On the Study of Mechanical Properties of Aluminum/Nano-Alumina Composites Produced via Powder Injection Molding

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ABSTRACT

Powder Injection Molding (PIM) is a precision manufacturing process used for production of advanced composites. Mixing of polymeric binder with metal powders, molding of feedstock, de-binding of brown parts and sintering of green samples are four main steps of this process. In the present study, the compounds containing multi-component binder system and aluminum/nano-alumina (0-9 wt.%) powders were prepared and used as feedstock. After that, the feedstocks were injected, de-bound and sintered for producing standard specimens. Finally, the sintered composites were produced with a maximum relative density of 97.7%. Afterward, the hardness, yield and ultimate tensile strength of the nano-composites were evaluated. The results showed that the relative density, hardness and strength of the manufactured composites increased due to the addition of nano-reinforcements. It is demonstrated that the effect of alumina on the density of PIM composites differs from that of conventional powder metallurgy. Scanning Electron Microscope (SEM) reveals that the agglomeration takes place in the sample containing 9 wt.% nano-alumina.

1. Introduction

The Aluminum Matrix Composites (AMCs) are desirable metal matrix composites for the automotive, aerospace, defense and electronic industries because of their low density, high specific stiffness, corrosion resistance, high toughness, fatigue resistance, controllable expansion coefficient, and high thermal as well as electrical conductivity [1-3].

The Powder Injection Molding (PIM) is an advanced powder technique that is commonly used for the fabrication of small and delicate composite parts. PIM can significantly decrease the production costs of composites for commercial applications [4]. Feedstock preparing, molding, de-binding and sintering are the four main steps of the PIM. In practical applications the demands for miniaturization, especially in mobile devices such as laptops and cell phones, result in production of heat sinks with different geometries and shape complexity through Al PIM [5,6].

In the case of structural applications, where higher strength and ductility are important, the use of nano-composites is reasonable [7]. Enhancement of the sinterability, improvement of the mechanical properties and fine microstructures are the most significant consequences of nanoparticles in powder technology [8,9]. The feedstock flow and mold filling requirements dictate that only particles or short fibers reinforced composites can be processed by the PIM [4].

Several studies have investigated the presence of additive particles in the flow behavior of powder-polymer mixtures and the properties of PIM products [8,10-15]. The presence of fine particles in the powder-polymer mixtures affects the rheological behavior, because nano-additives usually show poor
packing behavior and significantly influence the homogeneity and viscosity of feed-stocks [8]. Torque rheometry, rheological analysis of Al powder-polymer mixtures and the effect of alumina nanoparticles on the rheological behavior of feed-stocks were completely investigated in our previous studies [16,17].

The aluminum-based PIM composites were produced and evaluated by Liu et al. [18,19], Ahmad [20,21] and Adomphol et al. [22]. The sintering temperature, tin addition and heat treatment effect on the density and mechanical properties of 6061 alloy was investigated [18]. Liu et al. [19] also evaluated the mechanical properties and microstructure of injection molded AMCs reinforced with 10 %wt. AlN particles. Ahmad [20], reported the optimum injection parameters for achieving the highest level of fiber orientation in a given direction. He [21], also investigates and determines the injection machine parameters which lead to the formation of defects consisting of voids, cracks and blisters for Al-based material. Adomphol et al. [22], characterized the feedstock for powder injection molding of SiCp-reinforced aluminum composite. They found that the high solid loading was improved by the bulk density while the hardness values were observed to be similar. However, the effect of reinforcement on the mechanical properties of Al-\(\text{Al}_2\text{O}_3\) PIM nanocomposites has not been addressed yet.

The present study focused on the use of the PIM process for manufacturing the AMCs that were reinforced with nano-aluminum oxide. The \(\text{Al}_2\text{O}_3\) particles are favored as reinforcements because of their low price, superior high temperature mechanical properties and excellent oxidation resistance that avoid formation of the undesirable phases [23,24]. Furthermore, the effect of nanoparticles on the density and mechanical properties of molded Al-based composites was investigated.

2. Materials and Methods

\(\text{Al} (d_{50} = 25 \text{ μm}), \text{Sn} (d_{50} = 15 \text{ μm})\) and \(\text{Mg} (d_{50} = 11 \text{ μm})\) powders in commercial purity (supplier: Pourian Chem. Co.) were used as starting materials for preparation of pre-mixed \(\text{Al}-2\text{Sn}-1\text{Mg}\) (wt.%% powder). The addition of elements such as Mg and Sn as oxygen reactor and sintering activator can be aided by the densification of Al powder [18,19,25].

The chemical composition of the Al powder and particle size distribution parameters, obtained using a Malvern (ZEN3600) particle size analyser, are listed in Table 1.

### Table 1. The chemical composition and particle size distribution of powder.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Particle size parameters</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(d_{10})</td>
</tr>
<tr>
<td>Al</td>
<td>99.5</td>
</tr>
</tbody>
</table>

Then; 3, 6 and 9 (wt.-%) α-phase \(\text{Al}_2\text{O}_3\) (80 nm; >99% purity; supplier: US Research Nanomaterials, USA) was mixed with Al-based powder using a planetary high energy ball mill for 40 min in the presence of ethanol. The TEM image of alumina nano-sized powder is displayed in Fig. 1.

The binder system was comprised of three principal components: poly- propylene (35 vol.%) as a backbone polymer, paraffin wax (60 vol.%) as a plasticizer, and stearic acid (5 vol.%) as a surfactant. The multi-component binder results in gradual and selective binder removal during de-binding. A Brabender mixer (W50) with a pair of rotating blades was used to prepare the feed-stocks. The temperature, speed, and time were optimized during mixing to 180°C, 50 rpm, and 15-45 min, respectively. The mixing process continued until the torque stabilized at a steady state level. Then, the feedstock crushed into granules. The compositions of the prepared feed-stocks are summarized in Table 2. Fig. 2 exhibits, schematically, the materials and feedstock preparation steps.

The standard flat specimens [26] were injected using a Dynisco laboratory mixing molder. The binders were removed in two steps consisting of solvent and thermal de-binding. First, the injected parts were immersed in n-heptane solvent at 55 °C for 6 hours; then the direct thermal de-binding was done according to a heating cycle as shown in the left side of Fig. 3.
The parts were then heated from 500 to 620 °C at a rate of 5 °C/min and also were sintered at 620 °C for 1 hour in a nitrogen atmosphere (Fig. 3, right side). The heating regime was adjusted based on the binder decomposition temperatures. Thermal properties of the binder's constituents were determined by Thermal Gravimetric Analysis (TGA) equipment (PL-TGA) according to the ASTM E 1113 standard [27].

A scanning electron microscope (FE-TESCAN, Mira II, 15.00 kv) was utilized for microstructural investigation of the samples. The density was measured based on the Archimedes immersion technique.

**Table 2.** The different feedstock compositions for experiments.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Powder Loading (vol.-%)</th>
<th>Powder Composition (wt.-%)</th>
<th>Binder Volume (vol.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al60</td>
<td>100</td>
<td>Al 100</td>
<td>0</td>
</tr>
<tr>
<td>Al-3NP-60</td>
<td>97</td>
<td>Al 97</td>
<td>3</td>
</tr>
<tr>
<td>Al-6NP-60</td>
<td>94</td>
<td>Al 94</td>
<td>6</td>
</tr>
<tr>
<td>Al-9NP-60</td>
<td>91</td>
<td>Al 91</td>
<td>9</td>
</tr>
</tbody>
</table>

The hardness and tensile tests were performed according to MPIF 43 [28] and ASTM D 1708 [26], respectively.

### 3. Results and Discussion

Fig. 4 is a micrograph of the feedstock which shows the powder particles covered by a thin layer of polymeric binder.

Fig. 5 shows the optical images of the produced specimens. After sintering, the parts are free of defects such as cracks and blisters. The isometric and proportional shrinkage can be seen in the sintered parts. The powder densification takes place for all samples during the sintering cycle.

For example, Fig. 6 shows the SEM image of sintered specimen which in turn indicates the consolidated surface.

**Figure 2.** The schematic of feedstock preparation process.

**Figure 3.** The thermal de-binding and sintering heating cycles.

**Figure 4.** The SEM micrograph of the prepared powder-polymer mixtures.
The general microstructure, FE-SEM image of the produced nano-composites is presented in Fig. 7. The aluminum oxide nanoparticles can be discerned in this figure. Furthermore, an optical image is shown in Fig. 8, which in turn shows the general microstructure feature consists of the powder particles and the pores. The relative densities of the various composites after sintering are shown in Fig. 9 and are varied from 95.8% to 97.7%.

The density of alumina is 3.95 g/cm³ and consequently higher than Al powder. However, in conventional powder metallurgy, when the alumina content increases, the relative density of the Al-based composites decreases, as reported by Rahimian et al. [23]. The compressibility of the composite powder declines due to increasing the reinforcement, since the hardness of alumina is higher than Al, which results in increment of friction between particles. Inversely, in the PIM, the mold cavity is filled with a uniform and hydrodynamic pressure and the densification of the composite powder is not restricted by higher hardness of alumina. The nano-additives can fill the interstices among larger particles and increase the packing and relative density. However, in the PIM, the agglomeration of fine powders can obstruct more densification [8,12], as a
result of which, the relative density decreases with the addition of 9% nano-alumina. Figure 10 shows the distribution of reinforcement particles in two de-bound samples. The powder agglomeration can obviously be seen in the specimen containing 9 wt-% nano-alumina. When the fine powder ratio increases, more binder is required to provide essential flowability, because of the increased surface area. Therefore, it appears that in Al-9NP-60, there is an inadequate amount of binder for flowability and movement of the nanoparticles through the interstices of the Al powders. Consequently, the agglomeration of alumina and hence decreasing of relative density occur as the particle packing decreases. Decreasing the density in Al-9NP-60 can also affect other mechanical properties such as yield and ultimate tensile strength (refer to Figs. 11 and 12).

The hardness, yield and ultimate tensile strength (UTS) are shown in Figs. 11 and 12. Adding nano-alumina as reinforcement considerably enhances the mechanical properties of aluminum matrix as seen in the aforementioned figures (except Al-9NP-60). Generally, the nano-additives persuade sintering process, create finer microstructures and make better tolerance control [8,29]. It is described that the strength of an aluminum matrix increases with decreasing the reinforcement’s size from micrometer to nanometer, at least 20% [9]. In other words, the effect of reinforcement size on the mechanical behavior is recognized and proved [23,30]. It reveals that decreasing the particle size increases the mechanical properties of the composites.

This issue can be explained from two perspectives. First, with decreasing the reinforcement size to nanometer, the interface between the soft matrix and the hard nano-phase gets higher. Second, the strength of nanoparticles against fracture, under the loading, is higher than coarser particle due to few defects. Therefore, the nanoparticles have higher hardness and strength in comparison with the coarser particles [31].

As it can be seen, the hardness, yield, strength and UTS increase with addition of nano-alumina. In metal matrix composites, the dislocation movement is prevented by dispersion strengthening mechanism. Thus, the level of matrix strengthening depends on the distance, mode of distribution and the amount and size of the secondary phase [32].

![Figure 11. The hardness of Al-based composites against the nanoparticle contents.](image1)

![Figure 12. The strength of Al-based composites against the nanoparticle contents.](image2)
For particulate composites having uniform distribution of the secondary phase, the relation among interspacing of the reinforcement ($\lambda$), volume fraction ($f$) and diameter ($r$) is as below [33]:

$$\lambda = \frac{1 - f}{2fr}$$  

(1)

Therefore, the space between the second particles decreases with increasing the reinforcement weight fraction. On the other hand, the required stress for dislocation movement, between two adjacent alumina particles which determines the material strength, increases due to the less interspacing of particles [23]:

$$\tau_0 = \frac{\sigma_0}{\lambda}$$  

(2)

Where, $\tau_0$, $G$ and $b$ are the required tension stress for forcing dislocation to move through reinforcement particle, material’s modulus and Berger’s vector, respectively.

On the other hand, the Hall-Petch type expression for the hardness of the composite ($H_c$) is as below [34]:

$$H_c = \rho_{fc}(H_m + \frac{\phi_p^0.5(n_p-H_m)}{d^{0.25}})$$  

(3)

Where $\rho_{fc}$, $H_m$, $\phi_p$, $H_P$ and $d$ are the composite relative density, matrix hardness, volume fraction of particulate reinforcement, hardness of reinforcement and particle diameter, respectively.

The fracture strength of the composite ($\sigma_c$) is assumed to follow a relation analogous to the hardness [35]:

$$\sigma_c = \rho_{fc}(\sigma_m + \frac{\phi_p^0.5(\sigma_p-\sigma_m)}{d^{0.25}})$$  

(4)

Where, $\sigma_p$ and $\sigma_m$ are the fracture strengths of the matrix and particulate reinforcement, respectively.

According to equations (3) and (4), it is expected that the hardness and strength of a metal matrix composite increase with increasing the reinforcement volume fraction, as seen in above equations for Al-nano-alumina composite.

4. Conclusions

The mechanical behaviors of Al-based nanocomposites were studied in the present study. After the injection, the combination of the solvent and thermal de-binding was performed for the binder removal. The sound parts having relative sintered densities in the range of 95.8% to 97.7%, were produced. The mechanical properties of composites were improved due to the addition of nanoreinforcement. The agglomeration of nanoparticles, due to inadequate amounts of binder, was seen in Al-9NP-60 which caused a reduction in the Al-9NP-60 mechanical properties.

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References


