Production of al-si alloy feedstocks using the solvent hot mixing method

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Abstract. Powder injection molding is a promising low-cost technique for net shape processing of metal and ceramic components. This study aimed to investigate a new method for preparing aluminium (Al) – silicon (Si) alloy feedstock using the solvent hot mixing process. For this purpose, micron-sized Al-Si (20 wt. %) alloy powder was mixed with a binder consisting of 55 wt. % carnauba wax, 45 wt. % high-density polyethylene, and 3 wt. % stearic acid in a hot xylene bath. The scanning electron microscopy technique, thermogravimetric analysis, density measurement and torque measurements were used to verify the homogeneity of the feedstock. Moreover, the feedstock was chosen to perform the molding, debinding cycle and sintering. An Al-Si (20 wt. %) alloy part was successfully produced using this new method.

1. Introduction
Aluminum (Al) and its alloys are widely used in traffic, industrial production, electronics, communication, aeronautics, and military fields because of its superior properties such as low density, excellent specific mechanical properties, good resistance to stress corrosion, and high thermal and electrical conductivity [1-4]. Hypereutectic Al-silicon (Si) alloys and its composites have attracted much attention in electronic packaging applications due to their low density, high wear resistance, low thermal expansion coefficient and excellent thermal conductivity [5,6]. The requirement for packing materials is increasing, as electronic packaging has become an emerging technology featuring smaller size, higher integration, and complex geometries. Efforts are ongoing to fabricate hypereutectic Al-Si alloy and its composites using different technologies. Sumitomo Electric Industries, Japan, has developed an Al (60 wt.%) and Si (40 wt.%) composite for electronic packaging using the traditional powder metallurgy technology [7]. Hogg investigated the microstructure of a spray Al-Si (30 wt.%) alloy used in electronic packaging applications [8]. Zhang produced a 70 vol.% SiCp/Al-Si (12 wt.% ) composite for electronic packaging using pressure infiltration method [9]. Besides, Liang Tian produced an Al-calcium (Ca) composite used in national high-voltage system using the powder metallurgy and severe deformation method. This method can produce an extremely smooth interface, which is free of cracks and pores [10,11].

The powder injection moulding (PIM) is a near net shape technology combining the advances of conventional powder technology and plastic injection molding to mass fabricate small, complex, precision metal or ceramic parts [12-14]. This potential and attractive technology can be used for fabricating miniature and complex metal and ceramic packing materials. We would investigate the process of Al-Si (20 wt.%) alloy parts by PIM technology, and this study is the first part: preparing the
feedstocks. In general, the PIM process consists of four main steps: feedstock preparation, molding, debinding, and sintering [12,15]. In the feedstock preparation process, conventionally, the binder and the powder material are mixed thoroughly with a mechanical mixer at a temperature above the higher melting component of the binders [14-16]. It could realize satisfactory mixing performance, and obtain homogeneous feedstock. However, it needs complex mixer equipment and a high mixing temperature.

In this study, the Al-Si alloy feedstock was prepared using solvent hot mixing with a xylene solvent bath to simplify the mixing process of feedstock and reduce the mixing temperature. The proposed binder system was dissolved in a 110°C xylene bath and mixed using an electric stirring bar. Then, xylene was removed through distillation to obtain the feedstock. The scanning electron microscopy (SEM) technique, thermogravimetric (TG) analysis, density measurement, and torque measurements were used to verify the homogeneous of feedstock. Moreover, debinding and sintering were also conducted to show the feasibility of feedstock produced by solvent hot mixing.

2. Experiments

2.1. Materials

In this study, commercial air atomised Al-Si (20 wt.%) alloy powder having a mean particle size of 6.67 µm was used. The shape and morphology of the alloy powder are shown using the SEM micrograph in figure 1. The granule size distribution measured using a laser granulometry (BT-9300H) is shown in figure 2. Small amounts of pure magnesium (Mg) and tin (Sn) powders were used as sintering aids. Mg could react with the oxide, inducing an oxide film fracture and breakup [17-19]. Sn was a beneficial additive for the enhanced liquid-phase sintering of aluminium and its alloy. A trace amount of Sn could improve the wetting characteristics and behaviour of aluminium [20,21]. A multi-component binder system comprising 45 wt.% high-density polyethylene (HDPE), 52 wt. % carnauba wax (CW), and 3 wt.% stearic acid (SA) was used (table 1). HDPE was a minor binder component, which retains the form of feedstocks after solvent debinding and prior to sintering. CW was a major binder component, which could reduce the viscosity of the molding feedstock and promote flowability. SA served as a surfactant, which improved the interaction between the power and the binder.

![Figure 1. SEM micrograph of original Al-Si alloy powder.](image)

![Figure 2. Particle size distributions of Al-Si alloy powder.](image)

| Binder constituent          | Supplier                  | Density (g/cm³) | Melting point (°C) |
|-----------------------------|---------------------------|-----------------|--------------------|
| High density polyethylene   | Exxon Mobil               | 0.956           | 142                |
| carnauba wax (CW)           | LUSEN Chemical            | 0.990-0.999     | 82-86              |
| stearic acid (SA)           | JINDA shuangpeng oil company | 0.9408         | 56-69.6            |
2.2. Methods
In total, 85 wt. % of powder loading (82 wt.% Al-Si alloy, 2 wt.% Sn, and 1 wt.% Mg), and the binder is the rest 15 wt.%. The feedstock was prepared in a flask containing an appropriate amount of xylene at 110°C. At this temperature, the respective components of the binder could dissolve in xylene. At first, all of the binder components were added into the xylene solvent, and the solution was stirred at 300 rpm at 110°C using a stainless steel stirring bar. Until all binder components completely dissolved, the metal powder was gradually added into the solution and continually stirred for an additional 2 hours to homogeneous the mixture. Finally, the xylene was distilled off to obtain the feedstock.

The micromorphology of the feedstock using a SEM (Hitachi SU-8010), torque measurement using a rheometer (ARES—RFS), the TG analysis using a thermal analyzer (TGA, Q5000IR), and the density measurements using a densitometer (Quantachrome UPY-20T) were performed to study the homogeneity of the feedstock.

The feedstocks were injection molded into tensile test bars using a LX-MIM120 injection molder. Solvent debinding was performed in xylene at 60°C for 48 h. Thermal debinding and sintering were conducted in a thermal schedule as shown in table 2 in a glass tube furnace. The heating process was designed on the basis of TG analysis results of the feedstock. The furnace was evacuated to less than 5.0×10⁻² torr before commencing heating. Then, nitrogen was backfilled at 100°C and the nitrogen gas flow was maintained at 0.5 L/min for debinding and sintering. Some sacrificial Mg powders were placed beside the samples to scavenge oxygen.

3. Results and discussion

3.1. Homogeneity analysis
The homogeneity of the feedstock influenced the injection molding and sintering process[16,22]. Therefore, the homogeneity of the feedstock was verified by observing its micromorphology, torque value, density and TG analysis.

The SEM micrograph of the feedstock in figure 3 illustrates that the powder and binder were uniformly mixed in this feedstock without any obvious bubble and hole.

| Stage | Heating rate (°C /min) | Debinding/ sintering temperature (°C) | Hold time (min) |
|-------|------------------------|--------------------------------------|-----------------|
| 1     | 1                      | ambient temperature to 200           | 0               |
| 2     | 0.5                    | 200 to 500                           | 1               |
| 3     | 0.8                    | 500 to 550                           | 180             |
| 4     | furnace cooling        | ambient temperature                  | 0               |

Supati [23] observed variation in the torque value of the feedstock during dynamic rheology measurement to predict its homogeneity. If the torque of the feedstock had a steady value, uniform mixing was considered to occur [23]. As shown in figure 4, the torque dropped quickly at the beginning of the test, which, according to Ghanbari [22] was due to the loss of feedstock structure, resulting in the reduction of viscosity. Then, the torque remained stable. The stability of the torque meant the stability of the viscosity, and the homogenous of the feedstock.
Figure 3. SEM micrograph of feedstock produced by solvent hot mixing.

Figure 4. Torque rheological diagram of the feedstock at 160°C.

Figure 5 shows a comparison of the measured densities of the feedstock calculated using a nitrogen pycnometer. The standard variation of the pycnometer density measured in five random samples was extremely small, indicating a thorough homogeneity of the prepared feedstocks. Figure 6 shows the thermograms of the feedstocks measured in five random samples. The five curves displayed the same behavior and nearly overlapped. This phenomenon verified the excellent homogeneity of the feedstock again.

Figure 5. Densities of randomly selected portions of the feedstock.

Figure 6. Tg analysis of randomly selected portions of the feedstock. The heating rate was 10°C/min.

3.2. Debinding and sintering
The subsequent injection molding and sintering progress was conducted to investigate the feasibility of the feedstocks during the process. The mold injection sample called “green sample” is shown in figure 7(a), which illustrates that the green sample had no porosity and cracks on the surface. The mold part had remarkable properties.
The subsequent progress was binder removal. Traditionally, a combination of solvent and thermal
debinding process was used for this[14,24]. Solvent debinding was conducted by immersing the parts
into a bath with xylene at 60°C for 48 h; in general 8.20 wt.% of the feedstock could be extracted,
which is approximately 99.40 wt.% of the soluble ingredients of binder. After solvent debinding, the
green samples were free of defects and chosen for sintering. The solvent debinding sample is shown in
figure 7(b).

Thermal debinding and sintering were conducted in a single heating sequence. Knowledge of the
thermogram for the solvent debinding feedstock allowed one to predict the thermal decomposition
behavior of the binder in the feedstock. Figure 8 shows the weight loss when the solvent debinding
feedstock was heated at 10℃/min in nitrogen. Binder decomposition started at 300℃, and the
dissociation speed was low, between 300℃ and 400℃. When the temperature was more than 400℃,
the degradation rate obviously increased followed by a rigorous weight loss to about 92.6 wt.% at
about 490℃ and the binder was completely decomposed. This indicated that about 8.2 wt.% binder
was extracted after solvent debinding. The result was consistent with the thermograms of “green
samples”.

Figure 7. (a) Green sample, (b) solvent debinding sample, and (c) sintered sample.

Figure 8. TG analysis of the solvent debinding feedstock.

Based on the thermogram of the solvent debinding feedstock and taking into account that high
heating rates introduced cracks and blisters into the samples, the debinding and sintering thermal
cycle was established, shown in table 2. Figure 7(c) shows a sintered part. The sintered part
maintained the shape well and had a uniform shrinkage.
4. Conclusion
A homogeneous Al-Si (20 wt.%) alloy + Sn (2 wt.%) + Mg (1 wt.%) feedstock with HDPE, CW, and SA as the binders was manufactured using the solvent hot mixing method. The SEM, TG analysis, density measurement, and torque measurements verified the high homogeneity of the feedstock. An Al-Si (20 wt.%) alloy + Sn (2 wt.%) + Mg (1 wt.%) part was successfully produced by a process similar to PIM. The part exhibited satisfactory geometric stability and was free of distortion and macrocracks.

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