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A NOVEL TECHNIQUE FOR CARBON NANOTUBE REINFORCED METAL MATRIX COMPOSITE FABRICATION

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Nanotechnology has become widespread, encompassing a voluminous range of disciplines that are progressively important nowadays. With applications in materials, electronics, biomedicals, chemistry, and other related technology areas, the common factor is that the materials, techniques, devices and systems have at least one or more critical dimensions on the nanometer scale. The best-known nanomaterials, carbon nanotubes (CNTs) are the strongest and stiffest materials discovered in terms of strength and elastic modulus respectively. For that reason, usage of CNTs as reinforcements in composites, defined as common used materials consists of a combination of two or more different constituents with different properties introducing a performance of characteristics greater than the components taken separately without composing an alloy, is vital.

Until today, great deals of polymer matrix composite (PMC) fabrication studies were carried out. However, fewer studies are made in MMC fabrication area because of the difficulties such as wetting problems about CNT reinforced metal matrix composite (MMC) fabrication. Above all, most of the studies were related to powder metallurgy, which requires expensive tooling and much production time. Consequently, there is still an important deficiency in casting of CNT reinforced MMC fabrication.

In this study, a novel method for CNT reinforced MMC fabrication, vacuum assisted infiltration method with CNT preform reinforcement is studied; and fabrication of CNT reinforced aluminum (Al) matrix composites by a casting method is realized successfully. Furthermore, microstructures of these composites are investigated and success of the method reported. As a result, a new and economic fabrication process for solid and light-weighted material is introduced.

Keywords: Carbon nanotubes, Metal matrix composites, Fabrication, Casting, Microstructure.

Introduction

Composite materials are common used materials consist of a combination of two or more different constituenst with different properties introducing a performance of characteristics greater than the componenst taken seperately without composing an alloy. The "matrix" material is the continuous phase that holds the discontinuous phases called "reinforcements" together [1]. The discontinuous phases are usually involved to obtain better properties such as mechanical and electrical properties.

Experimental evidence of the existence of carbon nanotubes came in 1991 by the study of Iijima where MWCNTs were investigated by using a transmission electron microscope [2]. It is easy to imagine a single-wall carbon nanotube (SWCNT)[3]. Ideally, it is enough to consider a perfect graphene sheet rolled into a cylinder (Fig. 1) paying attention that the hexagonal rings put in contact join coherently, then to close the tips by two caps (unclosed nanotubes exists), where each cap is being a hemi-fullerene with the appropriate diameter.

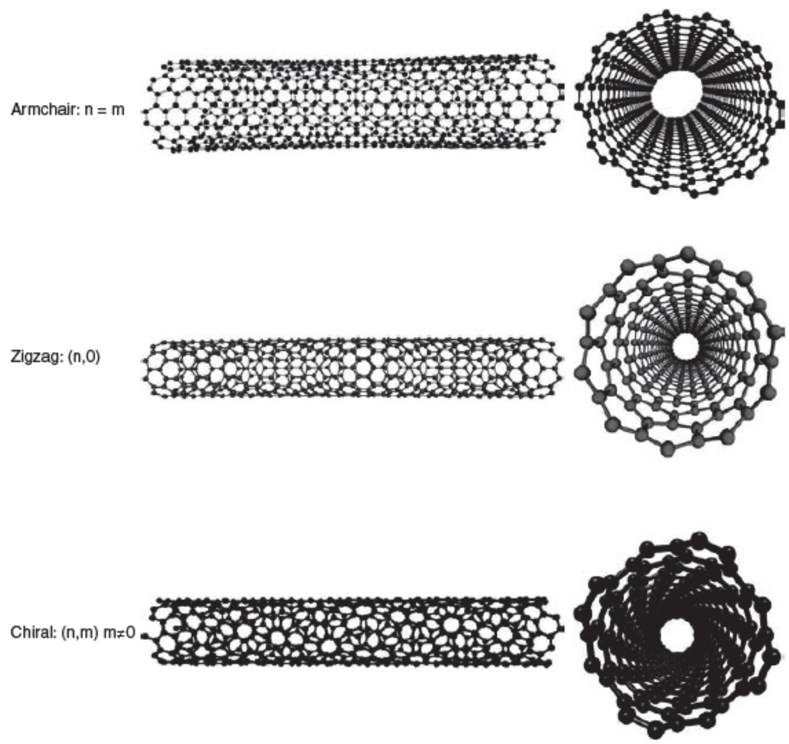

Figure 1. Examples of the three types of SWCNTs identified by the integers.

The strength of the carbon–carbon bond gives rise to the interest in the mechanical properties of carbon nanotubes [4]. Theoretically, CNTs should be stiffer and stronger than any known material. Simulation studies of Yakobson [5] and experiments of Falvo [6] demonstrate a remarkable "bend, don't break" response of individual SWCNT to large transverse deformations [4]. Young's modulus of a cantilevered individual MWCNT was measured from the amplitude of thermally driven vibrations observed in the TEM as 1.0 to 1.8 TPa. Apart from that, TEM-based tensile and bending tests gave more reasonable moduli and strength of MWCNT of 0.8 and 150 GPa, respectively.

MWCNTs and SWCNT bundles may be stiffer in bending compared to tensile strength because in tension, bundles are weaker due to "pull-out" of individual nanotubes. The stress–strain curves suggest that the load is carried primarily by SWCNT on the exterior surface of the tubes, from which breaking strengths from 13 to 52 GPa were revealed in the studies of Yu et. al.[7] On the other hand, the mean value of tensile modulus was 1 TPa, and the result is consistent with near-ideal behavior. With the same method, tensile strength of MWCNTs were measured between 11 and 63 GPa and Young's modulus between 0.27 – 0.95 TPa [8]. On a density-normalized basis the nanotubes look much better for reinforcement; because, the modulus and strength are, 19 and 56 times better than steel, respectively [4]. These specialities make carbon nanotubes the most rigid and strong reinforcement materials.

CNT reinforced polymer and ceramic composite studies are mostly preferred because of feasible manufacturing techniques compared to MMC studies [9**].** CNT reinforced Al studies were started with Kuzumaki et al. [10] by using powder metallurgy techniques. In most of the previous studies, CNTs or CNT containing carbon powders were mixed with Al or Al alloy powders using ball milling and solid state fabrication techniques were used to fabricate composites [11, 12, 13].

Liquid-state techniques are more often preferred because they are cheaper than solid-state techniques, easier to handle than are powders, the composite can be produced in a wide variety of shapes with casting methods. On the contrary, liquid-state techniques frequently suffer from incomplete control of the processing parameters, and undesirable chemical reactions between matrix and reinforcement. In this study, selection of a liquid-state fabrication technique is one of the main reasons because of the importance of economic production necessity.

In this study, a novel method for CNT reinforced MMC fabrication, vacuum assisted infiltration method with CNT preform reinforcement is studied; and fabrication of CNT reinforced Al matrix composites by a casting method is realized successfully. Furthermore, microstructures of these composites are investigated and success of the method reported. As a result, a new and economic fabrication process for solid and light-weighted material is introduced.

Theoretical Background

Liquid-state processing techniques are still being investigated and developed to combine the matrix and reinforcement together in desirable conditions. Four major categories are known: (1) Infiltration, (2) Dispersion, (3) Spraying, and (4) In-Situ Fabrication. Although these four categories can be used in composite materials, infiltration methods are the most appropriate technique to produce CNT reinforced Al matrix composites; because it provides opportunity to use porous reinforcement constituents such as CNT preforms.

Preform

In MMC material production, the infiltration of a porous preform, which is prepared mostly by using ceramic reinforcement components in the form of short fibers and/or particles, are carried out with molten light metal alloy like Al alloy represents one of the most tevarding techniques with regard to the range of the accessible properties of the composite material [14].

The preform manufacturing process has steps to carry out. Begining with the delivery of the reinforcing material, cleaning and dispersing of these reinforcing fibers or particles are done if needed. Next, these components are mixed with pore forming agent and binder. Later, shaping of the mixture is done in a mold and preform is left for drying. After dehydration, dry preform is cured in furnace to evaporate the pore forming agent and obtain final strength of the preform.

Infiltration Process

Infiltration process involves infiltrating a molten metal that flows interstices into a porous body to fill the pores and produce composite material. Metal infiltration method has been used since

1980s to strengthen porous metal parts; but in our case of using ceramic or carbon reinforcements, there is a wetting problem appears between ceramic/carbon reinforcement and liquid metal. Therefore, an external force can be applied to overcome the capillary and fluid-drag forces.

There are several types of infiltration that we may select the most appropriate one according to the application needs. In the use of cermets as reinforcements such as titanium-carbides of for metal-metal infiltration or some of the ceramic reinforcements in specific environments like infiltrating ceramic preforms by Al-Mg alloys between 750°C and 1050°C in nitrogen-rich atmosphere, it is possible to apply infiltration without external force. For some matrix-reinforcement systems, to overcome the poor wetting, applying vacuum around the reinforcement provides a pressure difference and drives metal flow inside the preform. This process mostly used in infiltration of Al or Mg into Al_2O_3 or SiC preforms. Another strategy to overcome poor wetting is to apply pressure on the matrix phase to fill the preform better with increased processing speed, refined matrix microstructure. This type of infiltration is mostly used in commercial applications and pore-free products can be manufactured. However, the high pressure range requires solid molds and a high-pressure source which means manufacturer needs extra systems that reveal uneconomical conditions. Vacuum-infiltration method usage is the best way known to reduce expenses in liquid-state composite material processing. Furthermore, there are other forces like vibrations, centrifugal forces, and electromagnetic body forces. Those forces depend on the matrix material structure or the geometry of the workpiece. In conclusion, vacuum assisted infiltration is convenient and the most economic method to fabricate CNT reinforced Al matrix composite materials. Tooling is going to be cost-effective and no extra pressure system or expensive molds would be required.

Experimental

In this study, vacuum assisted infiltration method with CNT preform reinforcement is studied; and fabrication of CNT reinforced aluminum (Al) matrix composites by a casting method is realized successfully. First preforms are produced. Next, one of the most used metal matrix materials; 6063 aluminum alloy is infiltrated into these preforms by using vacuum assisted casting machine.

Preform Production

Industrial type MWCNTs (10-30 nm diameter; ~2.1 g/cm^3 true density) with a purity rate of over 85% are provided from Chengdu Organic Chemicals Co. Ltd., SEM and TEM images of as-received CNTs are shown in Fig. 2. Furthermore, XRD, TGA and Raman Spectrum investigations were obtained to ensure the properties such as purity and chemical composition of CNTs are appropriate with our demand.

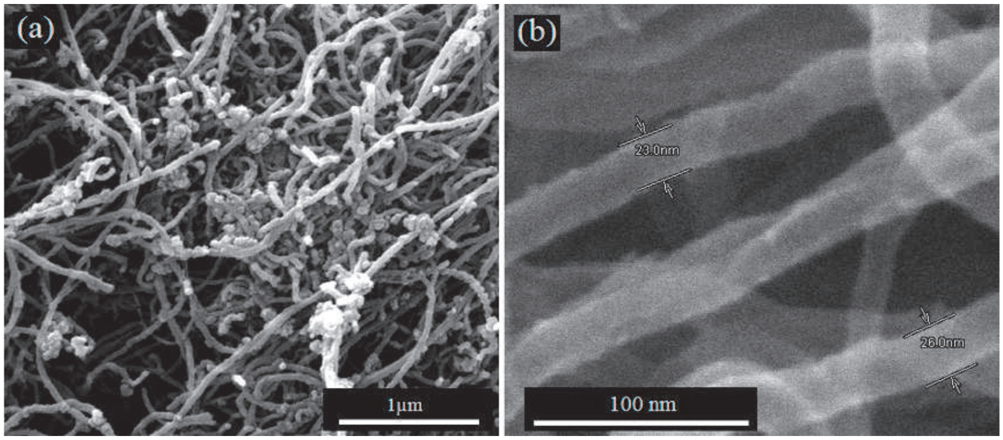

Figure 2. Electron microscope images of CNTs: (a) Secondary electron SEM micrograph of industrial type MWCNT's and (b) TEM micrograph showing the average diameter of MWCNTs is between 10-30 nm.

CNTs as-received, Poly Vinyl Alcohol (PVA) as a pore forming agent and colloidal silica (10 - 20 nm grain size; ~1.20 g/cm3 density) as binding agent are chosen as preform production materials. 6g CNT and 2ml colloidal silica are mixed mechanically with 10ml of 20% wt. PVA solution. This mixture is poured into a flexible mold shown in Fig. 3. to fabricate preforms (Fig. 4.). Next, these preforms are dried at room temperature for 48 hours. Finally, dried preforms are cured at 600°C to evaporate PVA and sintered at 1000 °C for 3 hours with a heating/cooling rate of 10 °C/min under vacuum environment.

Figure 3. Flexible preform mold.

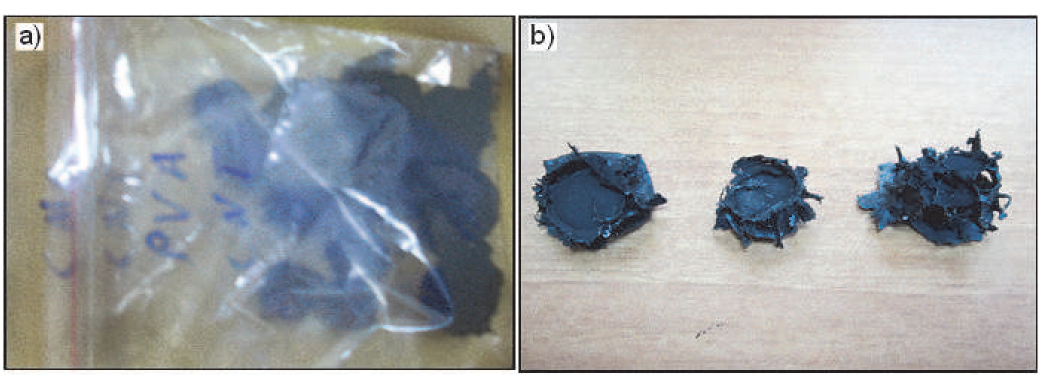

Figure 4. Preform samples (a) packed for usage after curing and (b) before curing.

Preperation of Mold

For vacuum assisted infiltration, wax pattern (20.1 mm in diameter, 40.2 mm in length without runner head) is prepared and mounted to the runner head as shown in Fig. 5 (a) and finally assembled to the flask. After preparation of flask, gypsum-bonded casting investment is prepared by mechanical mixation shown in Fig. 5 (c) and poured into the flask gently. During and after the pouring of gypsum slurry, flask is vibrated by a vibrator mechanism shown in Fig. 5 (b). Then, flask is dried at room temperature for 30 mins for solidification. After solidification, wax is removed and finally mold is cured with a heating step rising from room temperature to 780 °C before casting process.

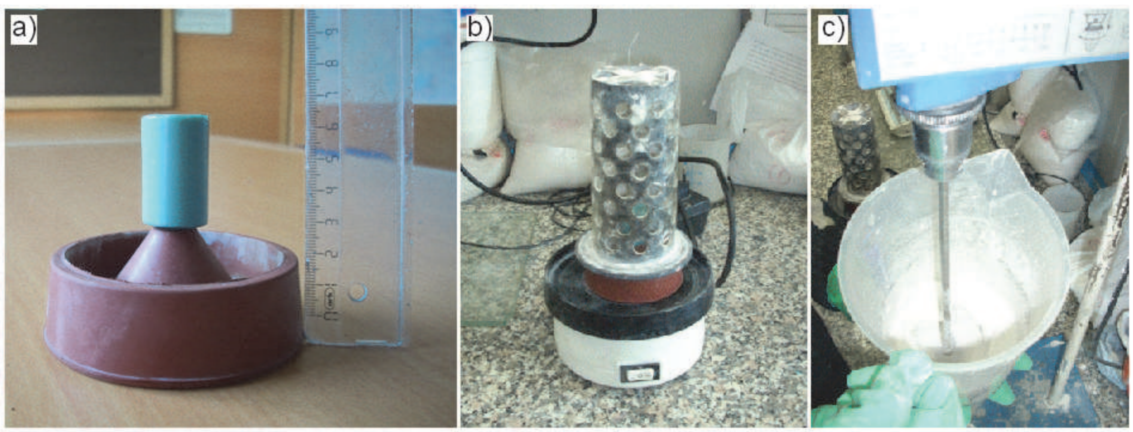

Figure 5. Materials and devices used for mold preparation:(a) wax pattern mounted to the runner head, (b) flask on the vibration machine and (c) preparation of gypsum slurry with mechanical mixer.

Vacuum Assisted Infiltration

Following the preparation of preforms and mold, molten 6063 Al alloy is prepared by melting 6063 Al bars in melting pot by using electric furnace in 800°C. Subsequent to reaching 800°C, flask cured to 780°C is mounted to the vacuum assisted casting machine, vacuum motor is operated and just before the casting process, preform is placed close-fit into the mold by using a lancet. Next, molten 6063 Al alloy is gently poured into the mold paying attention not to form turbulence in metal flow and deform the preform. After the solidification, flask is sunk into water and cast composite material is taken and cleaned. The vacuum assisted infiltration process is also presented in Fig. 6 and the original schematic diagram of fabrication system is shown in Fig. 7.

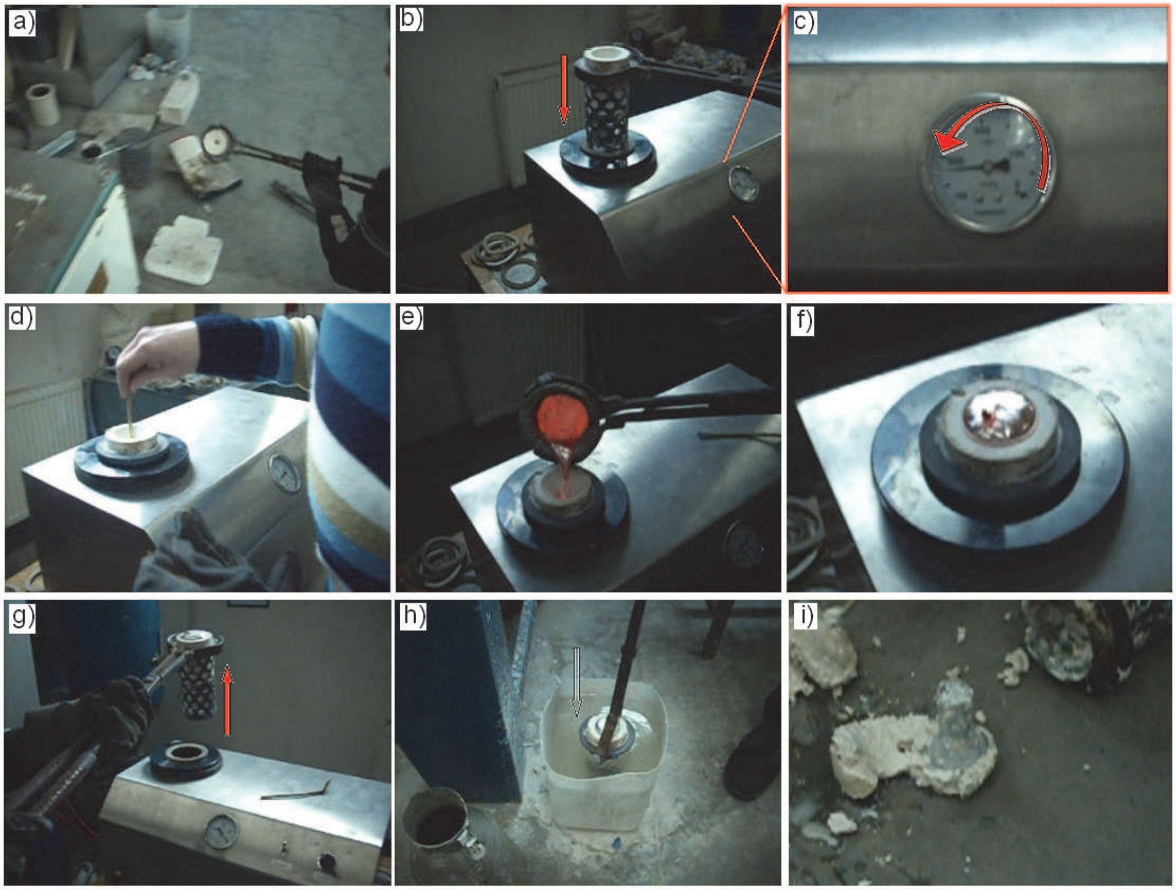

Figure 6. Vacuum assisted infiltration process steps: (a) Flask taken from furnace, (b) locating the flask, (c) vacuum pumping, (d) placing the preform, (e) pouring the molten metal, (f) solidification under vacuum, (g) removing flask for solidification in the air without vacuum, (h) sinking flask into the water and (i) cast composite with runner.

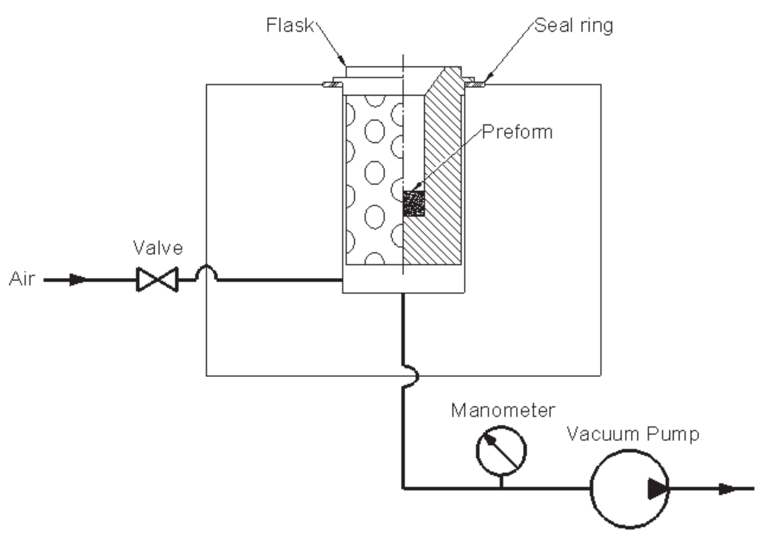

Figure 7. The schematic diagram of vacuum assisted infiltration system.

Microstructural investigations are performed by JEOL JSM-6335F NT and JEOL JSM-5410 LV scanning electron microscopes operating at 20kV and all results are given and discussed in results and discussion section.

Results and Discussion

Microstructures of CNTs are examined from their SEM and TEM images given in Fig. 2. Agglomeration of CNT bundles can be seen clearly from the SEM image. It's also possible to see ash existance from the SEM images. TEM image shows us the average diameter of CNTs used in our fabrication process. Besides, Raman spectrum of CNTs given in Fig. 8 shows us our MWCNTs (1582 cm^{-1} peak shows we have MWCNTs) have point defects (G+ band: 1352 cm^{-1} peak shows defects) affecting the mechanical properties. Nevertheless, properties would be enough for being stronger than conventional reinforcement materials. For a low-cost preform and composite fabrication process, industrial type MWCNTs are considerably practicable because of their properties mentioned. Thus, we may provide cheap and strong enough reinforcements.

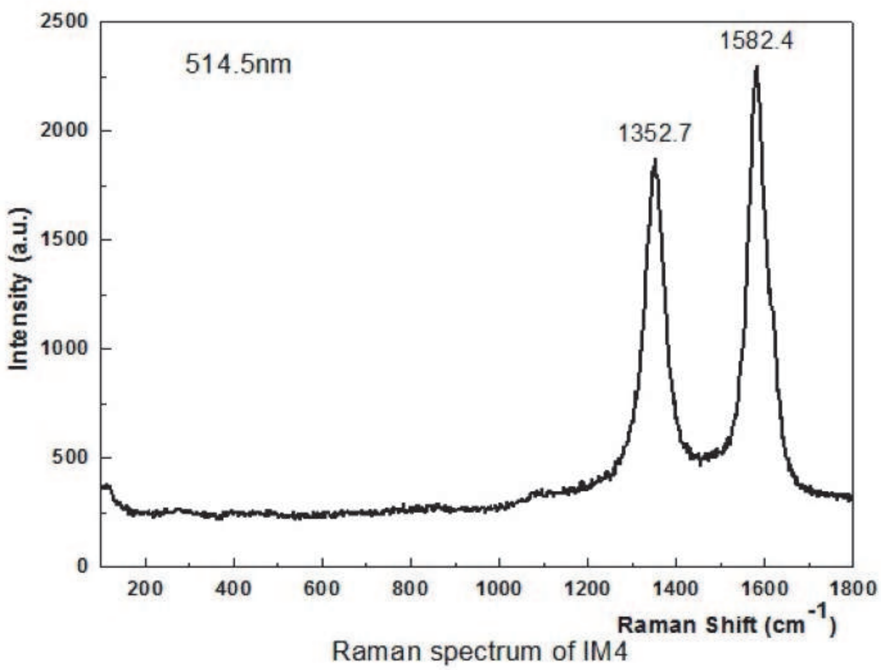

Figure 8. Raman spectrum of industrial type MWCNTs.

Commonly, in surveyed powder metallurgy studies, CNTs were milled with metal powders to attach CNTs to metal powders and also to split up CNTs into smaller parts to facilitate dispersion of CNTs in the matrix. In our process, CNTs are not split-up by any method because mechanical mixing process provides this effect enough to split-up and distribute CNTs in the preform.

In the course of fabrication process, the flask is heated without the preform inside due to the burning point of CNTs, and the preform is put into the mold immediately before pouring the molten aluminum alloy. For this reason, runner is made wide enough to provide the pass of the preform. Because of the density difference between Al and CNTs, rising of the preform during the casting process is an important problem to solve. Therefore, it is decided to obtain snug fit of the preform and mold cavity. Finally, casting and infiltration of the preform reinforced composites are successfully carried out.

After the fabrication of the composites, microstructural examinations are performed. Fig. 9 shows SEM images of CNTs/Al composite's both polished surfaces and fractured surfaces. According to the images, distribution of Al and CNTs in the composite is quite uniform in micro scale compared to the infiltration study of Zhou et al. [15] but not homogeneously distributed as much as the composites fabricated by powder metallurgy methods as expected.

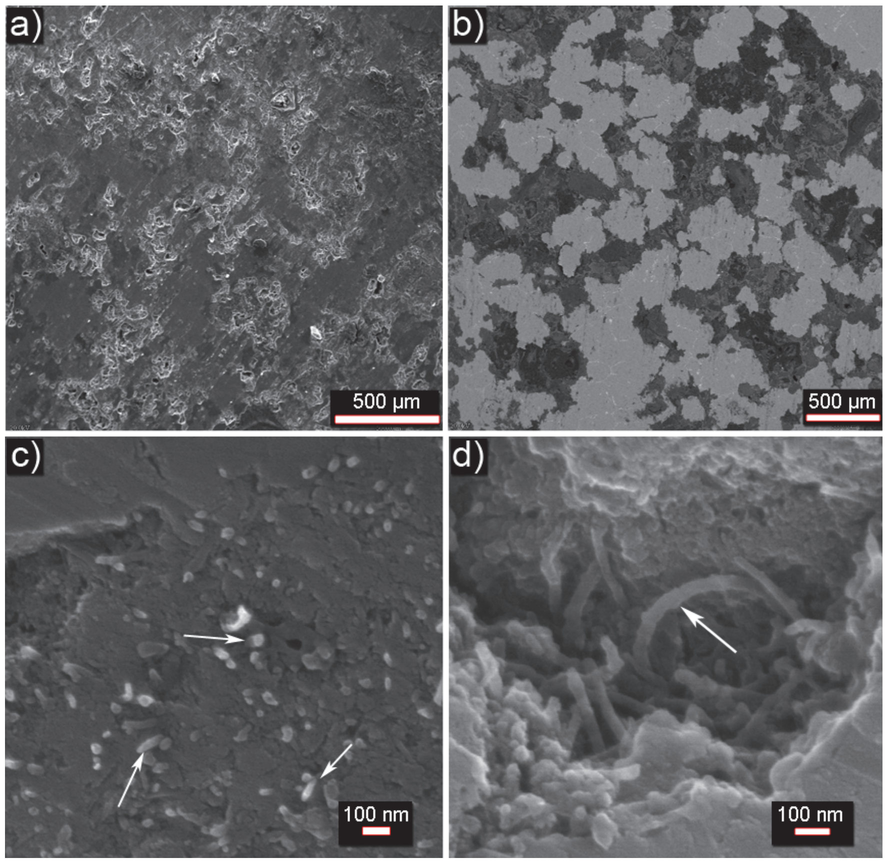

Figure 9. Distributions of Al and CNTs in composite were shown by: (a, b) SEM images of polished composite surfaces and SEM images of the fractured and polished surfaces of composites, (c) showing the pulling-out of CNTs between fractured surfaces and (d) showing the bridging of CNTs between different sides of matrix material.

It is known that the mechanical properties of composites are related with the influence of CNT length and CNT-matrix interphase [16]. SEM images of the fractured composite surfaces are given in Fig. 9 (c) showing the pulling-out of CNTs in matrix, which indicates the stress transfer by shearing between CNT and the matrix material. Furthermore, Fig. 9 (d) shows the CNT bridges between the fractural surfaces of the matrix material, which is related to transferring the stress and increase of fracture energy of the composite that improves mechanical properties [17]. With the existence of bridging and pulling-out of CNTs, the interface strength between CNTs and matrix material is confirmed. It was understood that CNTs are mostly embedded in the aluminum alloy matrix but still there are regions that obtains tangled CNTs, which is a disadvantaging result that worsen mechanical properties of composites.

Conclusions

In this study, CNT reinforced metal matrix composites are successfully fabricated by the infiltration of 6063 Al into the CNT preform using vacuum assisted investment casting process. As a result, a new and economic fabrication process for solid and light-weighted CNT reinforced MMC material is introduced. With the present study, results given below are observed as well:

1. CNTs were distributed quite uniform in 6063 Al matrix material but not uniform as powder metallurgy studies. Enhancement of distribution of CNTs is still being studied and going to be presented in our next studies.
2. CNTs are not split-up by any method to be shortened but they are shortened during the mechanical mixing of preform production materials. Furthermore, mechanical mixing has positive impact to dispersion of long CNTs in the matrix.
3. The mechanical enhancements of the composites are interrelated with the bridging and pulling-out of CNTs in the fracture surfaces. It is confirmed with the bridging that the interfaces between CNTs and matrix material bonded well enough. Thereby, increase in mechanical properties of the composite materials is possible with our method.

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