Studies on Al-MWCNT MMC surface coating on Aluminium substrates through friction surfacing process

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Abstract. In this study, Aluminium-Multi Wall Carbon Nano Tube (Al-MWCNT) metal matrix composite surface coating was fabricated by using solid state friction surfacing technique on Al substrate. The influence of process parameters on the coating dimensions, integrity and hardness was examined. The optical microscopy studies revealed that the coating integrity with the substrate is good with Trial-2 parameters i.e RPM 2500, Axial Load 700Kg and Traverse Speed 6mm/s. Grain refining due to the dynamic recrystallization was observed in the coating microstructure. XRD studies revealed that the MW-CNTs were distributed in to the coating and no detrimental intermetallic compounds were formed between Al matrix and MW-CNTs except Al\textsubscript{4}C\textsubscript{3}. The Scanning Electron Microscopic Studies reveals that the Al metal was severely deformed before forming the coating which is evident from the flow lines. It is further confirmed from the SEM studies that the MW-CNTs were dispersed uniformly within the coating and the nano size was retained in the coating without significant coarsening.

1. Introduction

The outstanding mechanical properties, low thermal expansion, high thermal conductivity, good electrical properties [1-2] of carbon nanotubes make them an excellent reinforcement in Al matrix to design high-performance metal matrix composites. Several processing techniques were investigated to synthesize the Al-CNT MMCs. These techniques including cold spraying [3], spray drying [4], Plasma spraying [5], Powder metallurgical route followed by hot isostatic pressing (PM+HIP) [6], Spark Plasma Sintering followed by hot extrusion (SPS + HE) [7], Powder deformation processing [8], and friction based solid state techniques such as Friction stir processing (FSP) to form surface composites [9 & 10]. The interfacial phenomena which includes wetting of the CNTs by Al matrix and chemical reactions at interface are crucial for the better functionality [11 & 12]

One of the most common problems in the processing of CNT reinforced-MMCs is the difficulty in dispersing the CNTs due to their attractive van der Waals interactions [13]. Therefore achieving an uniform dispersion of carbon nanotubes in a metal matrix is quite difficult. The other major challenges in preparing the Al-CNT composites include the following [14]

i. Fabrication of Al-CNT composites with higher vol % (>6) CNT having uniform dispersion
ii. Homogeneous dispersion while retaining the structural integrity of CNT
iii. Reduced damage of CNT during processing at higher temperatures and pressures
iv. Improving wettability of CNT with molten Al and its alloys for casting based techniques

As the Al-CNT MMCs were demonstrated for superior wear and Tensile properties [15 & 16] research was driven in to fabricate the MMC surface coatings.
Friction surfacing (FS) is a solid state surface coating technique which involves the generation of intense frictional heat between rotating consumable rod and the stable base plate. The tip of the consumable rod, after reaching a critical frictional temperature will be coated on to the substrate upon the traversing of the substrate. The process of friction surfacing is best understood with following schematic diagram in Fig. 1[17]. The coatings produced with this technique, are free from porosity, having worked structure rather than a cast structure, much finer grain size due to dynamic recrystallization effect and free from the unwanted inter-metallic compounds (IMCs) due to the higher diffusion rates.

In the recent studies friction surfacing is also using for fabricating the surface composites with varying volume percentage of the fiber [17 & 18]. This method of producing the surface composite coating is superior to the other conventional melting & spraying routes in the following aspects
a. Uniform distribution of the fibers due to severe plastic deformation and material flow
b. Effectively minimizes the coarsening of nano sized fibers/dispersants
c. The chemical stability of fibers and matrix are retained (or) Interfacial reactions were minimized due to lower diffusion rates at solid state processing

The present study aims for preparing in-situ, solid state Al-MWCNT composite surface coating on aluminium substrate. The MWCNTs were incorporated in to the consumable rod by drilling holes. The number and size of the holes can be varied to obtain the required volume percent (Vol%) of CNTs. In the current study it was aimed for approximately 4 Vol% of CNTs in the Al matrix. As the process is done almost in the solid state and involves severe plastic flow, the coatings are expected to have better dispersion, no interfacial reaction & nano size retention.

2. Materials and experimental methods

A friction surfacing machine (Fig. 2a) with 10kN Loading capacity and computer controlled 3 axes moment was employed to obtain the coatings. The substrate and consumable rod materials were taken in a well-polished condition and thoroughly cleaned to ensure the good bonding.

General purpose commercially pure aluminium plate with a nominal composition of Al-99.36%, Fe-0.45 and other trace elements was used as substrate. The dimensions of the substrate are Length 300mm X Width 200mm X Thickness 8mm, Al consumable rod with a nominal composition of Mg-0.55%, Si-0.75%, Mn-0.62%, Fe-0.37% and the balance is Al, in stress relieved annealing condition with Length 75mm X Diameter 20 mm were used in the present study.
The CNT reinforcement were packed inside 2mm diameter holes, drilled with 30mm depth from rubbing end of the consumable rod. The hole is drilled 3mm from the center of the rod. The hole configuration was shown in Fig. 2 (b).

Multi wall CNTs with Diameter 10-20nm, Length 3-8μm and Purity >90% from M/s NANOSHELL India Ltd, were utilized for the study. Fig. 3 will describe the representative image and the FTIR spectrum of MWCNTs from the supplier. These CNTs were filled in to the holes drilled in to the consumable rod, carefully and sealed with a thin polymer adhesive tape while fitting in to the spindle. PLC controlled machine was employed for the purpose of friction surfacing. The Al consumable rod which was reinforced with MWCNTs being mounted in a specially made holder that fitted to the spindle of the machine. Al Substrate consisting of square plate was laid on a platform which can be traversed. Friction Surfacing was performed by lowering the spindle with Al consumable rod until a contact was made with the Al substrate. The process parameters were entered in to the user interface program with help of a computer. The following two trials were carried out mainly varying the RPM from 2000 to 2500 and traverse speed from 5 to 6 mm/s, in the trial-1 & trial-2 respectively. This is to understand the influence of RPM and traverse speed on bonding characteristics and the bead dimensions.
Table 1. The Dimensions of materials and process parameters used in Trial-1 & Trial-2.

| Trial No | Rod Dimensions | Substrate Dimensions | Parameters |
|----------|----------------|----------------------|------------|
|          | Length (mm)    | Width (mm)           | Thickness (mm) | RPM | Load (kg) | TS (mm/s) |
| 1        | 75             | 20                   | 300         | 200 | 8         | 2000  |
| 2        | 75             | 20                   | 300         | 200 | 8         | 2500  |

Optical microscopy in un-etched and etched condition was carried out with Lieca metallurgical microscope. Micro hardness tester (Automatic Micro Hardness Tester, Omini Tech, India) was used for the hardness survey across the interface. Field emission scanning electron microscope (Merlin Compact, Carl Zeiss) was employed for sub microscopic images and energy dispersive spectroscopic studies. X-Ray diffraction machine (D8 advance, Bruker) with Cu Kα X-Ray radiation was used for the phase analysis. Table-3 will indicate the details of etching reagent used for the base metal and friction surfaced coating, along with its influence of revealing the micro-structure.

Table 2. Etching reagents used in the study.

| Material            | Etching reagent | Composition                  | Method                               | Remarks                                      |
|---------------------|-----------------|------------------------------|--------------------------------------|----------------------------------------------|
| Al consumable rod   | --              | 1 gram NaOH pellets + 99ml distilled water | For Al alloys, immerse or swab the sample up to 10-30 sec | Revealed the Grain boundaries of CP Al |
| Al-MWCNT coating    | Keller’s etch   | HF - 1ml, HCl - 1.5ml, HNO3 - 2.5ml, Distilled water - 95ml | For Al alloys, immerse the sample up to 30-180 sec | Revealed the Grains and phase boundaries |

Vicker’s micro hardness survey was conducted for comparing the hardness of coating and the substrate. The load on the Vickers micro-hardness indenter usually ranges from a few grams to several kilograms. 200 grams load was used in the current study for both base metal and coated samples. The actual indenter used is a square based diamond pyramid with an apex angle of 136°. The hardness survey was conducted systematically starting from interface with an inter indentation distance of 100µm from both coating and substrate.

3. Results and discussion

The process parameters used in both the trials have produced the coatings with the dimensions mentioned in the Table-3. It is evident from the results that the coating thickness is inversely proportional to the travel speed.
Table 3. Dimensions of the coatings obtained in Trial-1 and Trial-2.

| Coating Dimensions          | Trial No | Thickness (mm) | Width (mm) | Length (mm) |
|----------------------------|----------|----------------|------------|-------------|
|                            | 01       | 9.70           | 25.93      | 26.5        |
|                            | 02       | 6.52           | 23.1       | 24.4        |

3.1 Trial-1

A circular button type coating was deposited on the Al substrate with the experimented parameters. The features of the coating were described in Fig 4. The top view (Fig. 4a) and cross sectional view (Fig. 4b) of the coating indicates a central hollow space. There was bonding at the advancing side and the retreating side of the coating leaving an uncoated region at the central region. The central concavity of the consumable rod and its rough surface (Fig. 4c) is confirming the material transfer from rod to the coating.

The coating can be conveniently divided in to four regions for the better understanding of the coating features. Region 1 is un-bonded region at advancing side, Region 2 is a Central uncoated region, and Region 3 is a well bonded region followed by Region 4 which is un-bonded region at retreating side. The Advancing Side (AS) is the one where rod rotation and substrate movement are in the same direction. Retreating Side (RS) is the one where the rod’s rotation and substrate movement are in opposite direction. Friction surfacing process has an inherent feature of processing unbounded regions at both the AS & RS. This is due to the non uniform distribution of axial load on the consumable rod. In the present case, RS has shown less fraction of UN bonded region and more fraction of well bonded region. This is due to the more frictional heat, more plastic flow of the material and better bonding at RS [19]

Figure 5. Different regions in trail-01 coated sample.
The central unbonded region can be explained from the strengthening effect produced by the MWCNTs. The holes are nearer to the central region of the rod and the dispersion of CNTs is also more concentrated at the central region at the initial stages of the friction surfacing.

As per the studies on material transfer mechanism from rod to the coating [20] in FS process, a quasi liquid layer forms at the center of the consumable rod due to the intense frictional heat generation. This layer will be transferred from rod to the coating when the substrate is traversed. The thickness of the quasi layer also increases with increasing RPM of the rod. This mechanism is the main reason behind the slick concavity at the center of the consumable rod at the rubbing end. However in the present study, the slick concavity is not much prominent and in contrary there is a central UN coated region. This can be attributed to the fact that, the exceptional mechanical strength and the thermal conductivity of the MWCNTs present at the central region can contribute to dissipate the frictional heat to the nearby regions and retains the mechanical strength of the rod at central region. As a result the formation of the quasi liquid layer will be delayed and will be shifted to the CNTs free regions. Therefore the central region will result no materials transfer and leads to un-coated region. At the same time the side region to the center of the rod may leads to the formation of quasi liquid layer and leads to coating formation. The observed coating features are matching with the above predictions.

3.2 Trial-02

In view of the above discussion, the following process parameters were modified in the trial-02. The RPM is increased from 2000 to 2500, to promote the quasi liquid layer formation at the center. The traverse speed also increased from 5 to 6 mm/s, to reduce the thickness of the coating which in turn leads to better distribution of the axial load on the consumable rod.

It is evident from the above Fig. 6, that the parameters in trial-02 have resulted a reasonably good coating without gross defects as observed in the trail-01. A circular button type coating without a central defect was obtained. The coating thickness was reduced from 9.7mm to 6.5mm and the slick concavity of the consumable rod tip at the central region is more prominent. It is an indication of the material transfer from the central region. It is interesting to note that the coating width was reduced from 25.93mm to 23.1mm. This can be explained based on the concept of “real rotational contact plane”. Real rotational contact plane refers to the actual or instantaneous contact plane between the rotating consumable rod and the substrate during friction surfacing. The metal transfer will occur from the consumable rod to the coating through this plane. The area of the real rotational contact plane will be usually decreases with increase in rotational speed. Hence at higher rotational speeds metal transfer
is restricted to a smaller contact plane leading to narrower coatings. The above observations were made at macro level without the aid of a microscope.

3.3 Microstructural Studies

The microstructures of the consumable rod before and after the coating have been observed to find out the influence of friction surfacing process on grain size. Fig. 7a & b are the optical micrographs of the consumable rod in etched condition (Keller’s Etch) before and after the FS. The grain size reduction from $\approx 20\mu$ to $1\text{-}5\mu$ as a result of FS can be observed. This will be attributed to the dynamic recrystallization effect and the severe plastic flow of the material which are inherent features of FS. The low magnification scanning electron micrograph (Fig. 7c) of the coating reveals that the traces of severe plastic flow of material is clearly visible in the form of flow lines at retreating side of the coating. The interfacial region is showing that the rubbed material between the rod and the substrate has been expelled out of the coating region in the form of flash. That is the reason behind the outside flow lines. The material transfer happens from the slick concavity of the rod and leads to the formation of the coating. The wavy nature of the interface also ensures that there is enough penetration of the coating in to the substrate which leads to better bond strength. The coating was also subjected a hand chisel test and found that the bond strength is reasonably good.

Figure 7. (a) Optical Micrographs of the consumable rod before the coating (b) FS coating (c) Low magnification SEM image of FS coating for trail 2 coating.
Other important objectives of the study are dispersing the MW-CNTs in the Al matrix uniformly and avoiding the interfacial chemical reaction between the CNTs and Al matrix. The former objective can be examined with the help of higher magnification SEM image of FS coating in Fig 8. It is evident that the CNTs distribution is mostly uniform. However some MW-CNT clusters typically of 1-2μ size were identified in the coating. Non uniform distribution of the plastic strain may be a potential reason which is resulting from the higher coating thickness. Optimization of the process parameters to produce 2-3mm coating thickness such as higher axial loads and faster traverse speeds may be useful to achieve this.

![Higher Magnification SEM image of FS coating](image)

Figure 8. Higher Magnification SEM image of FS coating for trail 2 coating.

### 3.4 X-Ray Diffraction (XRD) Studies:

XRD studies of the Al base plate, Al consumable rod and FS coating were presented in the Fig. 9. The XRD patterns of the base plate and consumable rod shows only FCC Aluminum and the FS coating shows the Carbon and Al phases. This is a strong indication for the reinforcement of the MW-CNTs in the FS coating. The studies on the interfacial reactions between CNTs and Al [21] explains that the aluminium carbide i.e. Al₄C₃ is a very common compound forms in the Al-CNT MMCs due to the lower surface energy requirement (-12.7 kCal at 298K). This compound will usually forms on the defects such as ends of CNTs, surface of the MW-CNTs by CVD process and also on the amorphous carbon pre-cursor phase. The study also concluded that the processing temperatures higher than the 450°C will result the formation Al₄C₃ at the interfacial regions. The corresponding position of the peak for this compound in XRD is at around 36° of 2θ. The XRD studies of FS coating processing a peak position at 36.620 which is confirming the formation of Al₄C₃ phase. The frictional saturation temperatures in FS process, usually reaches 80-90% of the melting point of the consumable rod which is Al in the present case. Therefore it is reasonable to assume that the FS processing temperatures will easily exceeds the 450°C and there is higher possibility for the formation of Al₄C₃ phase.
3.5 Micro-Hardness survey

Al-MWCNT surface coating along with the substrate was subjected to micro hardness survey (Fig. 10) across the interface. The following HV\textsubscript{0.2} values were measured as an average of five readings. Substrate Hardness is 38.3, Al rod Hardness is 111.2 before the FS coating, Al FS Coating Hardness is 75.33 H\textsubscript{V} respectively. The hardness survey with square based diamond indenter with 200g load and 100\mu inter indentation distance was carried from al substrate to coating across the interface. The hardness survey has revealed that the substrate hardness was increased by 96.7% and the consumable rod hardness decreased by 33% after the FS. The reasons for the decrease in hardness are uncertain. This may be due to the precipitate coarsening during FS and relaxation of dislocation density due to the dynamic recrystallization during FS. A post heat treatment after FS may require for restoring the strength and hardness. The advantage of CNT insertion in the Al matrix is not fully realized due to non uniform distribution and the cluster formation.

Figure 9. XRD patterns of Al base plate (Top), Al consumable rod (Middle) and FS coating with MW-CNTs for trail-02.

Figure 10. Micro-Hardness survey of Al-MWCNT FS coating across the interface.
It is interesting to note that there is a diffused layer or mechanically intermixed zone up to around 400μm towards the Al base metal. A gradual increase of hardness from 40 VHN to around 80 VHN can be observed in this zone at the Al substrate side. This zone is a result of consumable rod penetration in to the base metal. It can also be observed that there is no sudden raise or drop of hardness at the interfacial region, which may be an indication that there is no significant amount of hard and brittle carbides formation at the interface.

4. Conclusions

1. Al-MWCNT in-situ surface composite coating was successfully fabricated by using Friction surfacing process at the experimented trial-02 parameters i.e. 2500 rpm, 700Kg axial load and 6mm/s traverse speed
2. The coating thickness up to 6.5mm thickness can be deposited on Al substrates with the careful adjustment of the parameters
3. The Al-MWCNT MMC friction surfaced coatings are metallurgically bonded with substrates without any gross porosity or cracks
4. The distribution of the CNTs is uniform on a gross volume however some few CNT clusters of 1-2μm size range were observed may be due to the non uniform distribution of the plastic strain through the coating.
5. There is enough evidence in the XRD studies that FS also could result the formation of aluminum carbide \( \text{Al}_4\text{C}_3 \), however further TEM studies are required to confirm the same.
6. There was an intermixed zone observed between FS coating and substrate up to 400μm due to the of high temperature strength of the coating material probably due to the MWCNTs

5. References

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