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Compocasting of A356-CNT composite

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Abstract: A356 aluminum alloys reinforced with carbon nano-tubes (CNTs) were produced by stir casting and compocasting routes and their microstructural characteristics and hardness were examined. In order to alleviate the problems associated with poor wettability, agglomeration and gravity segregation of CNTs in the melt, CNTs were introduced into the melts by injection of CNT deposited aluminum particles instead of raw CNTs. Aluminum particles with mean diameters of less than 100 µm were first deposited by CNTs using Ni-P electroless plating technique and then injected into the melt agitated by a mechanical stirrer. The slurry was subsequently cast at temperatures corresponding to full liquid as well as 0.15 and 0.30 solid fractions. The results show that addition of CNTs to A356 matrix can significantly refine both full liquid and semi-solid cast microstructures. Hardness of the samples is also significantly increased by addition of CNTs and A356-CNT composite cast at 0.3 solid fraction produces the highest hardness. **Key words:** A356-CNT composite; carbon nano-tube (CNT); compocasting; electroless plating; microstructure; hardness

1 Introduction

Metal matrix composites (MMCs) are an important group of structural materials used in automotive, defense and aerospace applications because of their low density, high specific strength and modulus, excellent wear resistance, higher service temperature and in general better physical and mechanical properties compared with the corresponding monolithic materials[1]. Among a variety of MMCs produced in last few decades, aluminum matrix composites reinforced with various particles have attracted many researchers.

In recent years, nano-sized particles have also drawn much interest as reinforcements in MMCs because of their superior properties compared with those of micro-sized particles[2-4]. Since the discovery of carbon nano-tubes (CNTs) and their novel properties by IIJIMA[5], many potential applications have been proposed and investigated for CNTs[6]. The high strength, elastic modulus, flexibility and unique conductivity of CNTs[7] along with many other fascinating properties have led to their use in a variety of nano-composite materials. Although various investigations on fabrication of Al-CNT nano-composite have been reported in recent years, so far most of the CNT reinforced composites have been produced by solid state processes[4, 8–11] which are not apt for production of large and complicated components. Although liquid state processes such as vortex method and squeeze casting[12–13] provide greater freedom in component design and manufacturing, very large specific surface area and high interfacial energy of CNTs result in their agglomeration and poor distribution in the melt. Therefore, special techniques are required for addition of CNTs to the melt.

Compocasting is a liquid state process in which the reinforcement particles are added to a solidifying melt while being vigorously agitated. It has been shown that the primary solid particles already formed in the semi-solid slurry can mechanically entrap the reinforcing particles, prevent their gravity segregation and reduce their agglomeration[14–16]. These will result in better distribution of the reinforcement particles. The lower porosity observed in the castings has been attributed to the better wettability between the matrix and the reinforcement particles as well as the lower volume shrinkage of the matrix alloy.

In this work, a special method for addition of CNTs to semi-solid metal slurries is introduced which would result in less agglomeration and better distribution of CNTs in the matrix. Also, the preliminary results on

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production of A356-CNT composites along with their microstructure and hardness evaluations are presented.

2 Experimental

A356-CNT composites were produced by a special compocasting method using A356 aluminum alloy as the matrix and multi-walled carbon nano-tubes (MWCNTs) as the reinforcement. MWCNTs with 95% purity and outer diameters in the range of 10–30 nm were acquired from Research Institute of Petroleum Industry (RIPI) in Tehran, Iran. A scanning electron microscopy (SEM) image of the as-received MWCNTs is shown in Fig.1.



Fig.1 SEM micrograph of as-received MWCNTs

Fig.2 schematically shows the experimental set-up used in production of the composites. It consisted of an alumina crucible placed in a muffle furnace, a coated injection tube for introduction of the reinforcement into the melt and a coated steel stirrer. The crucible was equipped with baffles and bottom pouring arrangement. Temperature of the melt was measured using a K-type thermocouple. Argon was used as the carrier gas for injection of the reinforcement into the melt[17].

It has been evidently shown that small size particles have high tendency for agglomeration at various stages during processing[18–19]. This problem is expected to pose a major obstacle for uniform distribution of CNTs in the melt as they have large specific surface area and high interfacial energy. In order to improve the wettability of CNTs with the melt and to reduce their agglomeration and obtain a good distribution of CNTs in the matrix, a special technique was used for addition of CNTs to the melt. In this work, CNTs were injected into



Fig.2 Schematic of experimental set-up used

the melt in the form of CNT deposited aluminum particles instead of raw CNT powder. The aim was to deposit dispersed CNTs on the surface of aluminum particles which were then injected and melted and gradually released the CNTs in the molten matrix alloy.

This was achieved by deposition of CNTs on aluminum particles of less than 100 µm in diameter using Ni-P electroless plating technique. The process consisted of first purification and pretreatment of CNTs and aluminum particles by degreasing, acid-treatment and ultrasonic cleaning, and then coating of aluminum particles with Ni-P-CNTs. A commercial electroless solution (Slotonip 70 A, Schloetter Company) was used electroless acid plating bath with sodium as hypophosphite as reducing agent and nickel sulphate as nickel source. The aluminum powder to CNT mass ratio of 6:1 was chosen for the electroless plating bath after preliminary tests. Table 1 shows the optimum operating conditions of the electroless plating process and the concentrations of the bath components selected after preliminary tests.

The CNT deposited aluminum particles were injected into the melt at a temperature above its liquidus

Table 1 Concentration of bath components and operating conditions of electroless plating process

Bath composition					Operating parameter			
ho(Nickel)/ (g·L ⁻¹)	ho(CNTs)/ (g·L ⁻¹)	$ ho(\text{Reductor SH})/(\text{g}\cdot\text{L}^{-1})$	φ(Stabilizer Slotonip 76)/ (mL·L ⁻¹)	φ (Addition Slotonip 77)/ (mL·L ⁻¹)	pH value	Bath temperature/°C	Deposition time/min	Stirring speed/(r·min ⁻¹)
6	1.25	40-50	5-8	0.1	5.5	80	60	500

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temperature (700 °C) while being isothermally stirred. 1%Mg (mass fraction) was added to the melt to increase the wettability between the matrix and the reinforcements. After completion of the injection, the slurry was cast into a steel die placed below the furnace, either at 700 °C or after continuously cooling to 610 °C and 601 °C, corresponding to 0.15 and 0.30 solid fractions (according to Scheil equation), respectively. Analogous castings but without reinforcement addition were also produced for comparison. Table 2 shows the experimental conditions used in different experiments.

 Table 2 Experimental conditions used in different experiments

Sample	φ(CNTs)/%	Reinforcement injection temperature/°C	Casting temperature/°C	Stirring speed/ (r·min ⁻¹)
A-0-0	0	700	700	500
A-15-0	0	700	610	500
A-30-0	0	700	601	500
A-0-2	2	700	700	500
A-15-2	2	700	610	500
A-30-2	2	700	601	500

The cast samples were first degreased and their density was measured using the Archimedes principle. Samples were then sectioned and effects of casting temperature and reinforcement addition on their microstructural characteristics and hardness were examined. Microstructural characteristics were studied using an optical microscope (OM) connected to an image analysis system, Philips XL30 scanning electron microscope (SEM) and Philips X'PERT MPD X-ray diffractometer (XRD) using filtered Cu K_a radiation (λ =0.154 2 nm). Microstructural characteristics studied included the CNTs distribution on the coated aluminum particles, the average secondary dendrite arm spacing (SDAS) for the samples cast from full liquid state and the average particle size of $\alpha(Al)$ grains for the samples cast from semi-solid state. SDAS was measured using linear intercept method. Equivalent circle diameter, D_{eq} , of each α (Al) grain was calculated using Eq.(1):

$$D_{\rm eq} = \sqrt{\frac{4A}{\pi}} \tag{1}$$

where A is the cross section area of the grain on the polished surface.

3 Results and discussion

Fig.3 illustrates the SEM images of aluminum particles before and after coating. It is shown that a proper mechanical interaction between aluminum particles and Ni-P-CNT composite coating has been achieved. It is also evident that the coating has increased

the average size of the aluminum particles. Higher magnification image of the area marked by the rectangle in Fig.3(b) is shown in Fig.3(c). Fig.3(c) reveals the characteristic morphology of the Ni-P electroless coating on the aluminum particle and, more importantly, a very uniform distribution of CNTs in the Ni-P-CNT composite coating. Due to gradual co-deposition of Ni-P and CNTs on the aluminum particles, no CNT agglomerates can be observed in the composite coating. It is expected that when such particles are injected into the melt, the high melting point Ni-P coating starts to dissolve in the molten matrix alloy, gradually releasing the CNTs into the melt. The Ni-P coating also formed on the individual CNTs would provide adequate wettability with the molten aluminum and a good bonding with the matrix. The stirring action of the stirrer is expected to uniformly distribute the CNTs in the melt and prevent their gravity segregation.



Fig.3 SEM images of aluminum particles: (a) Before coating; (b) After coating; (c) Higher magnification of area marked by rectangle in (b)

Fig.4 shows the XRD pattern taken from one of A356-CNT composites. Since the CNT content of the composite is only 2% (volume fraction), which is less than the limit of XRD resolution, neither CNT nor Al_4C_3 peaks are observed in the pattern. The major peaks observed are those of aluminum and silicon. Traces of the Spinel (Al-Mg) phase and aluminum oxide (Al_2O_3) phase are also observed in the XRD pattern.

Fig.5 illustrates the OM images of the cast samples. Figs.5(a), 5(c) and 5(e) show the microstructures of monolithic A356 aluminum alloy cast at 0, 15% and 30% solid fractions, respectively. Figs.5(b), 5(d) and 5(f) show the microstructures of A356-CNT composites cast at 0, 15% and 30% solid fractions, respectively. Dendritic microstructures of the samples cast from full liquid state and non-dendritic microstructures of those cast within the semi-solid temperature ranges are clearly visible. Fig.5 also reveals that microstructure of A356 alloy is significantly refined by addition of CNTs. In fact, results of image analysis show that for samples A-0-0 and A-0-2 which have been cast from above the liquidus



Fig.4 XRD pattern of A356-2% CNT composite



Fig.5 Typical micrographs of cast samples: (a) A-0-0; (b) A-0-2; (c) A-15-0; (d) A-15-2; (e) A-30-0; (f) A-30-2

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temperature, the average SDAS has decreased from about 32 μ m to about 13 μ m by addition of CNTs.

Fig.6 illustrates the effects of addition of CNTs on the average equivalent circle diameter (D_{eq}) of α (Al) particles in semi-solid microstructures. As it can be seen from Fig.6, composite samples have smaller α (Al) particles than their corresponding monolithic samples. The difference is more pronounced for sample A-30-2 which was cast at lowest temperature. Different researches have shown that wettability of aluminum melt and carbon or graphite reinforcements increases by application of a nickel coating on the reinforcements[1, 12–13]. It seems that dispersed Ni-P coated CNTs in the melt have been able to act as potent heterogeneous nucleation sites promoting grain refinement.



Fig.6 Average equivalent circle diameter of α (Al) particles of samples cast from semi-solid state

The measured density of the castings is reported in Table 3. It is shown that the densities of the composite samples are lower than those of the monolithic samples. This is mainly due to the presence of low density CNTs in the composite samples. However, it may to some extent be attributed to the possible higher porosity of the composite samples. Moreover, due to less solidification shrinkage and gas absorption, the densities of both semi-solid monolithic and semi-solid composite samples are higher than those of the samples cast from full liquid state.

Fig.7 shows the effect of CNT addition on the hardness of the cast samples. As it can be seen, hardness

Table 3 Measured densities of different samples

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Sample	Density/(g·cm ⁻³)
A-0-0	2.624
A-15-0	2.632
A-30-0	2.638
A-0-2	2.559
A-15-2	2.582
A-30-2	2.580



Fig.7 Brinell hardness of different cast samples

of all samples has significantly increased by addition of CNTs. This can partly be attributed to the decrease in the grain size of the A356 matrix of the composite samples. Furthermore, CNTs, like other reinforcements, strengthen the matrix by creation of a high density dislocations during cooling to room temperature due to the difference of the coefficients of thermal expansion between the CNTs and the matrix. Mismatch strains developed at the interfaces of CNTs and the matrix obstruct the movement of the dislocations, resulting in the improvement of the hardness of the composites.

Fig.7 also shows that hardness of composite samples has been improved by casting from the semi-solid state. This is attributed to higher density and less gas and shrinkage defects formed in the compocast samples, as shown by previous studies[14].

4 Conclusions

1) A356-CNT composites were successfully produced by a special reinforcement addition technique and compocasting route.

 Injection of Ni-P-CNT coated aluminum particles instead of raw CNTs as reinforcement particles seems to alleviate the problems associated with poor wettability, agglomeration and gravity segregation of CNTs in the melt.

 Addition of CNTs to A356 matrix can significantly refine both full liquid and semi-solid cast microstructures.

4) Among the compocast samples, the sample cast at 0.3 solid fraction produces the smallest average α (Al) particle size of about 37 µm.

5) Densities of the composite samples are less than those of the monolithic samples and densities of both monolithic and composite samples increase by casting from semi-solid state.

6) Hardness of the samples is significantly increased

by addition of CNTs and A356-CNT composite cast at 0.3 solid fraction produces the highest hardness.

References

- CHAWLA K K. Composite materials: Science and engineering [M]. 2nd Ed. Springer, 2001.
- [2] HEMANTH J. Development and property evaluation of aluminum alloy reinforced with nano-ZrO₂ metal matrix composites (NMMCs)
 [J]. Materials Science and Engineering A, 2009, 507: 110–113.
- [3] KOLLOA L, LEPAROUXA M, BRADBURYA C R, JAGGI C, MORELLI E C, ARBAIZAR M R. Investigation of planetary milling for nano-silicon carbide reinforced aluminium metal matrix composites [J]. Journal of Alloys and Compounds, 2010, 489: 394–400.
- [4] KWON H, ESTILI M, TAKAGI K, MIYAZAKI T, KAWASAKI A. Combination of hot extrusion and spark plasma sintering for producing carbon nanotube reinforced aluminum matrix composites [J]. Carbon, 2009, 47: 570–577.
- [5] IIJIMA S. Single-shell carbon nanotubes of 1-nm diameter [J]. Nature, 1991, 354: 56–58.
- [6] BAUGHMAN R H, ZAKHIDOV A A, HEER W A. Carbon nanotubes—The route toward applications [J]. Science, 2002, 297: 787–792.
- [7] CHEN W X, TU J P, XUA Z D, CHEN W L, ZHANG X B, CHENG D H. Tribological properties of Ni-P-multi-walled carbon nanotubes electroless composite coating [J]. Materials Letters, 2003, 57: 1256–1260.
- [8] TOKUNAGA T, KANEKO K, HORITA Z. Production of aluminum-matrix carbon nanotube composite using high pressure torsion [J]. Materials Science and Engineering A, 2008, 490: 300–304.
- [9] ESAWI A M K, MORSI K, SAYED A, ABDEL-GAWAD A, BORAH P. Fabrication and properties of dispersed carbon

nanotube-aluminum composites [J]. Materials Science and Engineering A, 2009, 508: 167–173.

- [10] KIMA I Y, LEEA J H, LEEA G S, BAIKA S H, KIMB Y J, LEE Y Z. Friction and wear characteristics of the carbon nanotube-aluminum composites with different manufacturing conditions [J]. Wear, 2009, 267: 593–598.
- [11] MORSI K, ESAWI A M K, LANKA S, SAYED A, TAHER M. Spark plasma extrusion (SPE) of ball-milled aluminum and carbon nanotube reinforced aluminum composite powders [J]. Composites: Part A, 2010, 41: 322–326.
- [12] RAY S. Synthesis of cast metal matrix particulate composites [J]. Journal of Materials Science, 1993, 28: 5397–5413.
- [13] HOKAED I A I, LAVERINYA E J. Particulate reinforced metal matrix composites—A review [J]. Journal of Materials Science, 1991, 26: 1137–1156.
- [14] FLEMINGS M C. Behavior of metal alloys in the semisolid state [J]. Metallurgical Transactions, 1991, 22A: 957–981.
- [15] NAHER S, BRABAZON D, LOONEY L. Development and assessment of a new quick quench stir caster design for the production of metal matrix composites [J]. Journal of Materials Processing Technology, 2004, 166: 430–439.
- [16] FAN Z. Semisolid metal processing [J]. International Materials Review, 2002, 47: 49–85.
- [17] GHAHREMAINIAN M, NIROUMAND B. Compocasting of an Al-Si-SiC_p composite using powder injection method [J]. Solid State Phenomena, 2008, 141/142/143: 175–180.
- [18] ROHATGI P K, SOBCZAK J, ASTHANA R, KIM J K. Inhomogeneities in silicon carbide distribution in stirred liquids-a water model study for synthesis of composites [J]. Materials Science and Engineering A, 1998, 252: 98–108.
- [19] KOBASHI M, CHOH T. The enhancement of wettability of SiC particles in cast aluminum matrix composites [J]. Journal of Materials Processing Technology, 2001, 119: 329–335.

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