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Synthesis and Characterization of Carbon Nanotubes Reinforced Aluminium Alloys through Spark Plasma Sintering

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Abstract

Spark plasma sintering is the promising technique to produce bulk composite materials. It is a very useful method to synthesize metal matrix composites with enhanced mechanical properties. The Final stage properties of processed materials through SPS are strongly related to the type of reinforcement and composition of reinforcement. In the present work, Aluminium –Silicon matrix composites reinforced with multiwalled carbon nanotubes are prepared through high energy ball mill and then sintered using spark plasma sintering. The SPS was carried out at 600oC at a heating rate of 50oC/min for 20 min under a vacuum of 50 MPa. Uniaxial pressure was applied to the powder mass throughout the SPS cycle and this reached a maximum value of 50 MPa when the desired sintering temperature was attained. The total processing time right from loading of the powder filled graphite die into the SPS chamber to ejection of sintered pellet from the die was less than 40 min. The microstructure and mechanical properties of these composites were characterized.

Keywords: *Carbon Nanotubes, Al-Si alloy, Mechanical alloying, Spark Plasma Sintering, Property*

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1. INTRODUCTION

Carbon nanotubes discovered by Iijima [1], finds a great application in developing high strength light weight alloys. Since CNTs exhibit high mechanical, electrical and thermal properties, it attracted by researchers to design nanocomposites with high specific strength and specific modulus. Although more developments in CNT based nanocomposites using metals, polymers and ceramics, but aluminium attracts intense interest due to good strength, low density and corrosion resistance properties [2-4]. The combination of unique properties of CNT and Al has significant potential in many weight receptive applications such as aerospace, defence etc., though still considerable research needs to be done to identify optimal fabrication route [5-7]. The key problem in fabrication of Al- CNT composites is the agglomeration of CNTs in the matrix. This is due to complicated perplexity of longs and smooth CNTs resulting from vanderwaals force of attraction[8]. The formation of carbide of aluminium is also one the obstacle in developing composites [9].

In the present work, CNTs reinforced Al-Si alloy (AA 4032) was synthesized by Spark Plasma Sintering (SPS) method. The distribution of CNTs in matrix alloy and microstructure relationship have been analysed by XRD, SEM and TEM. Mechanical properties such as compressive strength and hardness also measured as per ASTM standards.

2. EXPERIMENTAL PROCEDURE

The aluminium powder (AA4032) and the multi-walled carbon nanotubes (MWCNTs) were used as the preliminary materials

Table 1: Chemical Composition of AA4032

Element	Si	Cu	Mg	Ni	Al
Wt. %	11.5	1.0	1.0	1.0	bal

2.1 SYNTHESIS OF MWCNT

A manual metal arc welding machine was used in this work. Anode and cathode both made of graphite. The cathode is stationary one whereas the anode is moving towards the cathode. The anode was a cylindrical graphite rod (150 mm length with 10 mm diameter) and the cathode was a rectangular graphite plate (size: 150 × 100 × 10 mm). Distance between the two rod tips was maintained in the range of 1-2mm. Now, The DC arc discharge is applied between the two graphite rods. The high temperature generated by the arc causes vaporization of carbon atoms from anode into plasma. The carbon vapour then condenses and deposits on the cathode to form a cylinder with a hard outer shell (fused materials) and soft inner core containing nanotubes and nano particles. The high reaction temperature,

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because of using arc discharge, promotes formation of CNTs with higher degree of crystalline. Formed Carbon Nanotubes usually contain a large amount of impurities such as metal particles, amorphous carbon. They are carefully removed by appropriate chemical and physical techniques [10].

2.2 MECHANICAL ALLOYING OF AL-CNTS POWDER VIA HIGH ENERGY BALL MILLING

The chemical composition of Al-Si alloy used in current work is given in table1. Then four different weight percentages of CNTs (0.5, 1.0, 1.5, and 2.0) were added with Al-Si. A major obstacle to reinforce Al matrices with carbon nanotubes is the agglomeration and poor distribution CNTs within the matrix. Here by using mechanical alloying uniform distribution of CNTs within Al matrix is achieved. All the elemental powders are mechanically alloyed using Fritsch P5 high energy ball mill to produce nanostructured Al-Si/CNT composite. A ball-to-powder weight ratio of 10:1 was used. Most of the experiments were carried out at 300 rpm milling time upto 30 h. Toluene was added as a process control agent. Toluene prevents oxidation, excessive cold welding and also prevents powders sticking to the balls and the jar walls.

2.3 SINTERING

For the present attempt the temperature, load and holding times are optimized based on the literatures [11-15]. The SPS was carried out at 600oC at a heating rate of 50oC/min for 20 min under a vacuum of 50 MPa. Uniaxial pressure was applied to the powder mass throughout the SPS cycle and this reached a maximum value of 50 MPa when the desired sintering temperature was attained. The total processing time right from loading of the powder filled graphite die into the SPS chamber to ejection of sintered pellet from the die was less than 40 min.

The temperature, current, and displacement variation rate as function of time were recorded, as shown in Fig.1. The pictures show no variation in the parameters except the vacuum. There is little variation in vacuum which affect the temperature due to the presence of moisture. The first part of the curve is due to compact upsetting and conforming to the exact shape of the inner extrusion chamber. Figure 1 shows that the maximum pressure required to compact for the milled aluminum is slightly higher than that of CNT–Al at initial stages and there after it becomes constant.

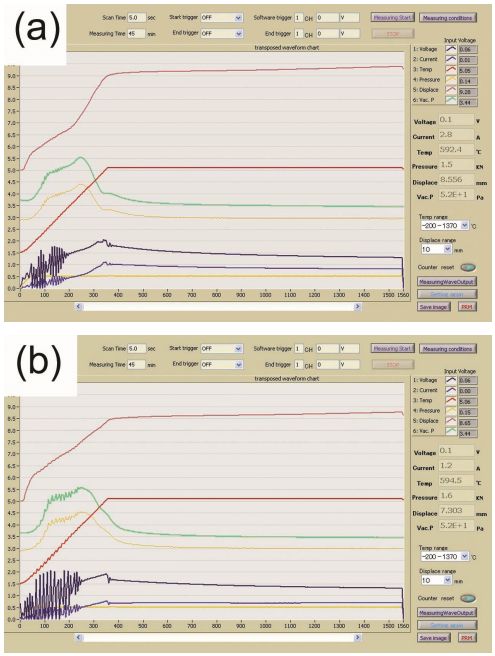

Fig 1. SPS picture the variation of the parameters (a) alloy; (b) composite

3. RESULT AND DISCUSSION

3.1 PHASE ANALYSIS BY XRD

Phase analysis was done by X-Ray Diffraction method. XRD patterns of Al-CNT composites are presented in Fig. 2. For Al-CNT composites, all the characteristic peaks of Al and Si were identified. No additional peaks were observed suggesting sintering of two phase mixtures without any undesirable interfacial reactions.

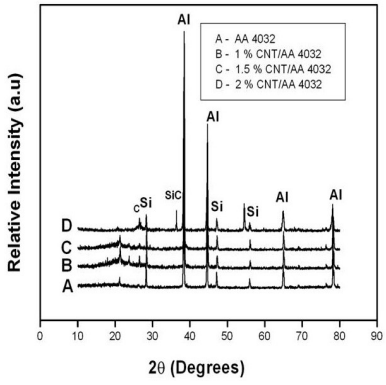

Fig 2: XRD Pattern of Al-CNT Composite

It is evidenced that no other intermetallics such as Al_4C_3 was formed during the sintering reaction. But there is a small amount of SiC formation is observed in the 2 wt. % MWNTs /AA 4032 composites. The size of the powders were measured

from XRD peak using Williamson Hall Equation. The grain size of the ball milled powder was 17nm after 30h.

3.2 MICROSTRUCTURAL ANALYSIS BY SEM

During milling, the aluminium particles were flattened under the impact of the balls, then started welding together to form large particles with a rough surface. As milling continued, it becomes smoother [16]. It has been proven in SEM analysis. Another advantage of using high energy ball milling is grinding. Because of their high impact energy, CNTs are embedded themselves into soft and ductile matrix through the solid diffusion process.

It has been proven that by increasing milling time, the CNTs will gradually lose its tubular structure, and after long milling time, 50 h, the tubular structure would completely disappear. To avoid this problem CNTs are added 29^{th} hour of operation in the present work[12].

Fig 3 shows SEM micrograph of the mixed powders after sintering. It can be clearly found that the density of the compacts is quite homogeneous and the morphology of AA 4032 powders are not changed relative to that of the raw powders due to the fact an equivalent pressure is applied around compacts, which is helpful for the plastic forming of the powders to reach full density. It can be seen from Fig 3 (a). The 2.0 wt. % carbon nanotubes reinforced AA 4032 composite after sintering with less density than base alloy. However, some micro-voids are found from Fig 3 (b), when 2.0 wt. % carbon nanotubes are added. This may be due to the fact that more quantity of CNTs impedes the densification process resulting in the decrease of the relative density of composites

3.3 MICROSTRUCTURAL ANALYSIS BY TEM

TEM micrograph of the AA 4032 alloy and composites are shown in Figure 4. It is clearly evidenced that CNTs are mixed with the alloy. The base alloy shows (Figure 4 (a)) Aluminium matrix along with silicon particles uniformly distributed throughout the matrix.

In Figure 4 (b), it is observed that CNTs are uniformly distributed inside the AA 4032 alloy matrix. But there exist a cluster of CNTs in the other TEM pictures (Figure 4. (c) and (d)) having higher concentration of CNTs. The CNTs are agglomerated individually due inter atomic force of attraction due to the Vander Waals force[17].

3.4 MICROHARDNESS

The hardness of the AA 4032 with different MWNT concentrations was also measured and plotted in Fig 5. It is important to point out that a substantial increase in hardness (155 HV) was observed for the composite sample, when compared with values for base AA 4032 alloy. These results make apparent the effect of the nanocrystalline state of the samples. As expected, MWNT had an important effect on hardness. It increased as the MWCNT fraction increased, reaching the maximum value of around 155 HV for the nanocomposite prepared with 30 h of milling time and 2 wt. % MWNT.

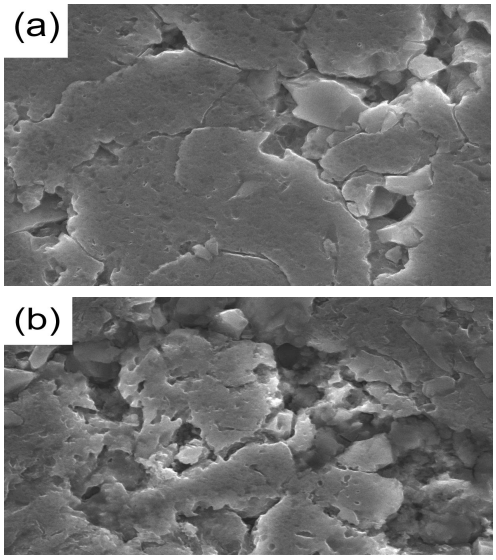

Fig 3: (a) Base Alloy (b) Al-CNT Composite

3.5 COMPRESSIVE STRENGTH

The compressive strength of the composites is plotted in the Fig 6. The fact that the prepared Al-CNT composite displays highly enhanced compressive strength and elongation with CNT addition indicates a resistance to plastic deformation in the stressed state due to difficulty in the rearrangement of dislocations[18-20].

This phenomenon increases dramatically in micro-ordered structures due to little generated dislocation (meaning limited movement of dislocations) reported by Oh et al. (2009). The CNTs used in the present work were selectively distributed around the boundary zone on the nanoscale.

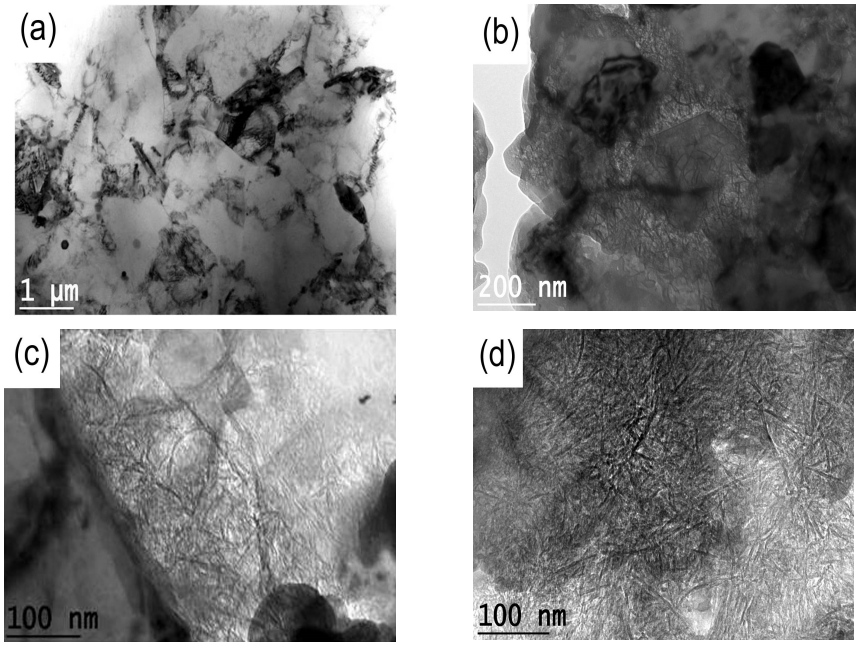

Fig 4: TEM micrographs: (a) AA 4032 alloy; (b) 1 wt. % CNT/AA 4032 (c) 1.5 wt. % CNT/AA 4032; (d) 2 wt. % CNT/AA 4032

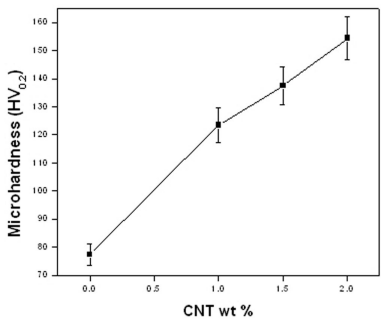

Fig 5: Microhardness of Nanocomposites

This may be one of the reasons for nanocomposite to have highly enhanced compressive strength and elongation. As a result, a remarkable enhancement in compression strength and less decrease in elongation of the Al-CNT composite could be achieved simultaneously. The maximum strength obtained is 50 % more than that of AA 4032 alloy.

4. CONCLUSIONS

The following are the conclusions drawn from the present work. Highly graphitized carbon nanotubes have been successfully synthesized by arc discharge technique

- Uniform distribution and nanostructure were obtained by mechanical alloying
- Degree of Nano size has been retained even after sintering at 600^0C by spark plasma sintering
- Better densification and high hardness were obtained by the addition of carbon nanotubes.

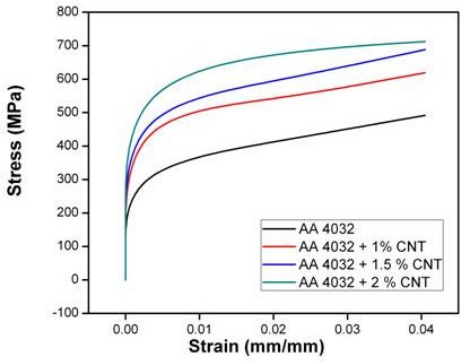

Fig 6: Compressive Strength of Nanocomposites

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