Multi-walled Carbon Nanotubes Reinforced-Based Magnesium Metal Matrix Composites Prepared by Powder Metallurgy

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Abstract. Nanostructured carbons, for example, carbon nanotubes (CNTs) arise much attraction in the last decades because of its remarkable physical and mechanical properties. The unique physical, chemical and mechanical properties of CNTs make them attractive for biomedical applications. CNTs have been used to modify conventional biomedical materials to enhance mechanical properties, biocompatibility, or to impart other functionalities. One of the metal materials which attract high attention in the biomedical field for orthopaedics application is Magnesium. Recently, many researchers are studying the magnesium reinforced with a different kind of reinforcement. As a lightest metal structure material, magnesium matrix composites show many advantages over monolithic magnesium and magnesium alloys. In this study, Magnesium metal matrix was reinforced by multi-walled carbon nanotubes (MWCNTs) in order to observe the physical and the mechanical properties of the composites. The MWCNTs-Reinforced based magnesium MMC was performed using powder metallurgy process with MWCNTs loading are: 0, 0.1, 0.2, 0.3 and 0.5 %. The temperature of the sintering process was conducted at 600°C by flowing argon gas during the process with the holding time of 2 hours. The experiment result exhibited that the porosity of MMC was increased with the reinforcement by the increasing of the loading MWCNTs observed by metallography and SEM. The mechanical properties showed that the loading of MWCNTs 0.1 % increased the micro-hardness of MMC about 19% compared to pure magnesium, with the peaks at the loading of MWCNTs 0.3 % which increased the mechanical properties about 0.31% at highest hardness value of 46.5 HV.

1. Introduction
In recent year, the biomaterial implant attracts a lot of attention. Biomaterial implant expected to be an aid for the human body and its performance. Biomaterials can be made by metal, ceramics, polymers and composites. The fundamental of biomaterial is compatibility within human body, non-toxicity, and osteo-integration. Materials for implant was also can be classified by its degradation performance bio-inert material and bio degradable materials. Bio-inert means it can be lasting as long as needed and
bio-degradable defines as the ability to degrade safely. The example of bio-inert is Metal such as Stainless Steel, Titanium Alloy, Cobalt-Chrome Alloy, and composites. Metal implants such as stainless steel, titanium are not degradable in human’s body which require advanced action to remove implant after human’s tissues healed. Bio-degradable its self can be classified as pure Metal, Metal - Alloy, and composites. Biodegradable metallic material took an important rule since traditional metal implant gives several notable problems. Some metals release toxic ions as a result of corrosion post-implantation, causing allergic reactions, local anaphylaxis and inflammation [1–4].

Magnesium (~ 1.74 g/cm³) is the lightest materials among several structural materials such as Steel (~7.7 g/cm³), Aluminium (~2.7 g/cm³), and Titanium (4.506 g/cm³). However, Magnesium has inferior physical and mechanical properties. Magnesium Tensile Strength is 160 MPa. Let’s we compare with other such as general steel (~370 Mpa), Aluminium (~310 Mpa), Titanium Alloy Medical grade (~950 Mpa).

It is not so common using pure Magnesium as a biomaterial since the low mechanical properties and very fast break down on the human body. Several non-toxic metals have been used for the alloying metal such as Ca, Sr, Zn, Si, Sn and Zr. Other than binary alloy of Magnesium, Magnesium metal matrix composite can be used and the physical, mechanical, and corrosion behaviour of pure magnesium can be enhanced or manipulated using reinforcement. A lot of reinforcement material have been utilized from bioactive glass, zinc oxide, hydroxyl Apatite, Carbon [3,5,6]. Magnesium-based composite is known to have high specific mechanical properties [7], low density, improved thermal and dimensional stability and better damping properties. Commonly, magnesium MMC reinforced with ceramic powder due to ease fabrication and low-cost production [8]. The use SiC [9] and Ti [10] increased the tensile strength however the ductility are usually sacrificed relative to the monolithic Mg. Solution to this problem is to look for further advancement in the properties of Nano-size reinforcement. Multiwalled Carbon nanotubes (CNT) with its electrical, mechanical, optical and other superior properties appear to be one of important element to various this application. Nevertheless, conventional carbon formulation may not be good enough for several applications such biomaterial implant. Class of carbon allotropes provides unique properties, Multi-walled carbon nanotubes are similar to hollow graphite fiber, except that they have a much higher degree of structural perfection, which are having a diameter of 10-200 nm [11–13]. Magnesium based composites can be tailored by using powder metallurgy followed by sintering at vacuum or inert gas [8], casting technology [14], and friction stir processing [15].

Powder metallurgy process performed to produce MWCNTs-Reinforced based magnesium MMC. Powder metallurgy simply means a method of a manufacturing process which pieces was delivered by blending certain metal powder such as Mg and CNT, compaction and sintered below the melting point. Improper selection of material may result in failure of the manufacturer requirements [16]. Proper material selection results in a good performance with minimum cost [17].

The objectives of this study were to characterize the physical and mechanical properties of metal matrix composites with MWCNT as reinforcement. Powder metallurgy was used to fabricate, and the attempts were made to compare the effect of increasing MWCNTs ratio on physical and mechanical properties of sample obtained.

2. Experimental

The starting material was Magnesium and MWCNTs in the form of powder. Magnesium composite (Mg-MWCNTs) containing pure magnesium 100% (diameter 60 – 300 µm, Merck USA), with MWCNTs (diameter of 20 – 40 nm, 90wt% of purity, Cheap Tubes Inc. USA) ratio of 0.1%, 0.2%, 0.3% and 0.5% (w.r.t Magnesium weight) was prepared using powder metallurgy. Magnesium powder was homogenously mixed with the MWCNTs by using Shaker mill and the respective weight percentages of MWCNTs w.r.t Mg was shown in Table 1. The ratio between the starting material and grind media (stainless steel ball) is 1: 2. Therefore, we prepared 1 gr of mixed powder and 2 gr of grind ball. The starting powder was mixed for 15 minutes.
Table 1. Designation of prepared sample

| Sample (Code) | Magnesium [gr] | MWCNTs [mg] |
|---------------|----------------|-------------|
| Mg            | 1              | 0           |
| Mg – 0.1% MWCNTs | 1            | 1           |
| Mg – 0.2% MWCNTs | 1            | 2           |
| Mg – 0.3% MWCNTs | 1            | 3           |
| Mg – 0.5% MWCNTs | 1            | 5           |

The mixed samples were then compacted at a pressure of 350 Psi. Compacted powder separated from compaction machine for further treatment as shown in Figure 1(e). Compacted billets were then sintered at 600°C by using tube furnace with Argon gas as protective atmosphere for 2 hours as shown in Figure 1(f). The microstructure of the sintered sample was studied by using metallurgical optical (MT7100, Meiji Technology) and electron microscope (JEOL JSM 6390, Japan). Hardness was measured by using Microvicker (Mitutoyo, HM-200).

3. Results and Discussion

Morphologies of the sintered samples were observed on the images acquired by optical and electron microscopes, as well as chemical composition by using EDAX. Figure 1 compare the morphologies as a function of MWCNTs weight content. The observed samples are not etched because we would like to examine the homogeneity and the rules of the MWCNTs addition. From the image below we may have said that by Increasing the weight percent of MWCNTs increased the affinity of closed porosity formation. The number of porosity was decreased followed by the increasing of pore diameter, as the MWCNTs content increased.
Figure 1 Surface observation by using optical microscope: (a) pure Mg (b) 0.1% (c) 0.2% (d) 50K 0.3% (e) 0.5% wt % of MWCNTs.

MWCNTs have large surface area. Therefore, it tends to interact each other MWCNTs to form MWCNTs aggregates rather than the interaction magnesium as matrix producing small clusters in the matrix. MWCNTs are stable materials as general carbon allotropy such as graphite, carbon active, and graphene. In order to make a good interface, MWCNTs needs to be decorated or functionalized with active functional group.

Figure 2 shows the electron micrograph of the sintered sample and the elemental spectra of the scanned area of the sample.

Figure 2. Electron micrograph of Sintered pellet showing clustering of MWCNTs

From the spectral element image derived from the EDAX, it shows that the MWCNTs are keep remain in the sintered sample. From the Figure 2, the fracture image of the sintered sample, MWCNTs exist in the form of agglomerates and generally placed in the grain boundary. As we mentioned before, lack of dispersion due to poor dispersibility of the MWCNTs in the magnesium matrix. That could be the reason as the amount of MWCNTs increased composite tends to be weaker, brittle and easily destroyed by an external force. Thus, it leads to poor mechanical properties of the nanocomposite.

Microhardness testing was used to determine the physical properties of the resulted sample. Microhardness of the measuring samples are shown as shown in Figure 3. Pure Mg has the lowest level of hardness compared to nanocomposite. It shows that hardness value increased as well as the weight ratio of MWCNTs. Magnesium matrix containing 0.3% of MWCNTs has the highest hardness value at the level of 46.5 HV compared to pure and other samples.
Compare to other typical experiment, we have a good agreement such as Meysam et al [5] for the work on the mechanical properties of magnesium matrix reinforced with hydroxyapatite and also N. Saikrishana et al. on their work on the investigation of the hardness of MWCNT/Mg Composites [18]. The mechanism of Strengthening on the Magnesium depends on the reinforced material. MWCNTs can be a grain refining agent during solidification, reducing interparticle spacing and small dimension and large surface area as mention in the work of [19].

4. Conclusion
Magnesium as degradable material is suitable for biodegradable implant application however pure magnesium provides low strength. The amount of MWCNTs in Mg matrix resulted the level of porosity increase. The pore size was also increased by increasing the MWCNTs content. Optimum strength of composite can be obtained at 0.3% of MWCNTs provides highest hardness value of 46.5 HV. Further treatment of MWCNTs in order to make sure the dispersion of MWCNTs in magnesium matric is good.

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