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Squeeze infiltration processing of nickel coated carbon fiber reinforced Al-2014 composite

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Abstract Ni-coated fibers are widely used to synthesize carbon fiber reinforces Al based composites. It is observed that during the pressure infiltration process, significant amount of damage takes place in the nickel (Ni) coating due to a difference in the thermal expansion coefficients of fibers and Ni-coating. A modified squeeze infiltration set up is studied in the present work to minimize the damage to the Ni-coating during the infiltration process. This process resulted in significant improvement in retention of the Ni-coating compared to the unmodified process. The solidification pattern in the matrix was established by Energy Dispersive Spectroscopic analysis, which suggests that solidification of primary α-Al started in the interfiber region. The Vickers hardness values for the unreinforced portion of the sample, the matrix regions within the fiber tows and at the fiber matrix interface were found to be 55, 72 and 87, respectively.

Introduction

The squeeze or pressure infiltration is a process by which metal matrix composites (MMCs) can be synthesized starting from a mechanically self-sustaining porous preform of a reinforcing phase, which is infiltrated by a liquid matrix phase [1, 2]. This processing route has enabled close control over chemistry, shape, volume percentage and distribution of the reinforcing phase in the synthesized MMCs and has become one of the principal synthesis methods [3, 4]. The squeeze infiltration process can produce net or near net shape composites. This is advantageous where it is difficult to machine the materials, especially fiber reinforced composites.

Al–C fiber composites are being commercially used in space and electronic industries and are attractive candidates for applications involving high specific strength and modulus and low coefficient of thermal expansion due to the presence of carbon fibers. For the two commercially important MMCs, Al–C and Al–SiC systems, synthesized using the casting route, the reactions between the matrix and the reinforcement taking place are [5]

$$4Al\ (l) + 3C(gr) \rightarrow Al_4C_3 \quad (1)$$

$$4Al\ (l) + 3SiC \rightarrow Al_4C_3 + 3Si \quad (2)$$

The existence of the reaction products such as Al_4C_3 at the interface is a drawback associated with MMCs synthesized via liquid state processing. It has been widely reported that the formation of this brittle compound at the interface has an adverse affect on the mechanical properties of the MMCs [6].

Squeeze Infiltration process involves application of hydrostatic pressure to fabricate components in a short duration of time. This reduces the time for chemical interaction between the matrix and the reinforcement

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and results in much lesser amount of Al_4C_3 at the interface [7]. The negative Gibbs free energy associated with the formation of Al_4C_3, as per Eq. 1, for the generally used processing temperature range (700–800 °C), can be calculated by Eq. 3.

$$\Delta G_{f^\circ}\,[\mathrm{kJ/mol}] = -266520 + 96.2T \quad (3)$$

At 800 °C the Gibbs free energy from Eq. 3 comes out to be –163,297.4 kJ/mol, which is a large negative number. In this study Ni-Coated Carbon fibers are used to reinforce Al-2014 alloy synthesized by squeeze infiltration method. Coating the carbon fibers with appropriate metals can reduce the formation of Al_4C_3 at the interface. Hence, Nickel coated carbon fibers are used in this study. It was observed in previous studies that the coating of carbon fibers is severely damaged during the squeeze infiltration method because high pressure is applied on the melt. A modified squeeze infiltration method is used to minimize the damage to the fiber coating to minimize the melt-fiber contact and obtain high quality composites. The microstructure of the material and hardness are studied to determine the interfacial reactions and interfacial products being formed.

Experimental

Materials

Aluminum alloy Al-2014 (provided by Alcoa) and Ni coated carbon fibers (provided by INCO) were used as the matrix material and the reinforcing fibers, respectively. The composition of the matrix alloy is given in Table 1. Al-2014 alloy has high modulus and tensile strength and has been used as the matrix material in synthesizing MMCs [8, 9].

The Ni-coating was deposited on 8 μm diameter carbon fibers using chemical vapor deposition (CVD) process. The PAN based fibers were pulled through the CVD chamber where Ni was deposited by decomposition of Nickel carbonyl gases in the absence of oxygen. In this process, the Nickel Carbonyls get adsorbed onto the carbon fiber surface and increasing temperature resulted in the release of carbonyl group. The electrical conductivity of the fibers was monitored to control the Ni weight content on the fibers. Some of the physical and mechanical properties of the base carbon fibers are listed in Table 2.

Synthesis method

A modified version of the commercially used squeeze cast method is used to fabricate composite samples, where the ends of carbon fibers extend out on both sides of the mold as shown in Fig. 1. This ensured that the ends of the carbon fibers were cooled due to a lower ambient temperature and heat is taken out of the system at a higher rate keeping the fibers at a lower temperature.

Table 1 Composition of Al-2014 alloy

Alloying element	Wt%
Al	93.5
Cu	3.9–5.0
Fe	< 0.7
Mg	0.2–0.8
Mn	0.4–1.2
Si	0.5–1.2

Table 2 Properties of base carbon fibers

Properties	Value
Tensile strength	3450 MPa
Young's modulus	217 GPa
Density	1.8 g/cm^3
Specific heat	921 J/kg K
Longitudinal thermal conductivity	0.54 W/cm°C
Axial thermal expansion	-0.1×10^{-6}°C

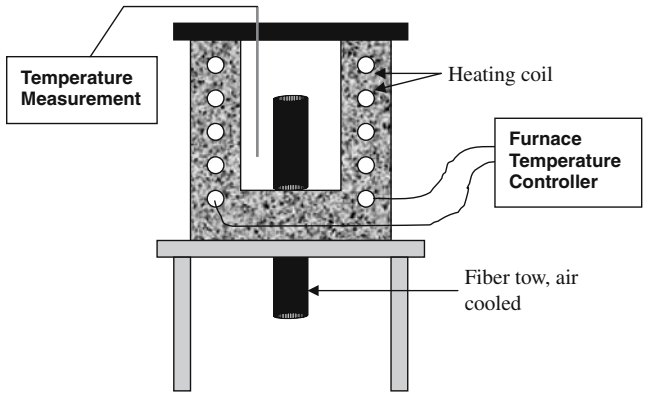

Fig. 1 Experimental setup with Ni-coated carbon fiber as reinforcement. The fiber bundle is extended out of the mold and air cooled during solidification

The process consisted of placing a tow, weighing 8 g and consisting of 420 mm long fibers (serving as a loose perform), in a high strength steel mold. The mold-fiber assembly was preheated in the nitrogen atmosphere to 550 °C to prevent freeze choking during infiltration. Nitrogen atmosphere was used to prevent degradation of the Ni-coating due to oxidation. The matrix alloy was melted in an induction furnace and poured in the mold and pressure was applied on the surface of the melt through a plunger connected to a hydraulic press to facilitate infiltration in the fiber tow. The pressurization cycle resulted in a maximum pressure of about 30 MPa in 30 s. The pressure was maintained for 1 min for complete solidification. The time–pressure profile for the processing is shown in Fig. 2.

The experiments resulted in $(80 \times 20 \times 50)$ mm^3 blocks of squeeze infiltrated Al-2014 selectively reinforced with loose tows of carbon fibers in a region of about 10 mm diameter. Since, loose tows of fibers are used as reinforcement, the fibers were pushed as a result of fluid flow due to the pressurization of the liquid melt during infiltration and solidification resulting in non-uniform distribution of carbon fibers in the matrix alloy. The primary purposes of the present work are to study the effects of the process parameters on the survivability of the Ni-coating on carbon fibers, interfacial reaction and solidification process. Hence, varying fiber distances is desirable so that the concentration of various elements can be measured at different location at varying interfiber locations.

Metallography

The fabricated composite was sectioned for microscopic analysis and hardness measurement. The specimens were mounted with dry phenolic powder in a Buehler compression mounting press. The mounted samples were polished using standard metallographic practice, using SiC grinding paper down to the grit size of 1200. The final polishing was carried out on a thin layer of high concentration of 1 μm size diamond suspension (METLAB) on a lapping film.

The micrographs of the samples were taken with the aid of a Clemex Vision Image Analyzer and a Scanning Electron Microscope (SEM). The elemental concentration was measured by Energy Dispersive Spectroscopy (EDS).

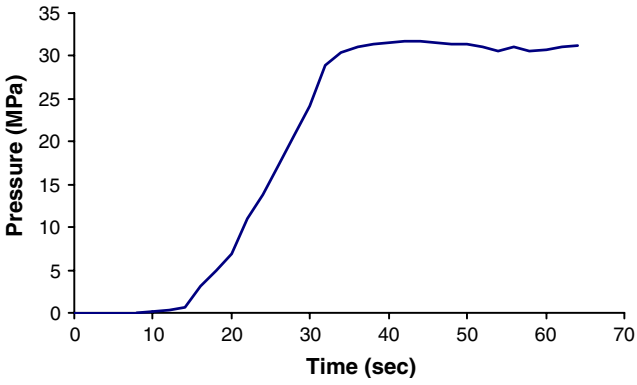

Fig. 2 Recorded pressure–time cycle during squeeze infiltration of Ni-coated carbon fiber with molten Al-2014 alloy

Microsegregation in cast MMCs

Developments of morphology and segregation pattern are interlinked phenomena leading to compositional variation in the microstructure. It has been well documented that an alloy microstructure is characterized by coring [10–12]. In dendritic solidification, the center of the dendrite is the purest metal (i.e., least solute content) because it marks the onset of solidification. The growth of dendrites leads to progressive increase in the solute content of the surrounding liquid. A dendrite is characterized by increasing solute concentration from its core to its periphery.

Scheil presented a relation given as Eq. 3, which describes microsegregation in binary alloys with the assumption that no diffusion in solid and complete mixing in liquid phase is taking place [13]. This equation relates solid-state composition (C_s) with the bulk liquid composition (C_o).

$$C_S = C_O k_e (1 - f_S)^{(k_e - 1)} \tag{4}$$

where k_e and f_s represent equilibrium partition coefficient and fraction of solid, respectively.

Fleming modified the Scheil equation to account for diffusion of solute in the solid phase and for small dendrite arm spacing in the casting [10]. Mathematically, the modified equation is given as

$$C_S = k_e C_O \left\{ 1 - \frac{f_S}{(1 + \alpha k_e)} \right\}^{(k_e - 1)} \tag{5}$$

where the coefficient α is related to the diffusivity and solute concentrations as given in Eq. 6.

$$\alpha = \frac{4 D_S t_f}{d^2} \tag{6}$$

In Eqs. 5 and 6 D_s, t_f and d are diffusivity of solute in the solid phase, total solidification time and dendrite arm spacing, respectively. Equation 7 is another

modification of Scheil's equation, which is proposed by Burton et al. and known as Burton–Prim–Slichter Equation [13, 14].

$$C_s = C_o k_{eff}(1 - k_e)^{\left(k_{eff}^{-1}\right)} \quad (7)$$

where, k_{eff} is the effective partition coefficient, accounting for incomplete mixing in the liquid phase. This equation accounted for incomplete mixing in the liquid phase [13]. Burton–Prim–Slichter equation has defined solute segregation by applying mass balance of solute across a thin strip of thickness, dx, and parallel to the solidification front. These equations will be used in the analysis of the experimental results.

Results and discussion

Microstructural analysis

The cross section of some of the Ni-coated carbon fibers used to fabricate composites is shown in Fig. 3. Discontinuities in the coating can be observed in some of the fibers. These discontinuities may be present due to the gas entrapment in the CVD process leading to improper bonding between the Ni-coating and the fiber. Figure 4 shows a micrograph of squeeze cast composite using the traditional process. Exfoliation and fracture of Ni-coating from some fibers can be observed in this figure. It is visible in Fig. 3 that some fibers have their coating already damaged before the composite fabrication, it is expected that these defects are not only carried over to the composites but also become pronounced due to the applied pressure in the infiltration process. However, the damage seems to be extensive in the squeeze cast composite shown in Fig. 4 and resulted from the processing parameters. A micrograph presented in Fig. 5 shows one fiber with damage to its coating. It has been reported that pressure of the order of 100 MPa can lead to damage in the fiber coating [15]. In the present work the applied pressures was only 30 MPa, suggesting that applied pressure alone was not responsible for exfoliation and fracture of the Ni-coating. There are several possible reasons that can contribute to damaging the Ni-coating and are discussed below.

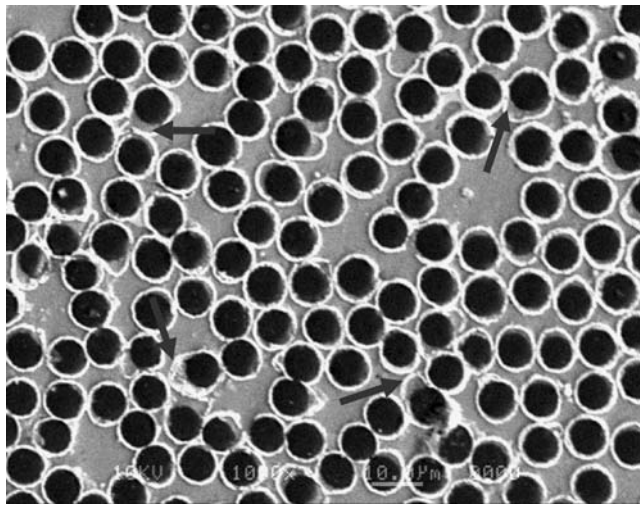

Fig. 4 A micrograph showing the retention of Ni-coating in squeeze infiltrated Ni-coated carbon fiber-2014 composite

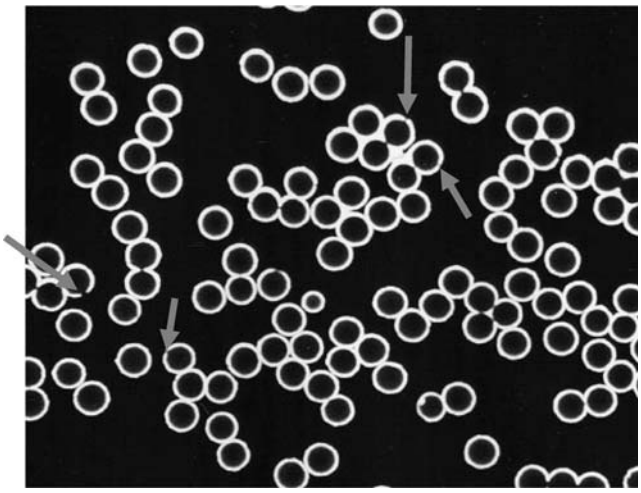

Fig. 3 SEM micrograph of Ni-coated carbon fibers showing discontinuity, marked by arrows, in the Ni-coating at a few locations

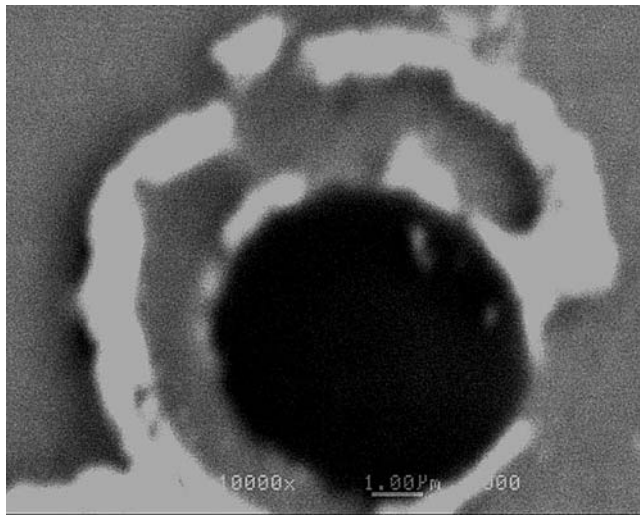

Fig. 5 High magnification SEM micrograph of squeeze cast sample showing the exfoliation and fracture of Ni-coating from the carbon fiber

Thermal stresses are generated at the fiber-coating interface due to the difference in the linear coefficient of thermal expansion (CTE) for Ni ($\alpha_{Ni} = 13.3 \times 10^{-6}°C^{-1}$) and carbon ($\alpha_C = -0.1 \times 10^{-6}°C^{-1}$). The expansion of Ni-coating will be 0.1 mm/cm and carbon fibers will contract by 7.75×10^{-4} mm/cm at the process temperature of 800 °C. The substantial difference between the expansions of the coating and the fiber generates thermal stresses at the Ni–C interface. Additional thermal stresses are generated due to thermal shock because of a temperature difference of 200 °C between the mold and the fibers. The stresses generated in the interface can be significant and with the combined effect of temperature effects and applied pressure, can lead to exfoliation or fracture in coatings.

Pre-existing discontinuities in the Ni-coating of fibers also affect the exfoliation. It is also known that CVD processing can result in air entrapment between the nickel coating and the carbon fiber surface. Upon heating the entrapped gas expands and could have caused exfoliation of the Ni-coating from the carbon fiber surface. The melt may enter the preexisting discontinuities under the applied pressure and can lead to exfoliation and fracture. This would be true because of the good wetting between the Nickel coating and the molten aluminum.

In an attempt to minimize the damage to the Ni-coating the synthesis process was modified and the carbon fibers were cooled at the ends to dissipate the heat and increase the cooling rate. Higher processing temperature leads to increased difference in thermal contraction of carbon fibers and expansion of Ni-coating. If the heat was dissipated through the fibers the difference in change in fiber and coating lengths would decrease and may result in lesser damage to the coating during the melt infiltration process.

The distribution of carbon fibers in a typical sample produced in this study using the modified squeeze infiltration process is shown in a micrograph in Fig. 6. Significant improvement is observed in retaining the Ni-coating on the carbon fibers due to the process modification. Retention of coating due to the heat dissipation through fibers suggests that the thermal expansion mismatch between fibers and coating and entrapped gas expansion are the possible parameters causing the coating damage in the unmodified process. The applied infiltration pressure does not have a detrimental effect on this composite. Due to the movement of loose fibers in the process of infiltration some matrix rich regions can be seen in Fig. 6. The fabricated sample exhibited a fiber volume fraction of about 48% in the reinforced region, measured using the image analysis.

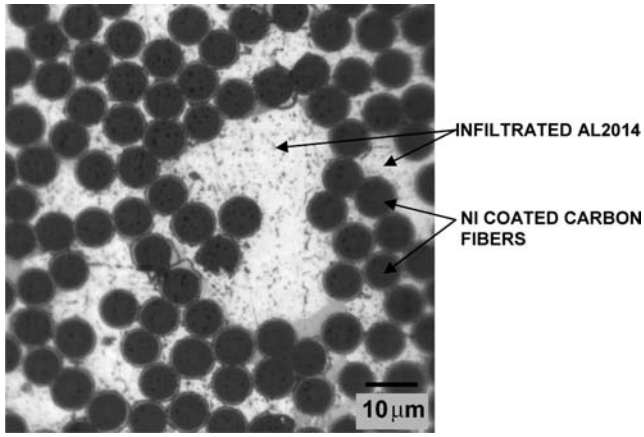

Fig. 6 Micrograph of an infiltrated sample showing complete infiltration of the fiber preform

Elemental analysis

Elemental analysis for Al, Ni and Cu for different interfiber spacing within the composite section was performed using EDS. The measured elemental counts are presented in Table 3. It is observed that Al concentration increased and Cu and Ni concentrations decreased with increase in the distance from the fiber surface. A sharp drop in copper concentration is observed in the matrix from the fiber surface to the center of the interfiber region (Fig. 7). This observation is in agreement with the published literature from the authors' and other researchers' groups [16, 17], where it is stated that in similar composites the primary

Table 3 Elemental count at different distances from the fibers surfaces

No	Interfiber spacing (μm)	Distance from fiber surface (μm)	Elemental count (%)		
			Al	Cu	Ni
1	3.1	0.5	47.3	2.8	49.9
		1.5	75.7	2.4	21.8
2	5.0	0.3	85.4	1.8	12.2
		2.5	98.5	0.6	0.8
3	13.1	0.5	76.2	1.2	22.6
		4.8	97.8	0.9	1.2
		6.5	98.2	0.9	1.0
4	14.1	0.8	71.4	1.8	28.8
		3.5	98.4	0.8	1.1
		7.0	98.7	0.6	0.7
5	18.8	0.8	80.5	1.1	18.4
		2.5	98.2	0.6	1.2
		4.5	98.9	0.5	0.6
		9.0	99.1	0.3	0.6
6	40	0.8	64.6	1.4	34.0
		6.0	97	0.6	2.5
		12.0	98.9	0.6	0.5
		20.0	99.1	0.5	0.4

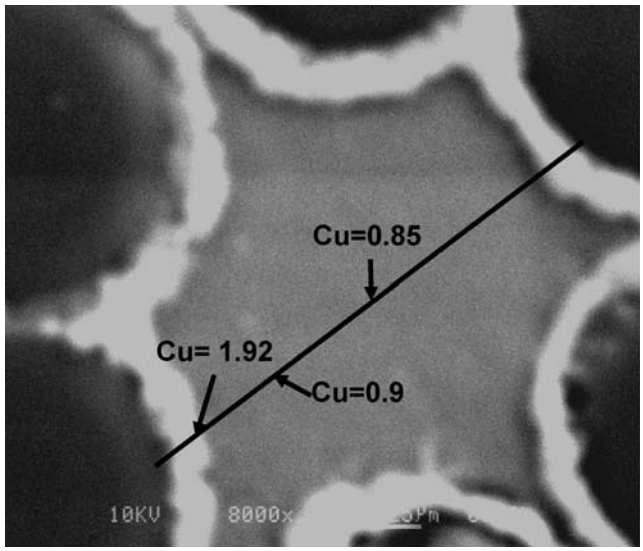

Fig. 7 SEM micrograph of a squeeze cast sample. The Cu count (%) is shown at 3 different locations in the micrograph for an interfiber spacing of 13.1 μm

α-Al tends to start growing between fibers and the last freezing solid with higher solute concentration is deposited close to the fibers. Cooling of fiber ends is carried out at room temperature; hence, this observation reveals that the cooling rates are not high enough to cause solidification to start at the fiber surface. At higher cooling rates the solidification may start at the fiber surface. In the Al–Cu system the eutectic mainly consists of $AlCu_2$. Similar EDS results have been obtained irrespective of the fiber volume fraction in the region of the composite examined. This analysis technique suggests that despite the cooling of fiber tow ends by extending them outside the mold into air, the primary phase does not appear to grow from the surface of the fiber into the interfiber region. If this were the case the highest copper content would have been observed in the center of the interfiber region. The copper count for an interfiber spacing of 18.8 μm was converted to weight percent using the software with the EDS setup. The variation of the solute content was compared to the values predicted using the Schiel equation and the Fleming equation.

Figure 8 illustrates the comparison between the calculated and the predicted values of copper content as a function of the distance from the fiber surface. The mismatch between the predicted values from various models and between the predicted and experimental values is more pronounced closer to the fiber surface than away from it. Table 3 shows that the Ni counts decrease by over 95% from the fiber surface to the matrix. This significant drop in Ni content suggests that only marginal dissolution of Ni takes place during

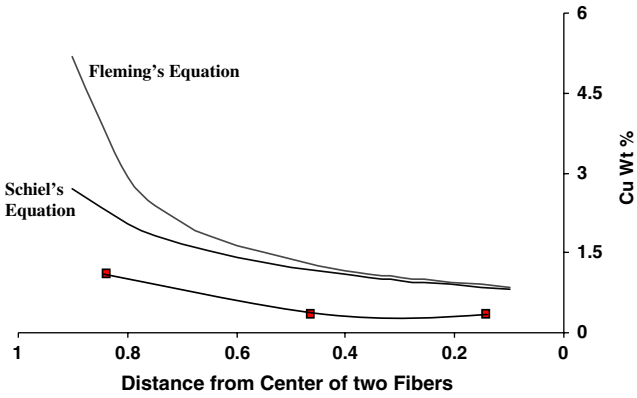

Fig. 8 Comparison of copper content measured using EDS with predictions from Scheil and Fleming equations. The interfiber spacing is 18.8 μm

synthesis. It is known that Ni reacts with Al melt to form Al_3Ni, which may precipitate either at the Al–C interface or in the matrix material [18, 19]. Since, Ni-coating does not dissolve completely in the melt in the present work and the melt does not come in direct contact with the fiber, the Al_3Ni phase would precipitate in the matrix alloy. Squeeze infiltration is a short duration process, limiting the time of interaction between the melt and the fiber coating. The drop in Ni count follows a power function $y = x^{(-0.5)}$ with respect to distance from the fiber surface. The retention of much of the Ni-coating on carbon fibers is important since it maintains the Ni–C interface and creates a Ni–Al interface instead of an Al–C interface, which causes formation of deleterious Al_4C_3 compound.

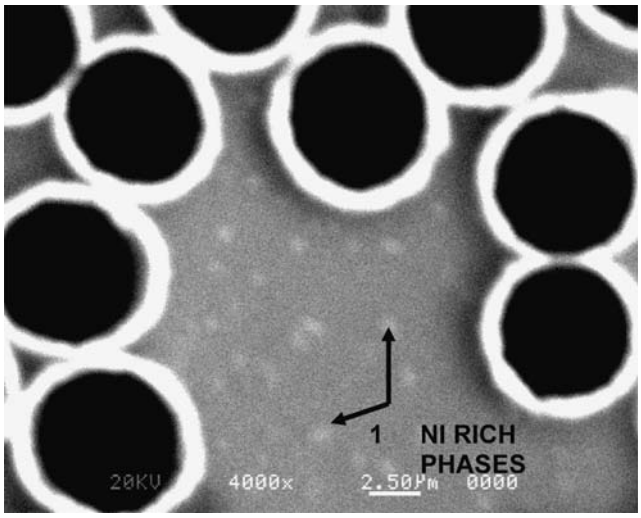

Fig. 9 SEM micrograph of squeeze cast sample highlights nickel rich phases

SEM micrograph presented in Fig. 9 shows the presence of white spots within the matrix region. An EDS scan of these spots (Fig. 10) shows a higher count of Ni in comparison to other areas in the matrix (Fig. 11), which primarily show presence of Al. Two factors contribute to the formation of these Ni-based compounds away from the fiber surface. The first factor is that during processing, there is contact between the solid Ni-coating and the molten Al. Since this process involves a short time cycle, only some of the Ni from the coating is dissolved in the melt. Some of this dissolved Ni then gets transported away from the fiber surface because of diffusion and convection caused by significant fluid flow within the molten metal resulting from application of high pressure. During solidification, various nickel aluminides can precipitate out from the melt and can therefore be located at regions away from the fiber as has been observed. The second possibility is that there is a Ni concentration gradient in the matrix as the distance from the fiber surface increases. This would result in diffusion of Ni into the molten matrix and upon solidification precipitate out as Ni rich compounds at various locations away from the Ni-coating.

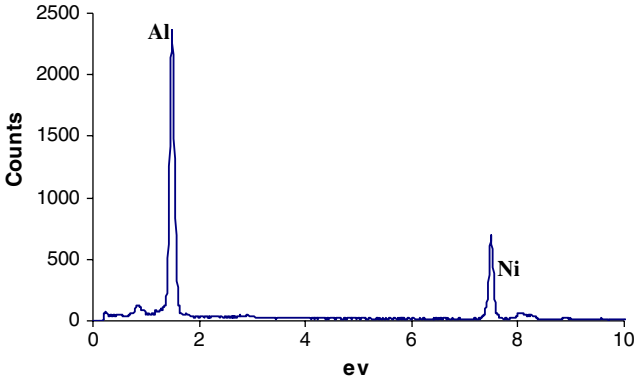

Fig. 10 EDS spectrum of the white spot in the matrix showing the presence of Al and Ni, thereby indicating the presence of Ni-based compounds

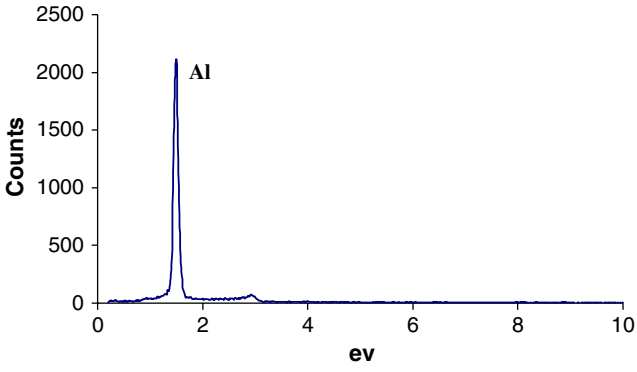

Fig. 11 EDS spectrum of the matrix in the reinforced section of the squeeze infiltrated sample showing the presence of Aluminum only

Hardness tests

The Vickers microhardness values for samples processed using the modified squeeze infiltration process are listed in Table 4. These values are average values of at least 5 readings. The results obtained show that the presence of the reinforcing phase increases the hardness of the matrix alloy. One reason for this could be the higher dislocation density in the composite section of the sample in comparison to the unreinforced alloy, due to the differences in the coefficient of the thermal expansion between Al-2014 ($\alpha = 22.9 \times 10^{-6}{}^{\circ}C^{-1}$) and the nickel coated ($\alpha_{Ni} = 13.3 \times 10^{-6}{}^{\circ}C^{-1}$) carbon fibers ($\alpha_C = -1.0 \times 10^{-6}{}^{\circ}C^{-1}$). This also explains the higher hardness value at the fiber matrix interface. It was found that primary α-Al precipitates in the interfiber region and the concentration of Ni and Cu increases near the fiber interface. Hence, presence of higher solute concentration cause the hardness to be higher near the fibers compared to the center between two fibers where α-Al exists.

Conclusions

The traditional squeeze infiltration process results in damage to the Ni-coating on the reinforcing carbon fibers during the MMC synthesis. The modified squeeze casting process adopted in this paper resulted in retention of much of original Ni-coating on carbon fibers. The retention of Ni-coating prevented contact between carbon fiber and matrix. The Al–C interfacial contact is undesirable due to the formation of Al_4C_3.

EDS analysis of the matrix solidification in the interfiber region between the fibers showed a decrease in both nickel and copper counts as the distance from the fiber surface increased. Vickers microhardness values of the squeeze-infiltrated sample indicated that the presence of the reinforcing phase made the alloy harder. The average hardness values of the unreinforced

Table 4 Vickers microhardness values for sample processed using the modified squeeze infiltration process

Sample type	H_v (Average)
Matrix alloy	55
Interfiber region	72
Fiber-matrix interface	87

portion of the sample, the matrix regions within the fiber tows and at the fiber matrix interface were found to be 55, 72 and 87, respectively.

Acknowledgments The authors would like to express gratitude to the NSF for funding this research under grant NSF CTS970045N, CMS9821057 and CTS000003N.

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