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Effects of milling and active surfactants on rheological behavior of powder injection molding feedstock①

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[Abstract] The effects of milling and active surfactants on the rheological behavior of powder injection molding feedstock were discussed. The feedstock consists of traditional compositional 90W-7Ni-3Fe powder mixture and a wax based polymer binder. Before mixing feedstock, the powder mixture was milled for different times in a QM-1 high-energy ball mill. The viscosity of the feedstock was examined in a capillary rheometer. The rheological behavior was evaluated from viscosity data. The results show that the feedstock belongs to a pseudoplastic fluid, milling decreases viscosity of the feedstock and the sensitivity of viscosity to shear strain rate. The flowability, rheology and powder loading of this feedstock are improved by milling. Active surfactants such as stearic acid (SA) and di-*n*-octyl-*o*-phthalate (DOP) have great influences on the rheological properties of the feedstock. DOP improves the flowability and rheological stability of the feedstock further.

[Key words] milling; active surfactant; rheological behavior
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1 INTRODUCTION

Powder injection molding (PIM) fits especially for manufacturing complex shaped parts of certain alloys with high performance[1]. However, due to the agglomerated irregular shape, fine particle size, high inner pores and specific surface area of the initial tungsten powder, the viscosity of the corresponding feedstock is very high, the powder loading ratio is very low; in addition, during sintering, the compact has larger shrinkage, which will result in distortion. Milling can improve powder characteristics greatly[2]. Moreover, the milled powder can be used to refine microstructure and enhance consolidation to reduce sintering temperature[3,4], which will decrease compact slumping and distortion induced by liquid phase sintering[5].

In this paper, the initial powder mixture is milled for different times, stearic acid and di-*n*-octyl-*o*-phthalate (DOP) are added to act as an active surfactant. The effects of milling and the active surfactants on the rheological behavior of the feedstock are investigated in detail.

2 EXPERIMENTAL

The metal powders used in the experiments were reduced tungsten, carbonyl iron and nickel powders. The mixture of 90W-7Ni-3Fe (mass fraction, %) powders were subjected to high energy ball milling from 0 to 20 h. Here tungsten ball was used, the mass ratio of ball to powder was 5:1, the rotation speeds of the sun disc and the jar was 200 r/min, the experiments were carried out in a high purity argon atmosphere to avoid oxidation. Then the as-milled powders were mixed with a wax based multi-component binder at 135 ℃ for 2 h to form homogeneous feedstock. And SA and DOP were added to the feedstock as active surfactants. The powder loading ratio was varied from 0.48, 0.49, 0.51, 0.54, 0.55 to 0.57. Finally the viscosity of the feedstock was examined by an Instron 3211 capillary rheometer, which has a radius (R) of 12 mm and a length (L) of 51.0 mm, giving a ratio $L/R = 42.5$, the entry and exit effects could be neglected. The information from capillary rheometry could be used not only to determine viscosity, but also to reveal the stability and homogeneity of feedstock and the extent of powder/binder separation.

3 RESULTS AND DISCUSSION

3.1 Pseudoplastic behavior

For a non Newtonian fluid, there exist $\tau = k\gamma^n$, where τ is the shear stress, γ is the shear rate, k is a constant, and n is a flow exponent. For a pseudoplastic fluid, $n < 1$, the viscosity decreases as the shear rate increases, which is desirable in PIM. Fig. 1 shows the viscosity variation of four kinds of milled (0 h, 5 h, 10 h, 20 h) powder feedstocks with shear rate. With the increase of shear rate, the viscosity decreases, which indicates that the flow exponent is less than one and the feedstock belongs to a pseudo-

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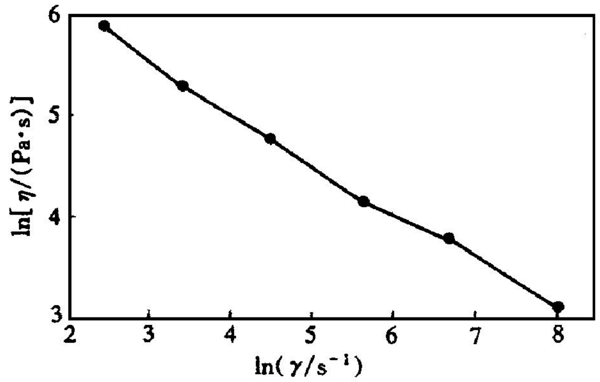

Fig. 1 Viscosity of feedstock vs non-Newtonian shear rate

plastic fluid.

3.2 Variation of viscosity with milling time

Fig. 2 shows the viscosity variation of the feedstock with milling time for the powder loading ratio (φ) of 0.51 and the shear rate of 140.40 s^{-1}. The results show that the viscosity decreases as milling time increases. The decrease in viscosity with milling indicates that the feedstock rheology is improved and the powder loading ratio can be increased. Powder factors have great influences on powder loading ratio and the amount of binder[6,7]. The powder loading ratio or the amount of binder is determined from the tap density of powder. Powder with high tap density will require less binder[8]. The spongy shape of the initial tungsten particles results in a substantial amount of binder being adsorbed to their interior, giving a low critical solid volume fraction. Milling improves powder characteristics. According to a recent theory[9], after milling, the spongy shape of the tungsten powder is deagglomerated, a new alloyed composite powder is formed due to repeated impact and cold welding between the different element powders. The composite powder has lower specific surface area. The decrease in specific surface area will increase the apparent density and tap density of the powder. The deagglomeration of the spongy powder improves the powder morphology. Therefore, sufficient milling is useful to improve the rheological behavior.

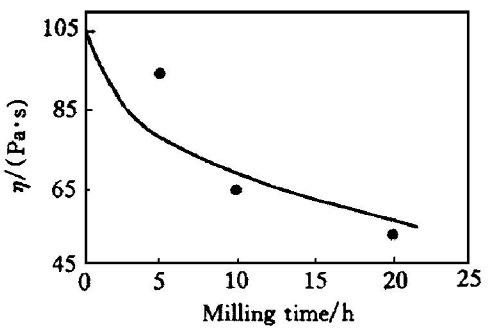

Fig. 2 Viscosity of feedstock varies with milling time

The value of n can be used to estimate the rheological behavior dependence on milling time. Table 1 shows the influence of milling time and shear rate on the flow exponent n.

Table 1 Values n of four kinds of feedstock after milling different times

Shear rate/ s^{-1}	n			
	0 h	5 h	10 h	20 h
42.12	0.642	0.557	0.461	0.545
140.40	0.633	0.572	0.535	0.483
421.20	0.502	0.466	0.511	0.495
1404.01	0.418	0.417	0.482	0.464

The results show that the value of n decreases as milling time increases. The viscosity decreases rapidly as shear rate and milling time increases. Therefore, milling is useful to increase powder loading, enhance flowability and mouldability, and also to form a more homogeneous feedstock. With the increase of milling time, the flow exponent varies slowly as shear rate increases. Therefore, the viscosity of feedstock becomes insensitive to shear rate for the as-milled powders, especially for 10 h of milling.

3.3 Dependence of viscosity on powder loading

Fig. 3 shows an example of viscosity of the milled powder feedstock varies with powder loading. The results show that the viscosity increases nonlinearly. The changes in viscosity with powder loading ratio corresponds to the following empirical formula[10]: $\eta = \eta_b A[(1-\varphi/\varphi_m)]^{-n}$, where η is the viscosity of feedstock, η_b is the viscosity of pure binder, A is a constant, m is an exponent. With the increase of powder loading, the viscosity increases rapidly. Fig. 4 shows the correlation of shear stress with shear rate at a temperature of 408 K and milling time of 10 h. The slop of line expresses the value of n. The results show that the value of n increases as powder loading increases. For the powder loading ratio of 0.48, 0.51, 0.54, 0.57, the values of n are

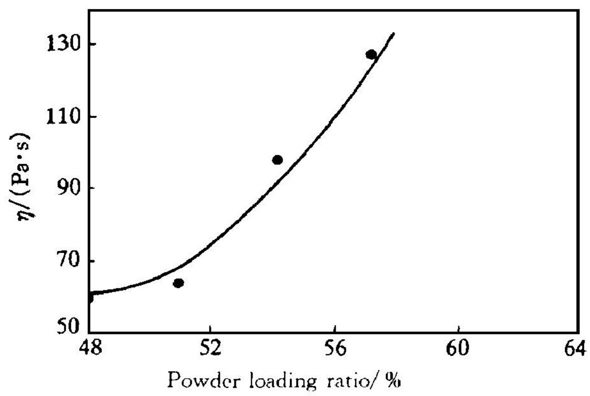

Fig. 3 Dependence of viscosity on powder loading ratio

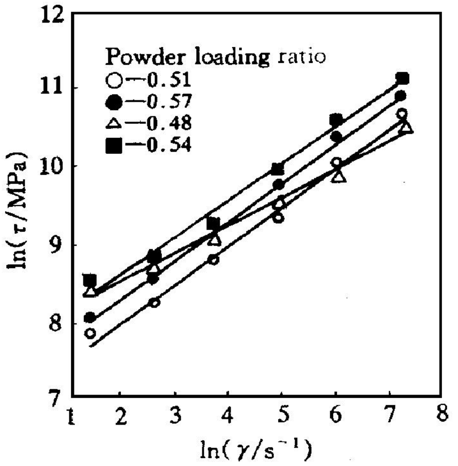

Fig. 4 Correlation of shear stress with shear rate at different powder loading ratios

0.331, 0.461, 0.507, 0.522 respectively. This indicates that the decrease of viscosity becomes slower as shear rate increases.

63.4 Effect of temperature on rheological behavior

The dependence of viscosity on temperature can be expressed by Arrhenius equation[10]

$$\eta(T) = \eta_0 \exp[(E/R)(1/T - 1/T_0)] \quad (1)$$

where $\eta(T)$ is the viscosity at a certain temperature T, E is the activation energy for viscous flow, R is the gas constant, T is the absolute temperature, η_0 is the reference viscosity at the reference temperature T_0. The flow activation energy (E) determines the sensitivity of viscosity to temperature. Large values indicate a high sensitivity of viscosity to temperature change. Fig. 5 illustrates the variation in viscosity with shear rate at temperatures of 393 K, 408 K, 423 K (φ= 0.51, milling time t= 10 h). The viscosity decreases as temperature increases. The difference in viscosity is large at lower shear rate. With increasing shear rate and temperature, the difference in viscosity becomes small, which indicates that the viscosity is more sensitive to shear rate at lower temperature. Fig. 6 is a plot of the natural logarithm of the viscosity of the feedstock against the reciprocal temperature. The flow activation energies (E) can be determined from these plots. For the milled powder

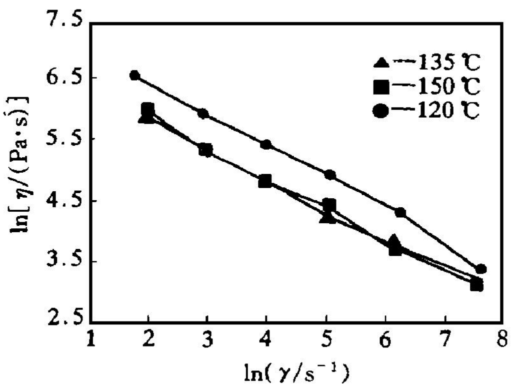

Fig. 5 Variation of viscosity with shear rate

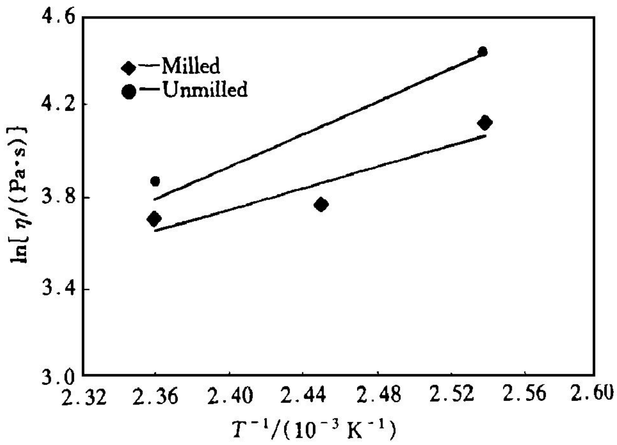

Fig. 6 Plot of natural logarithm of viscosity against reciprocal temperature

feedstock, the flow activation energy (E) is 18.0 kJ/mol. For the un-milled powder, the activation energy is 27.6 kJ/mol. Milling decreases sensitivity of viscosity to temperature, which suggests that the homogeneity of the feedstock can be enhanced by milling.

3.5 Effects of active surfactants on rheological behavior

Fig. 7 illustrates the relationship between the logarithm of viscosity and the logarithm of shear rate with SA and DOP surfactants at temperature of 408 K. At lower shear rate, the viscosity is close to each other. After adding DOP, the decrease in viscosity becomes slower, the flow exponent n increases from 0.461 to 0.539. Therefore, DOP decreases the sensitivity of viscosity to shear rate and enhances the flowability and rheological stability of the feedstock further.

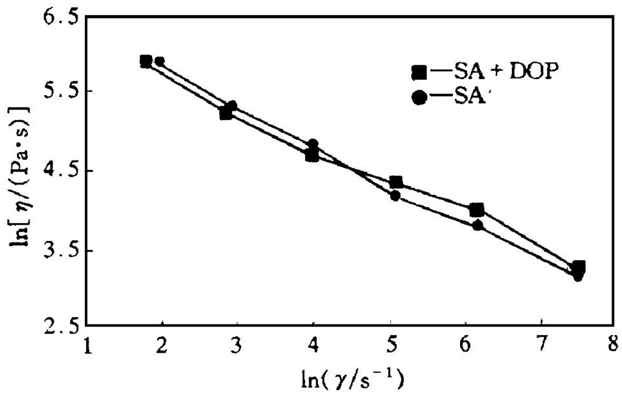

Fig. 7 Plots of logarithm of viscosity with logarithm of shear rate

Fig. 8 shows the influence of temperature on the viscosity of the feedstock with SA and DOP additives. The activated energy is 18.0 kJ/mol after adding SA. With a combination of SA and DOP as surfactants, the activation energy is 23.6 kJ/mol, which is higher than that of the feedstock only with SA, which indicates that addition of DOP increases

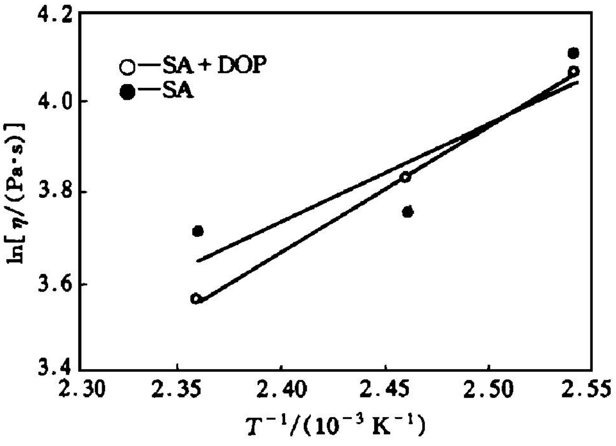

Fig. 8 Influence of temperature on viscosity of feedstock with different additives

the sensitivity of the viscosity to temperature, that is, the viscosity decreases greatly as temperature increases. By adding DOP, the flowability of the feedstock is obviously enhanced.

4 CONCLUSIONS

1) Milling of the powder mixture decreases the viscosity of the feedstock. After milling, the variation of viscosity to shear rate and temperature is less sensitive. Sufficient milling is useful to improve the rheological behavior of the feedstock.

2) DOP additive enhances the rheological stability to shear rate and the flowability of the feedstock at lower temperature further.

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