.1%, carbon 12.08%, and the rest were other elements, such as: O, Na, K, Co, Pd, Sn. The increasing size of MWCNTs indicates the presence of copper on the surface of MWCNTs. The average diameter of the 85 nm copper-clad MWCNTs increased compared to the average diameter of the initial MWCNTs (10–20 nm).

1 INTRODUCTION

Multi-walled Carbon nanotubes (MWCNTs) have been widely used in the manufacture of composites with aluminum matrices because MWCNTs have a high strength-to-weight ratio. Several previous studies have shown that the use of MWCNTs to strengthen the aluminum matrix is very effective. Most of these studies report using powder metallurgical techniques such as high energy ball milling followed by conventional and unconventional compaction and sintering techniques for sample preparation (Esawi, 2010, 2009). Of course, the Al-MWCNTs composite manufacturing process using powder metallurgy techniques, requires relatively expensive costs.

In the metal industry, casting is one of the techniques that can be used for the manufacture of metal matrix composites. The use of MWCNTs in the fabrication of aluminum-MWCNTs composites by casting process faces several obstacles. The main constraints are poor wetting which limits the dispersion of MWCNTs in molten aluminum as well as the problem of oxidation of MWCNTs at high temperatures which destroys the structure of MWCNTs (So, 2011). Recently, electroless coating has offered many advantages that enable it to work in harmony with MWCNTs in foundry engineering. Applying a metallic layeron the surface of MWCNTs can increase their wettability in molten metal and also helps in increasing their dispersion (So, 2011). In addition, it protects MWCNTs from oxidation at high temperatures.

In general, electrolytic plating has two main reactions occurring simultaneously, the oxidation of the reducing agent to generate electrons representing the anodic partial reaction and the reduction reaction of the metal ions present in the solution without electricity by the resulting electrons representing the cathodic partial reaction. Since electroplating occurs only on catalytic surfaces, the surface of MWCNTs

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must be catalytically made to be ready for electrocoating. The general scheme for surface catalyzing is the conventional two-step technique of sensitization and activation through aqueous solutions of Tin(II) chloride (SnCl2) and Palladium (II) chloride (PdCl) (Feng, 2004). This approach helps in depositing catalytic palladium particles on top of the MWCNTs. However, the optimization process of such catalyst deposition on MWCNTs is difficult due to the need to control the four main factors represented by $SnCl_2$ concentration $PdCl_2$ concentration, PH level for both solutions, and the resulting catalytic particle size. Such a process would be difficult to optimize when it comes to coating MWCNTs supplied from different sources due to the different surface area and volume ratios for different MWCNTs. However, electroless nickel and copper phosphorus have been reported in decorating MWCNTs following the previously mentioned catalyst system. After that, the coated MWCNTs were placed in molten aluminum which reported a promising improvement in the mechanical properties of the resulting composite (So, 2011).

One of the problems reported in this study for the previous zero-electric approach was the absence of a reaction stop mechanism to stop further copper deposition on top of the MWCNTs once the required copper layer was reached. This appears to be particularly important during the final filtration in the absence of sonication and stirring. Further copper deposits may lead to the formation of Cu-coated MWCNTs aggregates. The presence of electrolytes with low deposition rates makes it difficult to achieve a precise reaction stop mechanism. For electroplating copper, the key factor to increase the deposition rate is to increase the anodic partial reaction kinetics. By oxidizing more formaldehyde (reducing agent), more electrons will be generated and more copper ions will be reduced in the cathodic partial reaction.

The key parameter of formaldehyde oxidation is the pH value which is controlled by NaOH. As the pH value increases, the deposition rate increases. However, the pH reaches a threshold where it starts to fall when it reaches a value of 12.5. Conventional copper electrolytes rely on pH values and heating to control the reaction kinetics (Feng, 2004) and (Mishra, 1996). In this work, a room temperature copper-cobalt electrolyte having a high deposition rate was used. A new catalytic strategy using palladium-tin colloids was explored.

2 MATERIALS AND EXPERIMENTAL PROCEDURES

2.1 Materials

The multi-walled carbon nanotubes are widely supplied by Chengdu Organic Chemicals Co. Ltd., China (OD: 10 - 20 nm, length: 10 - 30 m and purity >98%) was used in this study. Colloidal palladium-tin drive was prepared with a composition of 0.5 g of palladium chloride (PdCl2), 50 ml of 37% hydrochloric acid (HCl), 200 ml of deionized water, 25 g of stannous chloride. Cupric Sulphate Pentahydrate (98.5% Assay) and Sodium Carbonate Anhydrous (99.5% Assay) were supplied by Bofa Laboratotium. Sodium Hydroxide (99% Assay) was supplied by Bofa Laboratotium. Potassium Sodium Tartrate Tetrahydrate otherwise known as Rochelle salt (99% Assay) is supplied by Bofa Laboratotium. Cobalt(II) Chloride Hexahydrate (99% Assay) was supplied by Bofa Laboratotium. Formaldehyde 37% in aqueous solution was supplied by Bofa Laboratotium.

2.2 Experimental Procedures

The process of coating the surface of MWCNTs with copper is carried out in three steps. Starting with the surface activation process of MWCNTs using Pd-Sn colloidal particles. The next step is the acceleration process to remove stanno hydroxide deposits on the surface of the activated MWCNTs. The last process, electroplating of Cu-Co on the surface of the catalyzed MWCNTs. The above procedure globally is shown in Figure 1

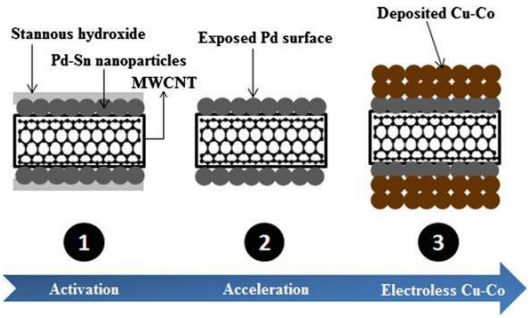

Figure 1: General Scheme of cu-co Electroless Plating on MWCNTs.

2.3 Activation of MWCNT's in Pd-Sn Colloidal Solution

The amount of MWCNTs used in this process wasset to 0.1 gram MWCNTs. MWCNTs is used when received without any function. MWCNTs were activated using a Pd-Sn colloidal solution adapted from the Plating on Plastics (POP) industry. The activation process was carried out in a mixture of 37.5 ml of Pd-Sn colloid solution, 37.5 ml of HCl (37%), and 175 ml of DI water. When using, mix 15% palladium-tin colloidal catalyst solution and 15% hydrochloric acid (37%) together, and balance with deionized water, then heated to 50 - 60 °C to get a better catalytic effect.

For activation, MWCNTs were dispersed with a magnetic stirrer in a colloidal solution for 30 minutes. After the stirring was completed, the treated MWCNTs were filtered using a 0.22 lm PTFE filter membrane on the microfiltration kit. The filtered MWCNTs were re-dispersed in DI water and filtered again to remove excess colloidal particles and residual colloid solution from activated MWCNTs. After filtration, MWCNTs were collected from the membrane using tweezers.

2.4 Acceleration of MWCNTs in a Mixture of Acids

The activated MWCNTs are then introduced intoa mixed acid solution known as an accelerator. The accelerator serves to remove excess tin hydroxideon the surface of the catalytic particles in theMWCNTs allowing the palladium surface to beexposed. The acceleration process will not removelead from the core of colloidal particles (Cohen, 1976). The acceleration process uses 55% (50 mL)HF acid in 500 mL DI water.

After acceleration, the MWCNTs were re-dispersed in water and filtered again to remove traces of the previous solution. Following the previous step, the MWCNTs surface becomes catalytic.

2.5 Electroless Cu-Co Plating of MWCNTs

The catalyzed MWCNTs were put into a 1 liter solution of Cu-Co electrolyte with concentrations as shown in Table I.

Table 1: Typical Concentrations of Cu-Coelectrolyte.

Copper-Cobalt electrolyte	Concentrations
$CuSO_4.6H_2O$	6.99 g/L
Na_2CO_3 $CoCl_2$	2 g/L
$CoCl_2.6H_2O$	1.09 g/L
$KNaC_4H_4O_6 \cdot 4H_2O$ (Rochelle Salt)	22.57 g/L
NaOH	4.5 g/L
Formaldehyde 37%	6 ml/L

All precursor powders were dissolved in DI water under magnetic stirrer for 5 min. After making sure all the powder is dissolved in the solution, formaldehyde is added to the solution. Subsequently, the activated MWCNTs were placed in an electroless bath under a magnetic stirrer for 10 min and the reaction started on the catalytic surface of the Pd-coated MWCNTs. Air bubbles began to emerge from the solution after the MWCNTs were added. This occurs due to the dissolution of hydrogen from the surface of the palladium and the oxidation of formaldehyde which produces hydrogen. Then the solution in a glass beaker was stirred using a magnetic stirrer for 30 minutes. When the air bubbles stop, it gives a good indication that the copper has completely covered the entire surface of the catalyst. In this case the copper surface became auto-catalyzed and the solution turned dark brown indicating the coverage of MWCNTs by copper. After stirring is complete, the copper-coated MWCNTs begin to accumulate on the bottom of the glass due to their increased density. Then the solution was filtered using a 0.22 nm PTFE filter membrane. The color of the filtered solution appears to be a light pink color indicating the consumption of all copper ions in the solution prior to filtration. The color of the copper-coated MWCNTs powder obtained, is shown in Figure 2.

The characterization of copper-clad MWCNTs was carried out at the Mechanical Engineering Materials Laboratory of Udayana University using scanning electron microscopy (SEM) analysis using (JEOL-JSM 6510 A).

Figure 2: Copper Coated MWCNT's of a Brown Color.

3 RESULT AND DISCUSSION

The addition of cobalt(II) chloride to an electroless copper solution helps in the autocatalytic reduction of copper ions in an electroless solution increasing the deposition rate tremendously. The use of colloidal Pd-Sn nanoparticle catalytic system limits the catalyst optimization process to two factors(colloidal particle concentration and solution volumerelative to the number of MWCNTs) rather than four factors in the predecessor system. In addition, the newsystem provides a fixed average size of the colloidal nanoparticles for better coating fit over MWCNTs. The optimized catalyst concentration and volume required to cover the surface area of a fixed number of MWCNTs helps in controlling the catalyst concentration-dependent initial copper deposition rate.

SEM image in Fig. 3 shows MWCNTs after being coated with copper. The increase in the thickness of the MWCNTs indicates the presence of copper on the surface of the MWCNTs. The mean diameter of the copper-clad MWCNTs was found to be 85 nm compared to the diameter of the initial MWCNTs, averaging 10-20 nm. The SEM images show a uniform layer that completely covers all the surfaces of the MWCNTs.

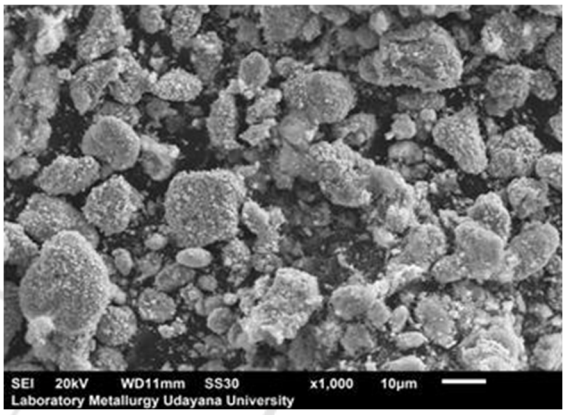

Figure 3: SEM Image of The Copper Coated MWCNT's.

To determine the percentage of the elements present, chemical analysis was carried out using energy dispersive X-ray (EDX). The spectrum obtained is shown in Figure 4.

The results of the analysis showed that the weight of copper was 84.10 % and 12.08 % C . Other elements such as Na, K,Co and Sn were found in minimal percentages as listed in Table 2.

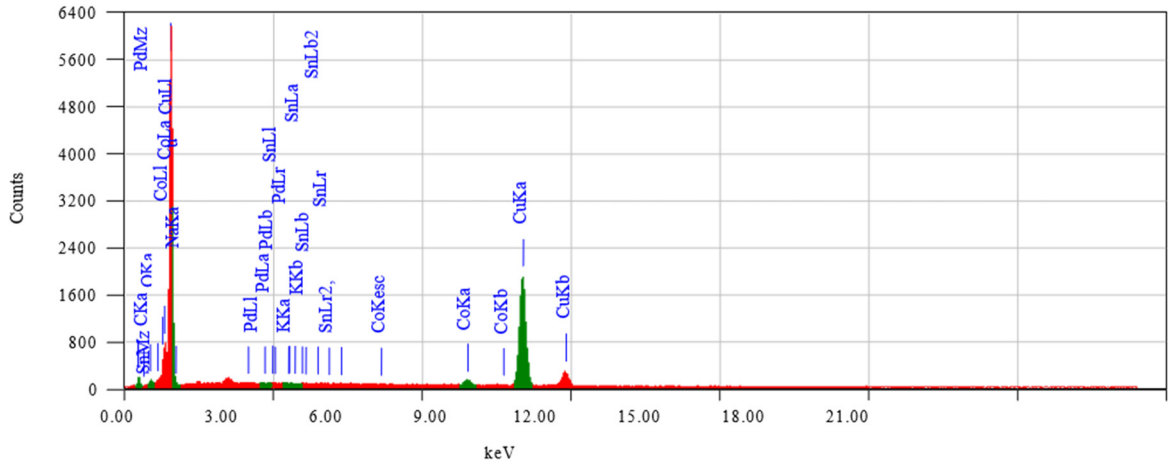

Figure 4: EDX Spectrum of Copper Coated MWCNTs.

Table 2: Edx Elemental Analysis of Copper Coated Mwcnt's.

Element	(keV)	Mass%	Sigma	Mol%	Compound	Mass%	Cation	K
C K	0.277	12.08	0.24	47.47	C	12.08	0.00	2.9938
O		17.81						
Na K	1.041	1.30	0.12	1.34	Na_zO	1.76	1.22	0.6077
K K	3.312	0.05	0.03	0.03	K_2O	0.07	0.03	0.0754
Co K	6.924	1.53	0.09	1.23	CoO	1.95	0.56	2.7533
Cu K	8.040	67.19	0.71	49.92	CuO	84.10	22.80	93.5240
Pd L								
Sn L	3.442	0.04	0.07	001	SnO	0.05	001	0.0458
Total		100.00		100.00		100.00	24.62	

ZAF Method Standardless QuantitativeAnalysis (Oxide)
Fitting Coefficient : 0.0326
Total Oxide : 24.0

The process of coating MWCNTs with copper produces different amounts of elements, compared to the results of previous studies (Elsharkawi, 2018). This is influenced by the type of catalyst, the type of accelerator, and the concentration of the solution used when immersing the MWCNTs. In this study, the SEM-EDX results showed that there was no Pd in the copper-coated MWCNTs powder. The use of a commercial Pd-Sn Colloidal Solution catalyst from Dupont gave a better effect, obtained elemental content of Cu 98.56% and Pd 0.43% (Elsharkawi, 2018).

4 CONCLUSIONS

In the electroless plating process of MWCNTs with Cu, it can be concluded that:

A. The factors that affect the morphology of the sample are; the composition of the colloidal palladium-tin catalyst, the type of catalyst, the activation temperature, the volume of the HF acid solution during the acceleration process, and the volume of the electrolyte solution bath.
B. The volume of the electrolyte solution bath is more in electrolytic coating, resulting in better samples.

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