Analysis of the rheological behavior and stability of 316L stainless steel–TiC powder injection molding feedstock

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Received in revised form 27 June 2005; accepted 27 June 2005

Abstract

An experimental rheological study has been performed to evaluate the influence of TiC addition on the rheological behavior and stability of 316L stainless steel powder injection molding (PIM) feedstock. The effects of TiC concentration, solid loading, shear rate and temperature were investigated via capillary rheometer method. The stability of feedstocks was evaluated quantitatively using “instability index”, which describes the threshold beyond which the variation of viscosity becomes unacceptable for PIM purposes. The results show that the rheological behavior of PIM feedstocks highly depends on the blend composition. The addition of TiC particles to the stainless steel powder increases the viscosity of feedstock at relatively low shear rates, i.e. <500 s⁻¹. Furthermore, the feedstock instability increases, particularly at higher solid loading. Nevertheless, with increasing shear rate and temperature, the viscosity decreases and the instability of feedstock improves. At relatively high shear rates, i.e. >2000 s⁻¹, the viscosity of composite feedstocks was lower than that of the mono-component SS feedstock due to the better particle packing efficiency. This article presents the rheological behavior of bimodal powder mixture of stainless steel and TiC powders prepared for PIM application. The influences of blend composition, i.e. the TiC concentration and solid loading, and the processing parameters, i.e. temperature and shear rate, are addressed.

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Keywords: Powder injection molding; Rheological behavior; Feedstock instability; Stainless steel; Composite

1. Introduction

Over the past decades, powder injection molding (PIM) has been established as a competitive manufacturing process for production of small precision components, which would be costly to produce by alternative methods [1]. The parts can exhibit complex geometries and the process circumvents the most common difficulties encountered in powder metallurgy, regarding geometry limitation as well as density gradients [2]. The PIM process involves mixing either metal or ceramic powders with a binder to produce a feedstock. During molding, the feedstock flows into and fills a mold under pressure to form a green part with the desired shape. The resulting part is then debinded and sintered to full or near full density [3].

In PIM process, the molding stage is a critical step for the fabrication of sound parts without cracks and distortions [3,4]. This step requires specific rheological behavior, so that the rheological characteristics of PIM feedstocks are of crucial importance. Non-homogenous flow and powder-binder separation can produce defects during molding, resulting in cracking and warpage during debinding and sintering, and ultimately poor physical and mechanical properties of the final PIM component [5,6]. Viscosity, density, thermal properties and pyrolytic behavior of a PIM feedstock determine its performance [7]. Amongst different parameters, viscosity is the single most important predictor of feedstock quality that influences the success of molding stage. It is known that a sound molded part would be obtained when the viscosity is controlled within a narrow range [5]. Therefore, the rheological behavior and stability of PIM feedstock are key features for successful manufacturing.

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0921-5093/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.msea.2005.06.057
Many experimental data about rheological characteristics of PIM feedstocks are available in the technical literature, e.g. [7–11]. Recently, Dihoru et al. [5,6] used neural network modeling to analyze the rheological behavior and stability of PIM feedstocks. Their model enables prediction of the viscosity when the powder characteristics, blend composition and shear rate are known. By evaluating the influence of shear rate and powder characteristics on the viscosity of feedstocks composed of binary blends of stainless steel (SS) powders, they examined the stability using “instability index” [5,6]. In the present work, this concept was used to investigate the rheological behavior and stability of 316L SS–TiC composite feedstocks. Recently, Loh et al. [12] and Supati et al. [13] have studied the production and characterization of SS–TiC composites. Nevertheless, generally not much research has been done on the production of composite parts by the PIM process. Consequently, there are limited data available particularly dealing with the characterization of composite feedstocks for powder injection molding.

This article evaluates the influences of TiC addition and processing condition on the rheological behavior, moldability and stability of 316L SS PIM feedstock. This involves measurement of the influence of temperature, shear rate, solid loading and TiC concentration on the viscosity of PIM feedstocks by using a capillary rheometer. The capillary test, which gives the fundamental rheological data of a viscous fluid, is currently realized as the best approach to predict the flow behavior during injection molding [11]. The information from this instrument can be used not only to determine viscosity, but also to reveal the stability and homogeneity of feedstocks and the extent of powder-binder separation.

2. Experimental procedures

2.1. Powder

The starting materials were commercially available gas atomized 316L stainless steel powder (Osprey Ltd., UK) and TiC powder (Sigma–Aldrich, USA). The characteristics of these powders are reported in Table 1. Fig. 1 shows SEM micrographs of the particles. As seen, the stainless steel particles are almost spherical whilst TiC particles are irregular. No evidence of severe powder agglomeration was observed during SEM observation.

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Shape</th>
<th>(D_{10}) (µm)</th>
<th>(D_{50}) (µm)</th>
<th>(D_{90}) (µm)</th>
<th>Apparent density ((\times 10^3) kg m(^{-3}))</th>
<th>Tap density ((\times 10^3) kg m(^{-3}))</th>
<th>Width of particle size distribution*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>Spherical</td>
<td>4.4</td>
<td>12.6</td>
<td>27.6</td>
<td>2.53</td>
<td>4.52</td>
<td>3.84</td>
</tr>
<tr>
<td>TiC</td>
<td>Irregular</td>
<td>1</td>
<td>4</td>
<td>9</td>
<td>–</td>
<td>2.24</td>
<td>2.68</td>
</tr>
</tbody>
</table>

* \(S_w = 2.56 \log (D_{90}/D_{10})\).
2.3. Feedstock

Binary powder blends composed of 3 and 5 wt.% TiC and 316L stainless steel were mixed in a Tumbler mixer for 20 min. The powder mixtures were then blended with the multi-component binder system to prepare feedstocks for PIM with solid loadings of 55 and 60 vol.%. The feedstocks are referenced here by their powder constitution and solid loading. For example, SS-3TiC-55 is the feedstock containing 3 wt.% TiC powder and has solid loading of 55 vol.%. The composition of investigated feedstocks is listed in Table 3.

In order to ensure adequate time for the binder to melt and homogenize, the binder components were initially blended at 100 °C (above the melting point of EVA) in a Haake rheocord 90 torque rheometer for 60 min. Afterwards, the composite powders were added to the binder in several stages to achieve homogenous mixtures. The mixing time was about 60 min.

2.4. Viscosity measurement

The viscosity of feedstocks was measured by an Instron 3211 capillary rheometer. A die with 0.08 mm diameter (D) and 2.56 mm length (L), giving a ratio (L/D) of 35, was used to give the mix a smooth and lamellar flow and minimum entrance corrections (Bagley entrance correction for stress due to funneling effect at the entrance) [10]. Because L/D is >20, the entry and exit effects can be neglected [8]. The test temperatures were 60, 70 and 80 °C that are beyond the melting temperature of the binder (Fig. 2). A period of 10 min was allowed to reach thermal equilibrium after charging the barrel. Shear rates ranging from 50 to 10000 s⁻¹ were applied. The measured shear rates were corrected using the Rabinowitsch derivation [14,15], as PIM feedstocks are considered to be non-Newtonian fluid.

3. Results

In Table 4, the viscosity of binder and feedstocks at different shear rates and temperatures are reported. The data

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>TiC content (wt.%)</th>
<th>Solid loading (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS-55</td>
<td>0</td>
<td>55</td>
</tr>
<tr>
<td>SS-60</td>
<td>0</td>
<td>60</td>
</tr>
<tr>
<td>SS-3TiC-55</td>
<td>3</td>
<td>55</td>
</tr>
<tr>
<td>SS-3TiC-60</td>
<td>3</td>
<td>60</td>
</tr>
<tr>
<td>SS-5TiC-55</td>
<td>5</td>
<td>55</td>
</tr>
<tr>
<td>SS-5TiC-60</td>
<td>5</td>
<td>60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Temperature (°C)</th>
<th>Shear rate (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>118.1</td>
<td>354.3</td>
</tr>
<tr>
<td>Binder</td>
<td>60</td>
<td>64.1</td>
</tr>
<tr>
<td>SS-55</td>
<td>60</td>
<td>448.1</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>40.4</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>42.2</td>
</tr>
<tr>
<td>SS-60</td>
<td>60</td>
<td>399.2</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>93.6</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>62.7</td>
</tr>
<tr>
<td>SS-3TiC-55</td>
<td>60</td>
<td>405.4</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>53.8</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>37.6</td>
</tr>
<tr>
<td>SS-3TiC-60</td>
<td>60</td>
<td>340.9</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>107.0</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>60.0</td>
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<tr>
<td>SS-5TiC-55</td>
<td>60</td>
<td>399.8</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>57.9</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>58.8</td>
</tr>
<tr>
<td>SS-5TiC-60</td>
<td>60</td>
<td>1258.6</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>207.9</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>54.5</td>
</tr>
</tbody>
</table>
Fig. 3. Viscosity of PIM feedstocks as a function of shear rate at temperature of 70 °C. (a) 55% solid loading and (b) 60% solid loading.

indicate the flowability of PIM feedstocks, in which, the lower value of viscosity shows the easier flow of feedstock. It is noticeable that the influence of TiC addition strongly depends on the testing condition, i.e. shear rate, temperature and solid loading, as presented below.

3.1. Effect of shear rate

Fig. 3 shows the viscosity of feedstocks as a function of shear rate at 70 °C. As seen, all the feedstocks exhibit a shear thinning or pseudo-plastic behavior, which is common for PIM feedstocks. This could be due to particle orientation and ordering with flow as well as breakage of particle agglomerates with release of fluid binder [3]. Nevertheless, one can notice that the blend composition has a great influence on the rheological behavior of feedstocks. The lower viscosity of feedstocks composed of mono-component SS powder (SS-55 and SS-60) as compared to the composite powders, particularly at lower shear rates, is noticeable. Additionally, the variation of viscosity versus shear rate in log–log scale is almost linear, which is an indicator of feedstock stability. When TiC powder was added to the blend, the resulting composite feedstocks exhibited higher viscosity, particularly at lower shear rates. A non-linear flow behavior of the composite feedstocks, i.e. a sudden drop in viscosity as the shear rate increases, is also noticeable. Similar behavior was observed at higher TiC concentration, particularly at low shear rates and higher solid loading.

To have better understanding about the effect TiC addition on the rheological behavior of feedstocks, the following formula can be used to relate viscosity to shear rate at a given temperature [8]:

\[ \eta = K \gamma^{n-1} \]

where \( \eta \) is the feedstock viscosity, \( \gamma \) the shear rate, \( K \) a constant and \( n \) is the flow behavior index, which is smaller than 1.

The value of \( n \), which indicates the degree of shear sensitivity, gives an important insight about the rheological characteristics of PIM feedstocks. The lower value of the flow behavior index means the more viscosity dependence to the shear rate [11]. Fig. 4 illustrates the effect of TiC addition on the flow...
behavior index ($n$) of feedstocks at 70 °C. Since the logarithmic diagram of $\eta$ versus $\gamma$ showed a non-linear behavior, the $n$ values were calculated at two regimes of low and high shear rates of 200 and 2000 s$^{-1}$. It is apparent that at low shear rates, the flow behavior index decreases with addition of TiC particles, particularly at the higher solid loading. This means that the viscosity is more sensitive to shear rate in the case of composite feedstock as compared to the mono-component SS feedstock. Nevertheless, at the higher shear rate (2000 s$^{-1}$) and at the lower solid loading (55 vol.%), the effect of TiC addition was found to be only marginal. When the solid loading increased to 60%, the influence of TiC is noticeable, somewhat similar to that of the low shear rate results.

3.2. Effect of temperature

Another important characteristic of PIM feedstock is temperature-dependence of viscosity. If the viscosity is very sensitive to the temperature variation, any small fluctuation of temperature during molding results in a sudden viscosity change. This could cause undue stress concentration in the molded part, resulting in cracking and distortion. In addition, a strong temperature-dependence of viscosity dictates smaller pressure transmission to the cavity, thereby promoting the possibility of the formation of shrinkage-related defects. Therefore, it is important to evaluate the dependence of viscosity to temperature.

Pure binder has a viscosity that usually varies exponentially with absolute temperature $T$ [3]. Therefore, the effect of temperature on the viscosity of feedstock was evaluated according to the following equation:

$$\eta = K\gamma^{n-1} \exp\left(\frac{E}{RT}\right)$$

(2)

where $E$ is a material specific constant which is termed the flow activation energy and $R$ is the gas constant. The small values of $E$ show a low sensitivity of viscosity to temperature, thereby minimizing stress concentration, cracks, and distortion in the molded parts. The flow activation energy of tested feedstocks as a function of shear rate is shown in Fig. 5. It is visible that the values of $E$ decrease as the shear rate increases, and that the addition of TiC has a positive influence on lowering the activation energy, particularly at high shear rates. Furthermore, at higher solid loading, the activation energy was found to be higher and the influence of TiC powder was more pronounced.

3.3. General rheological behavior

It is known that a feedstock viscosity with low temperature sensitivity and low sensitivity to shear thinning behavior is desire. In order to establish a general molding index, the model Weir proposed for polymers can be used [16]. In the present work, the influence of TiC addition on the rheological behavior of 316L feedstock was evaluated according to the following equation:

$$\alpha = \frac{n}{E\eta}$$

(3)

In the absence of problems such as jetting or high residual stresses, the higher value of $\alpha$ is desirable since feedstocks with low $n$ values are prone to powder-binder separation. If $\alpha = 1$ is assumed as a hypothetical reference feedstock, the relative $\alpha$ values of examined feedstocks at 70 °C for two reference shear rates of 200 and 2000 s$^{-1}$ and solid loadings of 55 and 60% would have been as what shown in Fig. 6.

Generally, the influence of shear rate on enhancement of the defined index is noticeable. Nevertheless, the higher solid loading led to lower $\alpha$ values, particularly at higher shear rates. Except that of solid loading of 55% and shear rate of 2000 s$^{-1}$, it is apparent that the addition of TiC degrades the rheological behavior. Therefore, it is preferable to use lower solid loading for the composite feedstock compared to the mono-component SS feedstock.
4. Discussion

4.1. Effect of TiC on the viscosity

The results presented so far indicated that TiC addition changes the viscosity of 316L SS PIM feedstocks (Table 4). The influence of TiC on the viscosity was found to be more pronounced at lower temperature and/or higher solid loading. One possible reason for this observation is related to the influence of TiC addition on the particle packing efficiency. The risk of powder agglomeration and powder-binder separation should also be considered. It is known that the variation of viscosity with solid loading, in very simple term, can be expressed by the equation [17]:

$$\eta = \eta_b \left( 1 - \frac{\phi}{\phi_m} \right)^{-2}$$  \hspace{1cm} (4)

where $\eta_b$ is the binder viscosity and $\phi_m$ is maximum solid loading. Factors that influence the ratio $\phi/\phi_m$ have a strong influence on the viscosity and flow behavior of the feedstock. For a given solid loading, an increase in packing efficiency increases $\phi_m$ and thus, the solid fraction ratio ($\phi/\phi_m$)
decreases. Under this condition, a decrease in the viscosity of the feedstock is expected. The results of powder density measurement according to the MPIF Standard [18] showed that addition of TiC improves the tap density of the powder mixture, i.e., the density of SS powder slightly increased from 4.52 g/cm³ (56.5% theoretical) to 4.67 g/cm³ for 3 wt.% TiC (59.5% theoretical) and to 4.73 g/cm³ for 5 wt.% TiC (61% theoretical) addition. It is known that in bimodal powder mixtures with two distinctly different particle sizes, having a high concentration of large particles, the tap density improves as the small particles fill the interstices between large particles [19]. Therefore, it is apparent that the concentration of the TiC in the powder mixture is lower than the peak packing density, i.e., there were enough voids between large particles to be filled with small particles. Therefore, in the case of homogeneous and non-agglomerated mixture of TiC and SS powders, the packing density increases as compared to the mono-component SS powder. This implies higher packing efficiency and thus lower feedstock viscosity [17]. However, as it is apparent in Table 3, a lower viscosity of composite feedstocks was observed at relatively high shear rate and temperature, even though, the effect was not very pronounced. With consideration that TiC addition improves the packing efficiency, this observation could suggest that other factors contributed to the flow behavior. Since the viscosity of feedstocks did not change significantly with TiC addition, the feedstock could be under-load. It is known that under-load and over-load feedstocks are susceptible to powder-binder separation. As Fig. 3 shows, the plot of viscosity versus shear rate in a log-log scale is non-linear for the composite feedstocks. This could be a sign of powder-binder separation that increases the viscosity of the feedstock due to enrichment with the powder, i.e., increasing its solid loading. On the other hand, an inverse relation between the viscosity and packing fraction with agglomerates size has been reported previously [20]. It is known that during mixing a hydrodynamic stress develops [17]. With increasing the shear rate, this hydrodynamic stress could exceed the cohesive strength of the cluster that results in deagglomeration to occur, and thus, the viscosity to drop down. When the temperature and shear rate are sufficiently high, i.e., in the absence of severe powder agglomeration, the higher packing efficiency of the composite mixture leads to lower viscosity (Table 4).

### 4.2. Stability of feedstocks

The variation of viscosity with shear rate represents one of the critical issues to be addressed in PIM. A feedstock is found to be more stable as the variation of viscosity with the shear rate is reduced [5]. Therefore, the stability of PIM feedstocks can be examined by evaluation of the rate of viscosity variation as a function of the shear rate. In Fig. 7, the plots of viscosity variations versus shear rate for the tested feedstocks are shown. Variable shear rate test at isothermal temperatures of 60 and 70 °C were conducted. At relatively high shear rates, when the rate of viscosity variation approaches zero, the feedstocks flow steadily through the capillary die. As the shear rate decreases, a dramatic increase of viscosity can be noticed. Here, the feedstocks may exhibit small regions with different particle concentration that can cause small variations in the viscosity at the microscopic level. In
other words, the heterogeneity of feedstock increases and the particles tend to agglomerate in clusters that entrap a part of the fluid binder \([6]\). Based on this consideration, it is apparent that the composite SS–TiC feedstocks are less stable than the SS feedstocks and this instability increases as the TiC concentration and the solid loading increases. Nevertheless, better stability was obtained at higher temperatures and/or higher shear rates. This difference between the flow behaviors can be explained by looking into the micro-rheology of such feedstocks. The increased instability exhibited by feedstocks made of composite powders (SS–3TiC and SS–5TiC) compared to the feedstocks made of mono-component SS powder, might be related to the segregation of particles of different size within the feedstock. The composite feedstocks made of blended powders of SS and TiC are more prone to concentration gradients in a variable shear regime, compared to the feedstocks made of SS powders. Such concentration gradients result in a viscosity variation, which increases the feedstock instability. By increasing the concentration of TiC, there is a higher risk of concentration gradients and powder agglomeration, particularly when higher solid loading was incorporated. Nevertheless, at higher shear rates, the breakage of agglomerates is more feasible. Therefore, as the shear rate increases, the rate of viscosity variation approaches zero, i.e. the more stability of feedstocks.

Dihora et al. \([5,6]\) introduced the concept of “instability index,” which exhibits the standard deviation of the rate of viscosity change. When this index exceeds unity, the non-homogeneous areas in the feedstock are sufficiently large to produce a significant variation of the bulk viscosity. Under this circumstance, the feedstock can be considered unstable and is subjected to segregation. This means that the lower the instability index, the less the viscosity fluctuations and the separation risk. Fig. 8 shows the influence of TiC addition on the stability of tested feedstocks at different temperatures. At 60°C, the values of instability index are close to or higher than unity (Fig. 8a). Therefore, at this temperature, the feedstocks can be considered unstable. With an increase in temperature, the instability index decreases considerably. However, the instability of SS–TiC composite is still higher than that of mono-component SS feedstocks (Fig. 8b and c). The results also determine that the effect of temperature on the stability is more pronounced for feedstocks with higher solid loading, particularly for those composed of bimodal powder mixtures, i.e. the SS–TiC composite feedstocks.

5. Conclusions

The rheological behavior and stability of feedstocks composed of 316L stainless steel and TiC powders were investigated. The findings are summarized as follows:

- All feedstocks exhibit a shear thinning or pseudo-plastic behavior. A non-linear behavior in the variation of viscosity versus shear rate in log-log scale was observed, particularly in the composite SS–TiC feedstocks with high solid loading.
- The addition of TiC powder increases the viscosity of SS feedstock at low shear rates. As the shear rate increases, this difference is diminished. Whilst at a relatively high shear rate, the viscosity of composite feedstocks was slightly lower than that of the mono-component SS feedstock, owing to higher particle packing efficiency of the composite powder.
- At low shear rates (<500 s\(^{-1}\)), the viscosity of composite feedstocks was found to be more sensitive to shear rate. As the shear rate increased, the effect of TiC addition was marginal at solid loading of 55 vol.%. In contrast, at the higher solid loading of 60 vol.%, the influence of TiC was noticeable.
- At relatively high shear rates (>500 s\(^{-1}\)), the composite feedstocks exhibited lower sensitivity to temperature as compared to the mono-component SS feedstock. This effect was more pronounced at higher solid loading.
- Generally, it is apparent that addition of TiC degrades the rheological behavior of SS feedstock at low shear rates.
- The instability indexes of composite SS–TiC feedstocks were found to be higher than that of the mono-component SS feedstocks. This means that the feedstocks composed of bimodal powder mixture are more instable. Increasing the temperature decreases the instability index considerably, particularly at higher solid loading.

Acknowledgments

The authors are grateful for the support of this work by the Office of Vice President for Research and Technology, Sharif University of Technology. They are also indebted to Dr. Thomas Hartwig from Fraunhofer Institute IFAM (Bremen, Germany) for helpful hints and discussions concerning the binder system and the sample preparation.

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