ENHANCING INTERFACIAL BODING STRENGTH BETWEEN MULTI-WALLED CARBON NANOTUBES AND ALUMINUM BY HOT EXTRUSION AND HEAT TREATMENT

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Keywords: Metal-matrix composites (MMCs), carbon nanotubes (CNTs), interface, reaction

Abstract
Thermal analysis (DSC), X-Ray diffraction (XRD) and SEM were used to investigate the CNTs-Al reaction and interfacial bonding in SiCw+CNTs/6061Al composites made by pressure infiltration. The results show that the reaction activation energy between CNTs and 6061Al is higher than that between CNTs and 2024Al. Reaction between CNTs and Al at temperature slightly below solidus temperature of 580 ^oC proceeds on a controllable way. After the as-cast composite was hot-extruded and treated at 580 ^oC for 1h, interfacial bonding strength between CNTs and Al was improved and Vickers hardness increased.

1 Introduction

Carbon nanotubes (CNTs) have high strength, modulus and unique physical and chemical properties and are demonstrated to be a kind of realistic reinforcement for various polymers[1, 2], ceramic[3] and metals[4-6]. For CNTs reinforced metals, it is a challenge to realize homogeneous dispersion, moderate CNTs-Al interaction and proper interfacial bond strength[4]. Various processes, such as high energy ball milling[7-9], semi-solid plastic extrusion[10] and pressure infiltration[11-14], have been used to fabricate CNTs reinforced metal-matrix composites (MMCs). To fulfill a complete metal infiltration into a reinforcement preform, the compressive strength of the preform (σ_c) need exceed the melt infiltration critical pressure (P_c)[11, 13]. However, the σ_c of CNTs preform is low and P_c is high, and thus only a partial infiltration of the preform was achieved[13]. Recently, whiskers with diameters of 0.1~1 μm were blended with CNTs to create a hybrid whisker/nanotubes preform. This hybrid preform showed a high σ_c and low P_c, and fully infiltrated by aluminum alloys[15].

Molten metals such as Al and Mg do not wet CNTs[16] and thus interfacial bonding strength between CNTs and Al and Mg metals is not high. Ci *et al*[17] reported that interfacial reaction between carbon nanotubes and aluminum enhance their chemical interaction and thus improve interfacial strength. Our previous studies also revealed that CNTs react with Al to form Al_4C_3[18, 19]. The reason for the improvement of CNTs-Al bonding is that C-Al reaction happens on the amorphous carbon, defect-rich sites or open ends of CNTs[17]. The nanoscale Al_4C_3 product on the surface of CNTs favors their bonding with Al matrix. Here, we make hybrid aluminum composites hybrid reinforced SiC whiskers and CNTs by pressure

infiltration, and study the modification of their interfacial bonding strength by partial reaction between CNTs and Al. The results show that interfacial reaction can be achieved slightly below the solidus temperature, and CNTs-Al bonding strength is significantly improved.

2 Experimental details

SiCw+MWCNTs/6061Al composite was synthesized by pressure infiltration method. The preforms used contain SiCw with diameter of 0.1-1 μm and MWCNTs with diameter of 0.06-0.1 μm. The volume ratio of SiCw and MWCNTs is 1:1 and overall volume fraction is 20%. During pressure infiltration, the preform and mold were preheated to 550 ^{o}C and kept at this temperature for 30 min. Then 6061Al melt with a temperature of 850 ^{o}C was poured into the preform mold and low pressure applied immediately to drive the melting aluminum alloy infiltrating into the hybrid preform. After infiltration, the applied pressure was raised to ~150 MPa and maintained at this pressure until the temperature of the mod is below 400 ^{o}C. The as-cast composite ingot was hot-extruded at 450 ^{o}C with an extrusion ratio of 16:1.

The as-cast and hot-extruded SiCw+MWCNTs/6061Al composites were heat treated at various temperatures to induce interfacial reactions between MWCNTs and aluminum. The differential scanning calorimetry (DSC) tests were carried out in a Netzsch STA-449C thermal analyzer, with heating rates of 5, 10, 20, 50 ^{o}C/min between 25-800 ^{o}C. The sample mass for DSC measurement is ~22 mg. A Philips X'Pert XRD with Cu Kα irradiation was used to analyze the interfacial reaction product after heat-treatment. The fracture surface of the composites was observed in a S-4700 field emission scanning electron microscope (SEM).

3 Results and discussion

3.1 Reaction kinetics between MWCNTs and aluminum

It is well known that carbon nanotubes can react with aluminum according to[18, 19]:

$$C+Al=Al_4C_3 \quad (1)$$

Here we investigated the reaction dynamic between MWCNTs and aluminum by heating the as-cast SiCw+MWCNTs/6061Al composite at different rates of 5, 10, 20 and 40 ^{o}C/min, as shown in Figure 1. For comparison aim, 6061Al and SiCw/6061Al composite was tested at a heating rate of 20^{o}C/min as well. It can be seen that 6061Al alloy and composites show an endothermic peak at ~650 ^{o}C corresponding to the melting of aluminum. The SiCw+MWCNTs/6061Al composite samples show an exothermic peak following the aluminum melting peak. The exothermic peak temperatures are 660.82, 671.82, 689.55 and 723.24 ^{o}C at 5, 10, 20 and 40 ^{o}C/min, respectively. This is in sharp contrast with 6061Al or SiCw/6061Al composite samples, which show no exothermic peaks in the DSC plots. Furthermore no reaction between SiCw and aluminum occurs can be detected below 800 ^{o}C. This implied that the exothermic peaks in SiCw+MWCNTs/6061Al composite samples were attributed to the reaction between carbon nanotubes and aluminum.

Figure 1 shows that the reaction between CNTs and Al happens immediately after aluminum alloy melts. This reaction activation energy can be obtained by Kissinger equation:

$$\frac{d(\ln\frac{T_p^2}{\beta})}{d(\frac{1}{T_p})}=\frac{E}{R} \quad (2)$$

where T_p is the exothermic peak temperature, β is the heating rate, E is activation energy and R is the atmosphere constant.

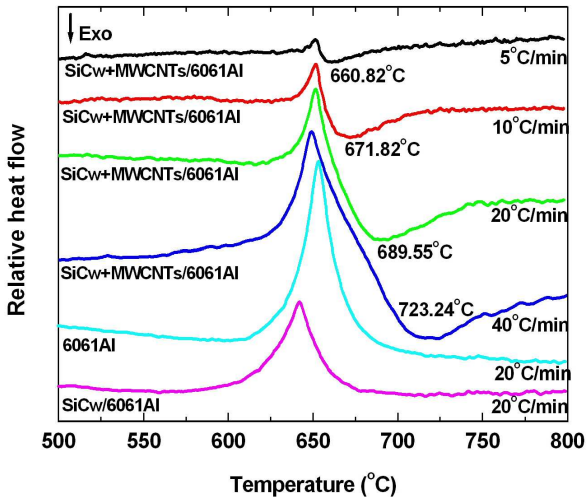

Figure 1. DSC curves of the 6061Al alloy, SiCw/6061Al and SiCw+MWCNTs/6061Al composites

$\ln(T_p^2/\beta)$ *versus* $1/T_p$ was plotted in Figure 2, and an reaction activation energy of 231.56 kJ/mol between CNTs and 6061Al can be obtained. This activation energy is higher than that between MWCNTs and 2024Al (194 kJ/mol)[18]. The reason for the higher activation energy between MWCNTs and 6061Al is thought to be due to higher melting point of 6061Al alloy and lower content of active element in 6061Al. This higher activation energy implies that reaction between MWCNTs and 6061Al is more difficult than that between MWCNTs and 2024Al.

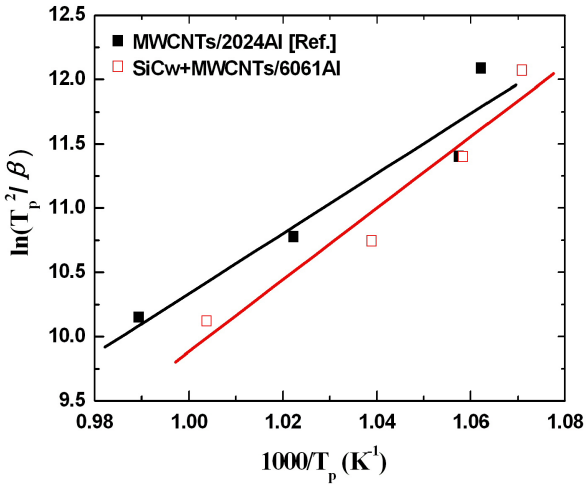

Figure 2. Plot of (Tp^2/ β) versus 1/Tp for the exothermic peaks in SiCw+CNTs/6061Al composites

3.2 Interfacial reaction products between CNTs and Al

The reaction product between CNTs and Al may be Al_2C[20] and Al_4C_3[17-19, 21]. The reason for the formation of these different kind products is still not clear. Here the reaction product of Al_4C_3 was identified, as shown in Figure 3. It can be seen that the as-cast composite contains two peaks (centered at 25.83° and 26.36°) corresponding to CNTs and graphite, respectively.

After the composite was kept at 520 °C for 5 h, the graphite peaks disappeared, while the CNTs peak remains. This implied that graphite is more prone to reaction than CNTs. After the composites were heat-treated at 640 °C for 1 h or 700 °C for 0.2 h, the CNTs peak disappeared as well and Al_4C_3 phase appeared. The Al_4C_3 peak after 700 °C 0.2 h treatment is stronger than 640 °C 1 h treatment.

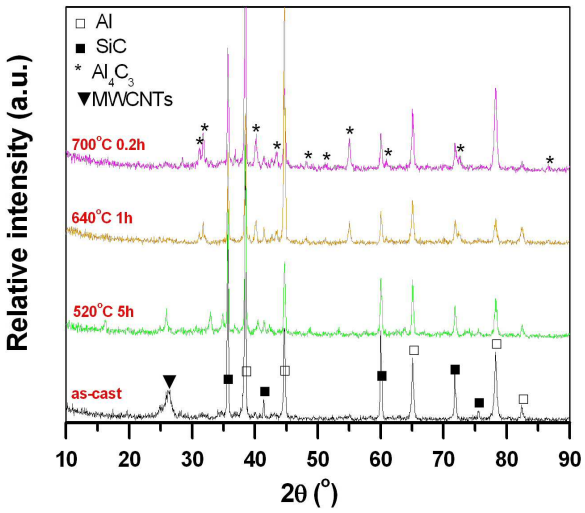

Figure 3. XRD spectrums of SiCw+CNTs/6061Al composites with various heat treatment conditions

Figure 3 showed that CNTs-Al reaction occurred above the solidus temperature of 6061Al. As the solid-liquid temperature of 6061Al is 580-640 °C. When the composite was treated at temperatures above 580 °C, melting of the matrix alloys happens and reaction between CNTs and Al is rapid (see Figure 1). This rapid reaction brings difficulty in controlling the interfacial reaction between CNTs and Al. In addition, micropores may appear during solidification of Al, and thus the composite strength is reduced. So we investigated the reaction tendency between CNTs and Al, at 580 °C for 0.5, 1, 1.5 and 2.5h, as shown in Figure 4. It can be seen that Al_4C_3 appeared at all time durations. At the same time, CNTs peaks remained after kept at 580 °C for 2.5 h, unlike the complete disappearance of CNTs peaks when kept at 640 or 700 °C (see Figure 3).

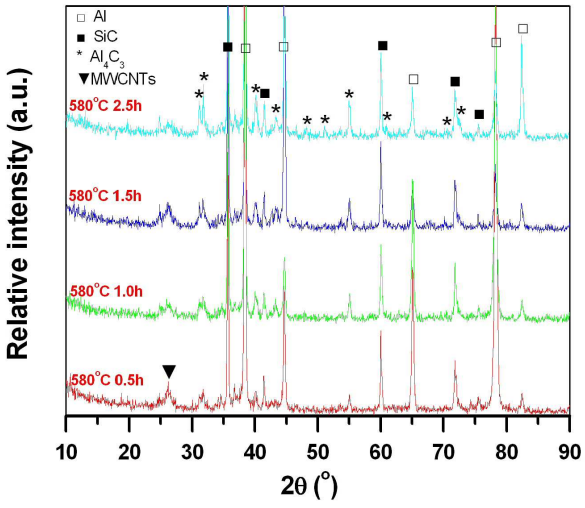

Figure 4. XRD spectrums of SiCw+CNTs/6061Al composites after various durations of heat preservation at 580 °C

3.3 Interfacial bonding between MWCNTs and aluminum

We check the interfacial bonding conditions by observation of the fracture surfaces. Figure 5 shows the fracture surfaces of the as-cast, hot-extruded and 580 ^{o}C 1h treat-treated states. The as-cast composite (Figure 5a, b) exhibited large number of naked SiCw and CNTs on the fracture surfaces. This showed a weak bonding between SiCw/CNTs with Al. After the composite was hot-extruded at 450 ^{o}C at a ratio of 16:1, the fracture surface contains very few SiCw or CNTs agglomerates, as can be seen in Figure 5c, d. Fracture and pull out of SiCw and CNTs can be seen. A lot of CNTs at the edge of dimples can also be observed. This revealed that interfacial bonding between CNTs and Al was improved after hot-extrusion. When this hot-extruded composite was further subjected to a treatment at 580 ^{o}C for 1h, the fracture surface show more signs of CNTs fracture and pull out (see Figure 5e, f).

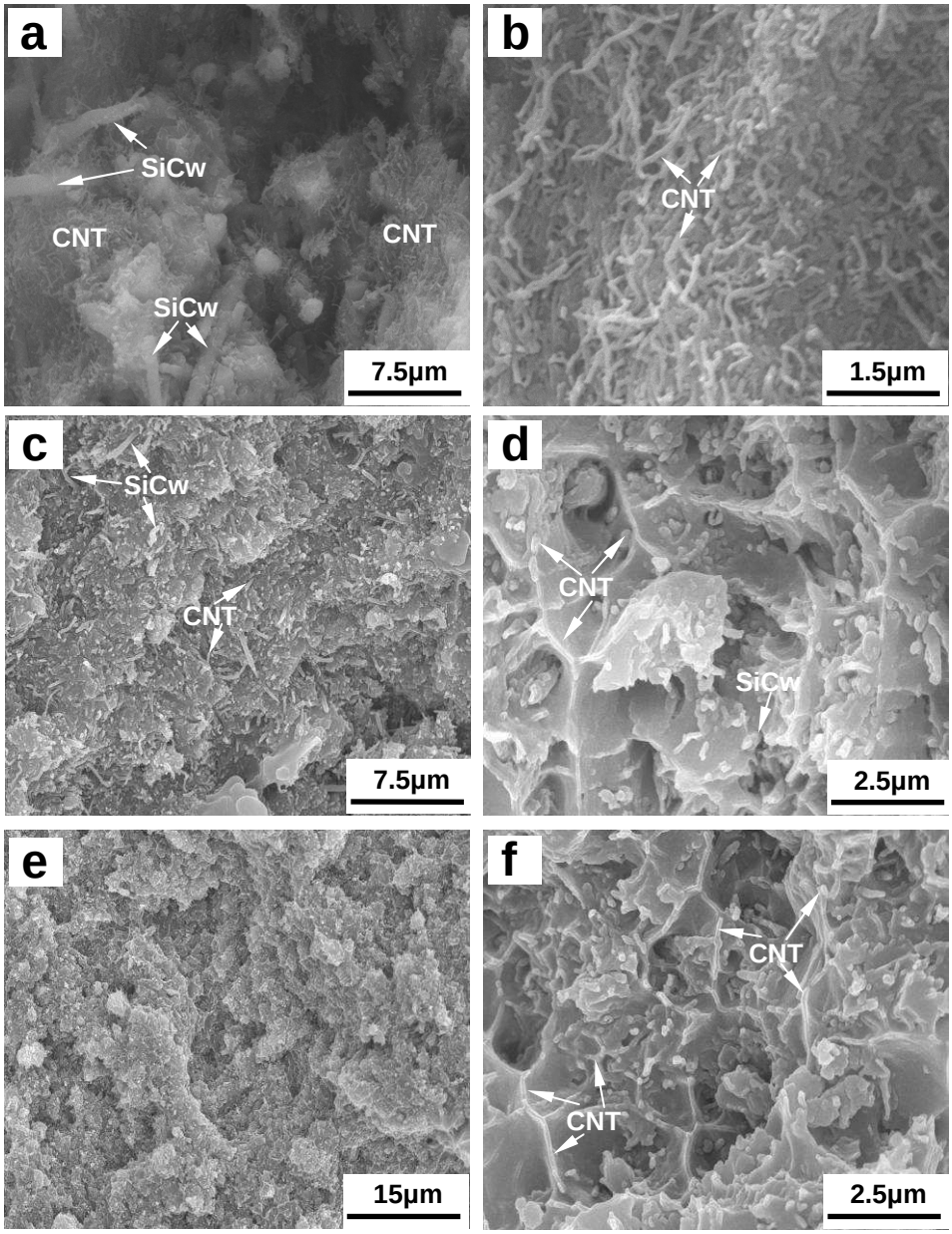

Figure 5. Fracture surface morphologies of SiCw+CNTs/6061Al composites with different conditions of (a,b) as-cast state, (c,d) hot-extrusion state and (e,f) heat-treatment at 580 ^{o}C for 1.0 h after hot-extrusion

Vickers hardness (HV) tests showed that the hardness of the hot-extruded and 580 ^{o}C 1h treated composites were 106.3 and 139.8. This improvement of hardness is attributed to the enhancement of interfacial bonding between CNTs and Al induced by treatment at 580 ^{o}C.

4 Conclusions

SiCw+MWCNTs/6061Al hybrid composites were fabricated by pressure infiltration and CNTs-Al reaction characteristics were investigated. The modification of CNTs-Al interfacial bonding was carried out by hot-extrusion and heat treatment below solidus temperature. The following conclusions can be drawn:

1) The reaction activation energy of CNTs-6061Al is higher than that between CNTs-2024Al.

2) Heat treatment for improving interfacial bonding between CNTs-6061Al at 580 ^{o}C is possible because the reaction control is reliable.

3) Hot-extrusion and heat treatment at 580 ^{o}C for 1h significantly enhance the interfacial bonding strength of CNTs-Al and thus improve the hardness of the composite materials.

Acknowledgements

National Basic Research Program of China (973 Program) (No.2012CB619600) and Aerospace Innovation Science and Technology (No.CASC200906) are greatly acknowledged.

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