Interface in carbon nanotube reinforced aluminum silicon composites: Thermodynamic analysis and experimental verification

Srinivasa R. Bakshi a, Anup K. Keshri a, Virendra Singh b, Sudipta Seal b, Arvind Agarwal a,⁎

a Plasma Forming Laboratory, Department of Mechanical and Materials Engineering, Florida International University, 10555 West Flagler Street, EC 3464, Miami, FL 33174, USA
b AMPAC and Nanoscience Technology Center, University of Central Florida, Orlando, FL 33816, USA

A R T I C L E   I N F O

Article history:
Received 13 January 2009
Received in revised form 10 March 2009
Accepted 11 March 2009
Available online 21 March 2009

Keywords:
Metal matrix composites
Surfaces and interfaces
Carbon nanotubes
Thermodynamics
Carbide

A B S T R A C T

Interface in carbon nanotubes (CNTs) reinforced aluminium–silicon composites are studied via thermodynamic and kinetic analysis. A pseudo-phase diagram has been generated based on the thermodynamic calculations to predict the type of carbide (Al4C3 or SiC) that would form at the matrix–CNT interface as a function of matrix composition and processing temperature. The pseudo-phase diagram is useful in high temperature processes like thermal spray forming. Critical thickness values for carbide nucleation suggest the formation of Al4C3 with Al–11.6 wt.% Si alloy and SiC with Al–23 wt.% Si alloy. Thermodynamic calculations show that the amount of Al4C3 increases with an increase in the CNT content. The computed results perfectly agree with the results obtained by XRD, SEM of fracture surface and high-resolution transmission electron microscopy (HRTEM) observations on Al–11.6 wt.% Si and Al–23 wt.% Si alloy reinforced with CNT.

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1. Introduction

Light weight and high strength metal matrix composites reinforced with carbon fibers have been used for many automobile and space applications [1–3]. In recent years, the focus has shifted to reinforcement of metal matrix composites with carbon nanotubes (CNTs) due to their strengths in excess of 100 GPa and stiffness of 1000 GPa which makes them superior to carbon fibers [4,5]. The major challenge has been to disperse and align the nanotubes in the metal matrix and the fabrication of bulk composites having the above-mentioned characteristics. Cha et al. [6] have shown extraordinary improvement of the yield strength (~200% increase for 10 vol.% CNT addition) in copper–CNT composites fabricated by the molecular mixing method. The increase in the strength was attributed to the uniform dispersion of CNTs. Choi et al. [7] have fabricated aluminium–CNT composites by extrusion of ball milled powders. Young’s modulus and yield strength increased by ~49% and ~46%, respectively, for the 4 vol.% CNT containing composite.

The fiber–matrix interface plays an important role in strengthening of the composite. The applied stress is transferred to the high strength reinforcement through the interfacial layer. So a strong interface would make the composite very strong but at the expense of ductility of the composite. A weak interface would lead to lower strength and inefficient utilization of fiber properties by facilitating pullout phenomena at low loads due to interface failure. Interfacial reactions and degree of wetting of the reinforcement (fibers) also affect the properties of the composite [8–10]. Formation of aluminium carbide (Al4C3) has been observed at the interface in liquid metal infiltrated aluminum silicon alloy composites reinforced with carbon fibers containing 7 wt.% [11] and 13 wt.% Si [12]. Vidal-Setif et al. have shown reduction in strength and premature failure of 75 vol.% carbon fiber reinforced A357 alloy due to formation of Al4C3 and presence of brittle Si particles [13]. So formation of Al4C3 needs to be avoided. This can be done by either by controlling the chemistry of the matrix or by using coated carbon fibers [14,15].

Recently there has been a lot of interest in fabrication of aluminum matrix composite reinforced with carbon nanotubes. Bulk aluminum–CNT composites have been fabricated using various processes like cold isostatic pressing followed by hot extrusion [16], pressureless infiltration technique [17] and thermal spraying [18–20] to name a few. In general, less attention has been devoted to the interfacial reaction between the metal matrix and CNT. It has been reported by some authors that no reaction product is observed [7,21]. It is very important to understand the interaction between metals and the new forms of carbon namely CNTs, from theoretical and practical viewpoint. Carbon nanotubes are made by rolling a sheet of graphene onto itself and hence outer shell is made up of the basal plane. So they could be quite stable chemically. Zhong et al. have shown from the changes occurring in the intensity of (1 1 1) peak of the XRD pattern of Cobalt, after a 10-h annealing treatment with various forms of carbon at 1000 °C, that the interaction of layered graphite was the lowest followed by single walled CNT.
multiwalled CNT and activated carbon in respective order [22]. Layered graphite has perfect structure of sp² hybridized carbon atoms arranged in ABABAB... stacking sequence which would make it less reactive chemically. Defects in activated carbon and in nanotubes provide sites for chemical reactions to occur. Xu et al. have reported carbide formation in Al–CNT composites fabricated by hot pressing at 520 °C with Al:C atom ratio of 1:1 and 1:2 from EDS results in SEM [23]. Ci et al. have demonstrated the formation of aluminum carbide on annealing CNTs, on which aluminum was deposited by magnetic sputtering process, at temperatures above the melting point of aluminum [24]. On the other hand, formation of silicon carbide (SiC) was shown to occur thermodynamically, kinetically and experimentally by Laha et al. from our research group, due to reaction between CNT and molten hyper-eutectic (23 wt.% Si) aluminum silicon alloy during plasma spraying [25]. Recently, we observed that Al₄C₃ forms at the interface due to the reaction between CNTs and molten eutectic (11.6 wt.% Si) aluminum–silicon alloy during plasma spraying of spray dried composite powders [26]. Hence, the matrix composition has a significant effect on the interfacial carbides forming in the composites. Different interfacial carbides may result in significantly different mechanical properties of the composites as the shear strength of the carbides determines the stress that could be transferred to the CNTs. It is critical to understand the underlying thermodynamics and kinetics of this effect to precisely control the reactions at the interface between CNT and alloy matrix. Also the mechanism of growth of the carbides needs to be understood. To the best of our knowledge, such a study has not been carried out for Al–Si alloy composites reinforced with carbon, be it fiber, graphite or CNTs.

This study highlights the effect of CNT and Si content on the interfacial reaction in Al–Si composites. Thermodynamic and kinetic analysis predicts which carbide will form for a given processing temperature and alloy composition. Particular interest is devoted to the interfacial phenomena occurring in Al–11.6 wt.% Si alloy and CNT composite. High resolution transmission electron microscopy has been carried out to study the interfacial reactions to validate the theoretical predictions.

2. Experimental techniques

Spray drying was used to fabricate spherical composite agglomerates of 40–80 μm diameter, of aluminum–11.6 wt.% silicon alloy particles (1–3 μm in diameter) with uniformly distributed CNTs. The CNTs employed were more than 95% pure and had a diameter of 40–70 nm and length 1–3 μm. Plasma spraying was used to fabricate thick coatings (up to 5 mm thick) containing 5 wt.% and 10 wt.% of CNTs. The microstructure of the coatings was dual phase: (i) matrix containing uniformly distributed CNTs and (ii) CNT rich clusters. The microstructure and processing details are provided elsewhere [26]. Transmission electron microscopy was carried out using a Philips/FEI Tecnai F30 field emission gun transmission electron microscope operating at an accelerating voltage of 300 kV. The samples for TEM were prepared by grinding the plasma sprayed deposits down to less than 100 μm using abrasive paper followed by punching 3 mm diameter discs which were then subjected to dimpling at the center using a dimple grinder (Model 656 Mk3, Gatan, Inc., CA, USA). The final thinning was carried out by twintjet polishing (Model 110, E.A. Fischione Instruments, Inc., PA, USA) using a 30 vol.% mixture of 6N HNO₃ in ethanol as the electrolyte until a hole was formed. Thermodynamic calculations were done using thermo-chemical software and database FactSage™ [27]. Images of the crystal structures were obtained using the free software Mercury 1.4.2 developed by the Cambridge Crystallographic Data Centre (Cambridge, UK) while the crystallographic information file for Al₄C₃ was obtained from the International Union of Crystallography (IUCr) database.

3. Results and discussion

3.1. Thermodynamic analysis of carbide formation

When molten aluminum silicon alloy reacts with carbon in CNT, there is a possibility of formation of silicon carbide (SiC) or aluminum carbide (Al₄C₃) at the matrix/reinforcement interface. The chemical reactions and the corresponding free energies have been represented by the equations below:

\[
\frac{4}{3}[\text{Al}]+C = \frac{1}{3}\text{Al}_4\text{C}_3, \quad \Delta G_{\text{Al}_4\text{C}_3}^{\text{r}} = \Delta G_{\text{Al}_4\text{C}_3}^{\text{0}} + \frac{1}{3}RT \ln \frac{a_{\text{Al}_4\text{C}_3}}{(a_{\text{Al}})^{\frac{4}{3}}} \quad (1)
\]

\[
[\text{Si}]+C = \text{SiC}, \quad \Delta G_{\text{SiC}}^{\text{r}} = \Delta G_{\text{SiC}}^{\text{0}} + RT \ln \frac{a_{\text{SiC}}}{a_{\text{Si}}} \quad (2)
\]

Here the square brackets [] represent that Al and Si are in the molten Al–Si solution and \(\Delta G^{r}\) refers to the standard free energy of formation per mol of carbon, \(\alpha\) denotes activity, \(R\) the universal gas constant and \(T\) the absolute temperature at which the reaction takes place. Representing the equations per mole of carbon makes it easy to study which carbide will form preferentially. For a given alloy composition and temperature, only one of the reaction (1) or (2) will occur depending on which has a more negative free energy change. The thermodynamic properties of CNTs were assumed equal to graphite due to lack of the data for CNTs. This gives us a comparative analysis for the two competing reactions which might be accurate for the CNT–alloy system as well, because for both graphite and CNTs the reacting planes are the same (the (000 1) basal and the (1 1 0) prism planes). It is assumed that CNTs are pure and activity of carbon can be taken as 1. The activity of Al₄C₃ and SiC can also be taken as unity since there was no evidence of formation of ternary aluminum silicon carbides which would affect the activity of any of them [26]. The activity (\(\alpha\)) is equal to atom fraction (\(\chi\)) only for ideal solutions. From the reported thermodynamic values for the Al–Si system [28,29] it is observed that both Al and Si show negative deviation from ideality. Using the activity of Al and Si for various alloy compositions at different temperatures, the free energy of formation of Al₄C₃ and SiC was computed using the ‘Reaction’ module of FactSage.

Fig. 1 shows the free energy of formation of the carbides per mole of carbon as a function of alloy composition at different temperatures. It is observed that at an experimentally measured temperature of 2300 K, which is typically attained by the molten particle during plasma spraying [26], the free energy of formation of Al₄C₃ increases with increasing Si content and becomes positive for Si content >34.8 wt.% (34 at.%). This indicates that Al₄C₃ formation is thermodynamically not feasible at 2300 K for Si content >34.8 wt.%. Also it is seen that the free energy of formation of SiC becomes more and more negative with increasing silicon content of the alloy. It is observed that at 2300 K, for alloys with Si content <21.6 wt.% (21 at.%), \(\Delta G_{\text{SiC}}^{\text{r}}\) is positive which indicates that the formation of SiC is thermodynamically not feasible. The open circles in

![Fig. 1. Free energy of formation of Al₄C₃ and SiC per mole of carbon as a function of alloy composition.](image)
Fig. 2. Plot showing the alloy compositions for which free energy of formation of either carbide at various temperatures are equal. For a given temperature of reaction, all compositions to the left of the line will lead to formation of Al$_4$C$_3$ while alloy compositions to the right will show formation of SiC.

Fig. 3. Equilibrium mole fraction of Al$_4$C$_3$ vs. Si wt.% in the alloy at various temperatures for 10 wt.% CNT composites.

The interaction time of powder particle with the heat source during plasma spraying is very small (0.1–1 ms) compared to the time required for other synthesis processes (e.g. hot pressing, sintering, extrusion, etc.). Hence, kinetics becomes very important in predicting CNT/Al–Si matrix interface reaction during plasma spraying. Wetting is related to the surface energies by the Young’s equation and the Young–Dupre relation given below:

\[
\cos \theta = \frac{\gamma_{SV} - \gamma_{LV}}{\gamma_{LV}} \quad (3)
\]

\[
W_A = \gamma_{SV}(1 + \cos \theta) \quad (4)
\]

Here $\theta$ is the contact angle and $\gamma_{SV}$, $\gamma_{LV}$ and $\gamma_{LS}$ are the solid–vapor, liquid–solid and liquid vapor surface energies and $W_A$ is the work of adhesion between the liquid and the substrate. It is seen from (4) that the smaller the contact angle, the higher is the work of adhesion and better is the wetting characteristics. The work of adhesion has been calculated as 200 mJ m$^{-2}$, 1156 mJ m$^{-2}$ and 1300 mJ m$^{-2}$ for Al–C, Al–Al$_4$C$_3$ and Al–SiC systems, respectively [30,35]. The surface tension of CNTs ($\gamma_{SV}$) is 45.3 mJ m$^{-2}$, which is similar to carbon fiber [36]. It has been shown that a liquid with surface tension between 100 mN m$^{-1}$ and 200 mN m$^{-1}$ results in good wetting with CNT [37,38]. Molten aluminum silicon alloys have surface tension...
of $\sim 800 \text{mN m}^{-1}$ [39]. The surface tension of Al–Si alloys does not vary significantly with the composition since the surface tension of Si and Al are similar. Hence, it is expected that the wetting between Al–Si and CNTs will be poor. Landry and coworkers observed that Al–Si alloys do not wet graphite in the beginning and exhibit a large contact angle of $\sim 160^\circ$ [30]. It is noted that contact angle strongly depends on the temperature, substrate surface roughness and the atmosphere during the test. In the case of Al–Si alloys and graphite, the contact angle reduces with the formation of Al4C3 or SiC as interfacial reaction product. Al4C3 and SiC formation reduces contact angle to 45$^\circ$ and 38$^\circ$, respectively [30]. Hence, formation of interfacial carbides favors wetting and infiltration of liquid melt into CNT clusters. Fig. 5 shows that the CNT cluster has been infiltrated by Al–11.6 wt.% Si melt suggesting occurrence of reactive wetting. Thus reactive wetting is an important phenomenon for infiltration of the clusters.

As with any nucleation phenomena, a critical dimension is associated with carbide nucleation too. The critical thickness for carbide formation is given by the equation [35]

$$t_{\text{Crit}} = -V_M \frac{\Delta G'}{\Delta \gamma'}$$  (5)

Here $V_M$ is the molar volume of the carbide formed, $\Delta G'$ is the free energy of formation per mole of carbide and $\Delta \gamma' = (\gamma_{\text{MC/CNT}} + \gamma_{\text{MC/Alloy}}) - (\gamma_{\text{Alloy/CNT}})$ is the increase in total surface energy as a result of formation of new interfaces. MC stands for metal carbide. There is no free energy barrier for carbide nucleation for negative values of $\Delta \gamma'$. When the thickness of carbide is lower than the $t_{\text{Crit}}$, the carbide is unstable and would dissolve back into the molten alloy. The mechanism of growth of SiC in case of Al–23 wt.% Si alloy was discussed by Laha et al. [25]. A similar kind of mechanism will hold true for the growth of Al4C3 at the interface of Al–Si alloy and CNTs. This is illustrated in the schematic in Fig. 6. When carbide thickness reaches $t_{\text{Crit}}$, further growth is energetically favorable this results in the decrease in contact angle and increase in reactive wetting. Smaller $t_{\text{Crit}}$ values therefore indicate easy formation of carbide as well as better wetting. But once Al4C3 is formed, it acts as a barrier for further reaction to occur. Further reaction leading to growth of Al4C3 is possible by two mechanisms. The perpendicular growth of the carbide will occur by reaction at the (a) Al4C3/CNT interface that will be governed by the diffusion of Al through Al4C3, and (b) at the Al4C3/Al–Si alloy interface which will be governed by the diffusion of C through Al4C3. The atomic radius of Al atom is 0.125 nm while that of carbon is 0.07 nm. Hence, it is expected that diffusion of the smaller carbon atoms from the CNT to the Al4C3/Al–Si alloy interface would be the dominating mechanism for perpendicular growth of Al4C3. The data on diffusion of Al and C in Al4C3 is not available. The lateral growth of the carbide is governed by the reaction at the triple points. So the larger the spreading, the larger will be the area of the triple points and hence the extent of reaction and formation of Al4C3.

It is evident from Eq. (5) that large negative free energy ($\Delta G'$) of formation and small increase in interfacial energy ($\Delta \gamma'$) will
yield smaller $t_{\text{Crit}}$ and better wetting. A lower value of carbide/CNT ($\gamma_{\text{MC/CNT}}$) and CNT/molten alloy ($\gamma_{\text{MC/Alloy}}$) interfacial energies will result in lower $\Delta \gamma$. Lower carbide/CNT interfacial energy is possible in case of coherent interfaces which will promote oriented growth of carbides over the CNT. There is a lack of experimental data for the interfacial energy values. The surface energies of a compound can be computed using ab initio methods [40] for crystallographic planes terminated by different kind of atoms. From the compilation of activity vs. at.% by Desai [28] for Al–Si alloys and using FactSage, the value of $\Delta G_f$ per mole of Al$_4$C$_3$ and SiC were calculated and then $t_{\text{Crit}}$ was calculated. $\Delta \gamma$ has been assumed to be 1000 mJ m$^{-2}$ [25,35]. Fig. 7 shows the variation of critical carbide thickness with alloy composition at 1700 K. It is observed that for Al–11.6 wt.% Si alloy, Al$_4$C$_3$ has lower critical thickness compared to SiC while the reverse is true for Al–23 wt.% Si alloy. The $t_{\text{Crit}}$ values indicate that Al$_4$C$_3$ formation is favored from the kinetics point of view for an alloy composition of 11.6 wt.% Si while SiC is favorable when alloy composition is 23 wt.% Si. This justifies the experimentally observed formation of the type of carbide with different silicon content of matrix in our present study and Laha et al. [25].
tributed and have a higher probability of coming in contact with the molten alloy and reacting to form carbide phase. HRTEM images of the plasma sprayed Al–11.6 wt.% Si composite containing 5 wt.% CNT is shown in Fig. 11. A coated and reacted CNT is seen in Fig. 11 where reaction products are marked by the arrows. There is an approximately 5 nm thick coating on the CNT surface which is greater than the critical thickness for Al$_4$C$_3$ formation at 1700 K (∼0.65 nm). This indicates that reactive wetting occurs resulting in uniform coating of the CNT with the molten alloy. Fig. 12 shows HRTEM images from plasma sprayed Al–11.6 wt.% Si composite containing 10 wt.% CNT coating. A clean interface between Si and CNT in Fig. 12a indicates that no reaction has taken place between CNT and Si, even when they are in intimate contact. This confirms the predictions from thermodynamic calculations presented previously. Fig. 12b shows the formation of Al$_4$C$_3$ at the Al–CNT interface in the composite. The thickness of the carbide layer as shown by the white arrow is found to be approximately 6 nm.

No orientation relationship between Al$_4$C$_3$ and CNTs was observed. This is in contradiction to observed orientation relationship of (0002)$_C$ // (0003)$_{Al_4C_3}$ [41] in carbon fiber aluminum composites. The lack of orientation relation between Al$_4$C$_3$ and CNTs is attributed to structural configuration. Growth of carbide phase is attributed to the crystal structure of Al$_4$C$_3$, which has a rhombohedral (space group R$3m$) structure as shown in Fig. 13. It is made up of alternating layers of Al$_2$C and Al$_2$C$_2$ with Al atoms having tetrahedral C coordination. C atoms have octahedral (C$_1$ in Fig. 13) and trigonal bipyramidal (C$_2$ in Fig. 13) coordination with Al atoms [42]. Al$_2$C layer is close packed with C in octahedral voids formed by close packed aluminum atoms. So it is expected that the lateral diffusion of carbon atoms by an interstitial mechanism would be favored through the Al$_2$C$_2$ layer. As seen from the figure (0003) plane of Al$_4$C$_3$, has a hexagonal arrangement of carbon atoms similar to that in graphite. However, it is to be remembered that the C–C distance in graphite is 1.42 Å while it is 3.33 Å in Al$_4$C$_3$. Thus Al$_4$C$_3$/CNT interface is expected to be strained without any orientation relationship.

Formation of nano-size layer of Al$_4$C$_3$ at the interface has been shown to be beneficial for the mechanical properties for Al–SiC composites by increasing the interfacial bonding [43]. Kwon et al. have suggested that Al$_4$C$_3$ formation helps in load transfer to CNTs by pinning the nanotubes to the matrix [44]. So the formation of controlled amount of interfacial products might help in the improvement of the mechanical properties. Mechanical testing of
bulk samples (our future studies) would answer the effect of Al₄C₃ content on the macro-scale properties of the composites.

4. Conclusions

Thermodynamic analysis has been performed to predict interfacial reaction between Al–Si alloys and CNTs. It is shown that during the process of plasma spraying, formation of Al₄C₃ is thermodynamically feasible in case of the reaction between Al–1.16 wt.% Si alloy and CNT while SiC is found to be feasible for Al–23 wt.% Si alloy. A pseudo-phase diagram is generated from the computed thermodynamic data, which can be used to predict the type of interface carbide that will form for any alloy at a given processing temperature. It has been shown that the critical carbide thickness for Al₄C₃ is lower than SiC for 1.16 wt.% Si alloy while it is reverse for 23 wt.% Si alloy at 1700 K further supporting the formation of the observed carbides. X-ray diffraction and SEM of fracture surface validates formation of Al₄C₃ with Al–1.16 wt.% Si as matrix. HRTEM images further validate the results obtained from the theoretical predictions.

Acknowledgements

Authors would like to acknowledge financial support from National Science Foundation CAREER Award (NSF-DMI-0547178). Srinivasa Rao Bakshi would like to acknowledge Dissertation Year Fellowship from the University Graduate School at Florida International University.

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