

Dispersive and rheological properties of Mg-PSZ feedstocks for precision powder injection molding

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The effects of various surfactants on the dispersive and rheological properties of ZrO_2 and MgO mixtures in heptane, melt wax and feedstocks were investigated. Several properties of the mixtures were tested to reveal the stabilization in various non-polar binder systems. The feedstocks which contained the surfactant (FP1) with an ester function group produced the highest critical solid loading (56.6 vol%) and least dimensional variation ($<0.07\%$) among five formulations, either choosing from SA, FP1 or NZ38 surfactant. The sintered PSZ (partially stabilized zirconia) samples could reach 99% theoretical density (T.D.) and an average fracture strength of 345 MPa. Dual surfactants, containing FP1 and SA, were also tested, resulting in feedstocks better in rheological properties and homogeneity. The surfactant FP1 apparently improved the homogeneity of the powders in the feedstocks, and consequently refined the properties of parts in the stages of injection molding and sintering.

Key words: Mg-PSZ, surfactant, feedstock, dispersion, homogeneity.

Introduction

Ceramic injection molding (CIM) has been developed in combination with plastic and powder technologies in the past two decades. CIM could quickly fabricate high-performance ceramic parts because of its manufacturing advantages, especially of near-net-shape processing capability. In addition to dimensional accuracy, the advantages also include the ease of complex shape manufacturing, and suitability for mass production [1, 2]. By the integration of these processing advantages, this method can appropriately reduce manufacturing cost.

Zirconia is a high temperature material with excellent thermal insulation properties. One of the ZrO_2 formulations, MgO-doped partially stabilized zirconia (Mg-PSZ), is especially corrosion resistant to basic slag in the continuously casting process of molten steel. For the past two decades, zirconia materials (PSZ and tetragonal zirconia polycrystals, TZP) have been greatly improved in toughness [3, 4]. The transformation toughening occurring at ambient temperature has made these materials very attractive in several structural applications.

The homogeneity and dispersive properties of feedstock are important to IM parts. Lenk and Krivoshchepov [5] used chloroform as a model medium to study the adsorption and viscosity of ceramic powder in a non-polar media. The dielectric constant of chloroform is comparable to that of paraffin wax, which is often used

as a carrier in ceramic feedstocks. This result revealed that the more the adsorption density, the more effective is the reduction in the yield stress. Liu and Tseng [6] studied the rheological behavior of non-aqueous ZrO_2 suspensions, and showed that the shear viscosity and yield stress decreased appreciably with a surface coverage by the pre-adsorption of an effective surfactant.

The presence of powder agglomeration caused a remarkable change in the powder-packing structure. The agglomerated particles suspended in a suspension would cause an increase in viscosity at a given shear rate. Irregular powder packing reduces the volume fraction of free flowing solvent because the solvent is entrapped within the agglomerates [7]. If a surfactant is adsorbed at a solid-liquid interface to reduce the particle interaction, it is expected to increase the effective solid loading and reduce the viscosity of the feedstock [6, 7].

One of the important aspects in ceramic injection molding (CIM) is the kneading process, and this has been pointed out by many reports [8-10]. Wu and Wei [8] reported that the different kneading sequences also affected the homogeneity of a feedstock. Homogenous feedstocks prepared by a designed kneading process showed a better fracture strength and Weibull statistics. Although the previous paper has investigated the effects of surfactants on Al_2O_3 feedstocks, little dispersive information is available on a surfactant for MgO/ ZrO_2 powder mixture to prepare Mg-PSZ feedstocks [1-6]. In this study, we intend to establish effective methods to understand the dispersive properties of the powders in non-polar solvents and wax systems, in order to select effective surfactants in terms of the properties of the dispersion, mixing, kneading, and dimensional control.

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Experimental Procedure

Materials and material processing

– Materials

The raw materials used in the study include ZrO_2 powder, MgO powder, polypropylene (PP), paraffin wax (PW), surfactants and n-heptane solvent. The ZrO_2 powder (EF) was a commercial powder supplied by Z-tech Co, USA. The MgO powder was also a commercial powder made by Shin-Mei Co., Taiwan. Polypropylene (PP, Formosa Plastic, Taiwan) and Paraffin wax (PW, Nippon Serio, Japan) were used as backbone-polymer and plasticizer, respectively. Stearic acid (SA, Nacalai Tesque, Japan), hydro-stearic acid (HSA, TCI, Japan), FP1 (ICI, England) and NZ38 (Ken-React, USA) were used as surfactants.

D-134 (Dai-Ichi Kogyo Seiyaku Co., Ltd., Japan; 2 wt%) was added to EF zirconia slurry. D-134 as a dispersant is an ammonium salt homopolymer with a 2-propenoic acid group. The slurry was milled for 24 h. The time of milling process was through 23 h, then MgO was added. The slurry was dried at 100°C by a Z-blade machine for 4 h. The dried powder mixture was called “MH”.

The solid content in the feedstocks of Mg-PSZ was kept within 53–57 vol% according to the results by a torque rheometer. The polymeric ingredients were used in a mass ratio of PP:PW:surfactant = 25:70:5.

The notations, SA, FP1 and NZ38 in feedstocks, mean that only a single surfactant was added to the feedstocks, and the amount of the surfactant in the feedstock was 0.8 wt% on powder. The notations of FP1/SA and NZ38/SA mean two surfactants had been added to the feedstocks, and the amount of each surfactant was 0.4 wt% based on the powder mixture.

– Kneading and Granulation

A twin Σ -type kneader (Ray-E Manufacture Co., Tainan, Taiwan) was used with a mixing bowl of 650 ml and operated at a rate of 35 rpm. In the beginning of the kneading process, the MgO/ ZrO_2 powder mixture was preheated to 175°C for 1/2 h in the kneader. PP was first added to the mixture. After kneading for 60 min, PW and SA were added and the temperature of the kneader was reduced to 160°C and held for 30 min. The dough-type mixture was then granulated in the mixing bowl as the temperature of the bowl was reduced to 70 °C.

– Injection Molding

An injection molding machine (CDC9000 SM50, CHEN HSONG, Co.) was operated at injection pressures of 40–40–69–54 MPa. The barrel temperatures were set at 165–165–170–170°C and the temperature of the hot sprue was set at 160°C. The mold temperature

was maintained at 50°C. The mold was designed to have twin cavities with dimensions of 4.00×5.15×49.95 mm³.

– Debinding and Sintering

An organic solvent n-heptane could extract soluble PW and SA from IM parts. The solvent debinding was conducted at 50°C and held for 2.5 h in n-heptane. More than 80 wt% of soluble binders could be extracted. After drying, the samples were subjected to thermal debinding in an air furnace according to the previous conditions [8]. Subsequently, the samples were heated at 10 K·min⁻¹ to 1600°C or 1700°C, then sintered for 1 h.

Characterization

– Sedimentation experiment

The suspensions for sedimentation experiments were prepared by mixing 54 ml heptane or melted wax at 70°C with a specified surfactant and 1.5 g EF, MgO powder, or a mixture of EF/MgO (MH). The suspension of melted wax was stirred at 70°C for 40 min. The sedimentation height ratio of H_t/H_0 was measured after 7 days. The states of the supernatant were categorized into clear, scattering and cloudy, which corresponded to various degrees of dispersion.

– ζ -potential measurement

The electrophoretic mobility of the suspended particles was measured by a Zeta-Meter (ZM3+, USA) instrument. The applied potential was 6000 V, and the run time was 20 s. The suspensions were always dispersed in an ultrasonic bath (Model RK103, Bandelin Sonorex, Berlin, Germany) for 30 min. Suspensions with a solid content of 100 ppm were prepared in order to measure the electrophoretic mobility, and then the electrokinetic (ζ -) potential was calculated.

– Torque and capillary rheometry

A torque rheometer was assembled from a kneader (PBV-01, Japan), a torque transducer (NEC San-Ei mold, Japan), and a signal amplifier (NEC AS2103, Japan). A capillary rheometer (Rosand RH7, England) was used and operated at 170°C with extrusion rates from 200 to 1500 s⁻¹. The diameter of the capillary was 1 mm.

– Material properties

The green density of the IM samples could be obtained by a water replacement method (Archimedes' method). The fracture strengths of the IM sintered bodies were measured by a four-point bending test method according to ASTM372-73. The sintered samples were surface ground by a 325-mesh diamond wheel following this standard. A four-point fixture with upper and lower spans of 10 mm and 30 mm was mounted on a dynamic testing instrument (MTS810, MTS., USA) for the four-point bending test.

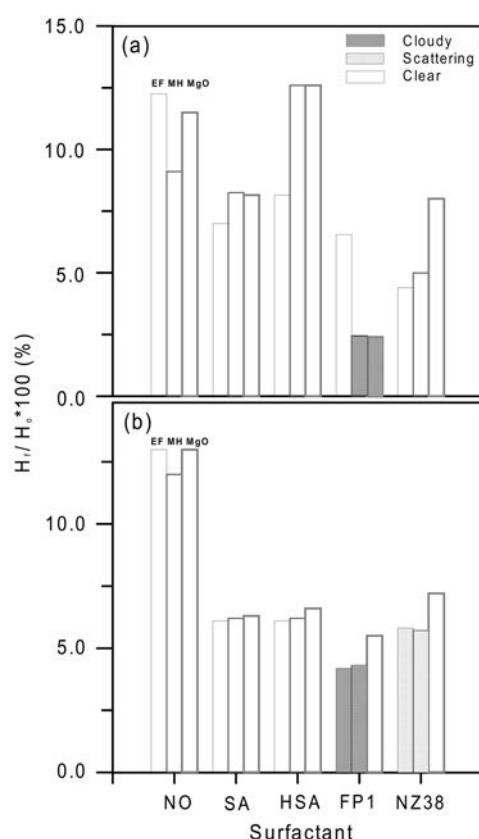


Fig. 1. Sedimentation results of the EF, MH and MgO powders with different surfactants in (a) heptane (22°C); (b) melted wax (70°C) for 7 days.

Results and Discussion

Dispersive Properties in Organic Solvent

Three types of powder were tested either in heptane or a melted wax solution. The sedimentation results are reported in Fig. 1, which shows that the H_t/H_o of MH and MgO powders with FP1 surfactant is the lowest (2.5%) and the supernatant is in a cloudy state. The suspensions of the rest changed from a scattered state to a clear state after sedimentation for 7 days. Four surfactants are not effective for the dispersion of EF powder, and their solutions are clear after 7-day sedimentation. It implies that no surfactants are adsorbed onto the surface of the EF zirconia powder in heptane.

Figure 1(b) gives the results depicting the sedimentation results of EF, MH, and MgO in melted wax with different surfactants. Without any surfactant in the suspension, EF particles settle rapidly and the supernatant of the melt wax is clear. The sedimentation height ratio H_t/H_o of the EF suspension with FP1 surfactant decreases below 5% and has the best defloculated effect in the melted wax system.

The suspensions of melted wax with SA and HSA were all in a clear state. Liu and Tseng [6] reported that HSA containing a carboxyl group (-COOH) and a hydroxyl group (-OH) is better at the dispersion of

ZrO₂ powder in a toluene suspension than SA with a -COOH group. However, the dispersive results of EF and MgO with HSA or SA are nearly identical in the wax suspension.

NZ38 is only effective at dispersing suspensions of EF and MH, but not MgO. Both EF and MH suspensions show scattering in the supernatant after sedimentation for 7 days. Hunt et al. [11] pointed that their coupling agent with an alkoxy functional group reduced the viscosity of their feedstock. The surfactant adsorbed on powder changes from physical to chemical adsorption at 120°C for 24 h. This implies the coupling agent of NZ38 molecules has a better wetting effect /or dispersion effect for the ZrO₂ powder. In the present study, the sedimentation of NZ38 feedstock is not the best after 70°C for 7 days.

All suspensions with FP1 show a relatively low H_t/H_o and a higher packing density. It is the best dispersion agent for a wax-based suspension. These suspensions also appeared to be cloudy. FP1 containing an ester group was easily adsorbed on ZrO₂ powder.

As shown in Fig. 1(b), MgO powder with any of the other surfactants cannot be dispersed well and the suspensions always show a clear state after the test. This result predicts that the functional groups of the surfactants except FP1 cannot modify a MgO surface in the wax-based suspension. The strong basic surface of MgO does not easily adsorb these surfactants, except FP1.

Figure 2 shows the sedimentation height as a function of MgO content in suspensions of an EF/MgO mixture with FP1 dispersant. When the amount of MgO increases, the EF suspension with 5% FP1 increases its sedimentation height in the wax, implying a reduction of the dispersive effect. The state of a wax suspension transformed from cloudy to scattering with 3% of MgO. As the content of MgO in the wax become $\geq 5\%$,

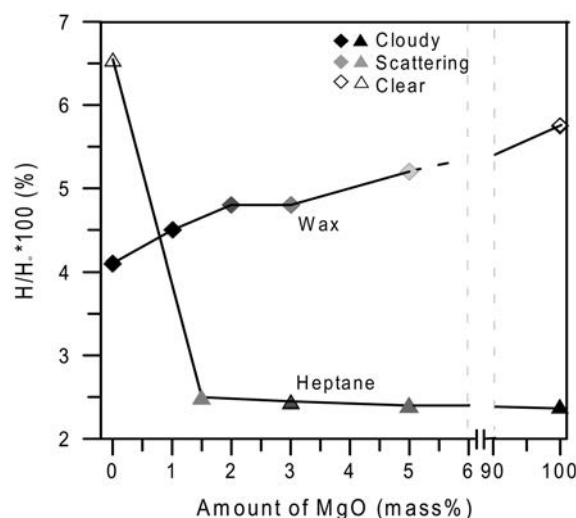


Fig. 2. Sedimentation height ratio of EF/MgO mixture suspension as a function of the amount of MgO in the melted wax and heptane containing 5 mass% FP1.

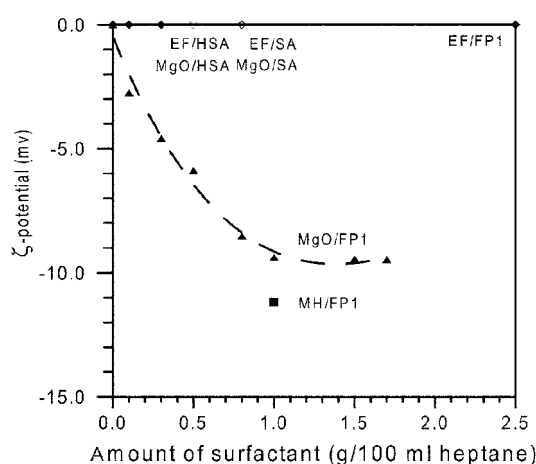


Fig. 3. ζ -potential of the powders (EF, MgO and MH) as a function of the amount of surfactants (SA, HSA and FP1).

the suspension of EF/MgO coagulates and settles rapidly. The suspension containing only MgO shows a clear state. The sedimentation behavior of the heptane-based suspension is the opposite. When the amount of MgO increases, the sedimentation height ratio reduces in heptane-suspensions.

The electrokinetic (ζ -) potential of powders was measured with different surfactants in heptane, as shown in Fig. 3. Most significantly MgO and MH powders turn from neutral to a strongly negative ζ -potential with FP1 in heptane. However, the ζ -potential of EF and MgO powder is zero in the heptane suspensions with SA, and HSA. This evidence strongly suggested that the FP1 dispersant is anionic when dissolved in heptane, and can be adsorbed on the positively-charged MgO surface, but not adsorbed on neutral ZrO_2 surface. The ζ -potential of 10 mV implies that electrostatic repulsive is available on the MgO or MH powders. The repulsive force between MgO particles offers good dispersion in the heptane solution. This also explain why the supernatants with HAS and SA were clear in the heptane suspensions, since no repulsive force was available.

Previous results appear to show that the dispersion of EF/MgO suspensions containing FP1 in the wax are inconsistent with those that in heptane. The adsorption of protons and hydroxyl groups on powder surfaces essentially shows an acid-base reaction [12]. Meguro and Esumi [13] reported that the order of electron donicity is as follows: $\text{MgO} > \text{Al}_2\text{O}_3 > \text{ZrO}_2 > \text{SiO}_2$. Stearic acid which is a carboxylic acid shows the exception of an unsaturated carbon-to-carbon double bond. Moreover, according to the report by Moloney et al. [14], the interaction of the carboxylic acid dispersant in polar conditions is strongly adsorbed with Lewis base sites on the ceramic powder in a non-polar organic media. FP1 is polyester also containing carboxylic acid functional group bonded with CH_3 . Therefore, MgO is the most preferred ceramic for the adsorption of FP1 in heptane. The reason is that MgO easily donates the

proton to produce a base site. FP1 shows Lewis acid tendency and to adsorb on MgO due to a dipole acid-base reaction, but not on ZrO_2 which shows most likely acidic sites. Thus, FP1 cannot adsorb on ZrO_2 to reach a dispersive state.

However, in the wax-base system, the FP1 adsorbs on ZrO_2 surfaces to form a cloudy state, but not on MgO (Figs. 1 and 2). There are two possible reasons. First, the carboxylic acid group of FP1 is difficult to accept e^- in melting wax. In other words, FP1 become "cationic". Secondly, according to Fowkes' [15], paraffin wax is neutral and a non-polar carrier. FP1 tends to dissolve in the melting wax but still shows Lewis base characteristics, which in turn easily reacts with ZrO_2 in weak acidic conditions in the wax. The MgO with strong Lewis base characteristics is difficult to adsorb FP1 in the wax.

Kneading Behavior of Feedstocks

Figure 4 shows the state of the mixtures with SA and SA/FP1 additions as a function of kneading time with a torque rheometer tested at 175°C . The torque profiles show an increase of the torque value over the first few minutes, because the polymer mixture changes from a

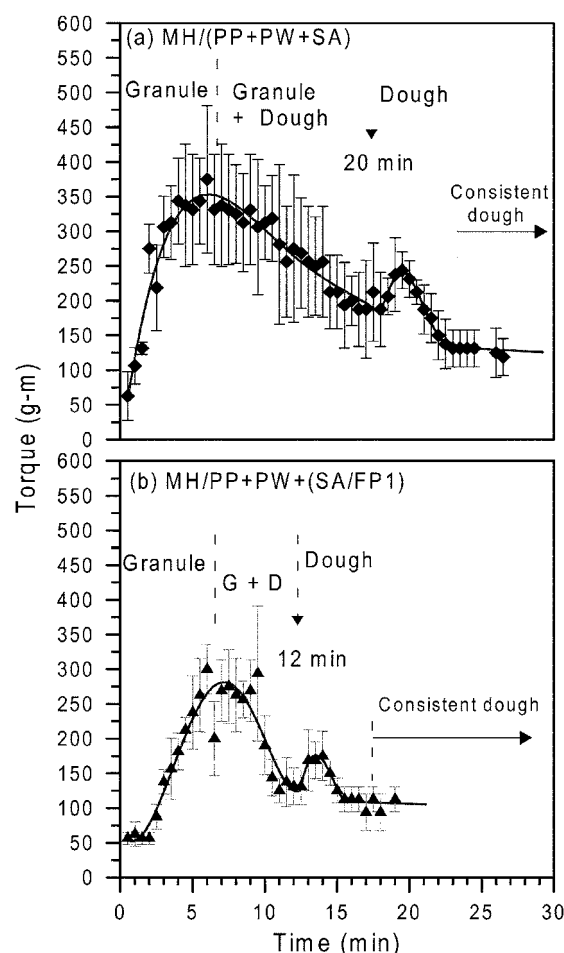


Fig. 4. Torque of the mixtures with (a) SA or (b) SA/FP1 as a function of kneading time.

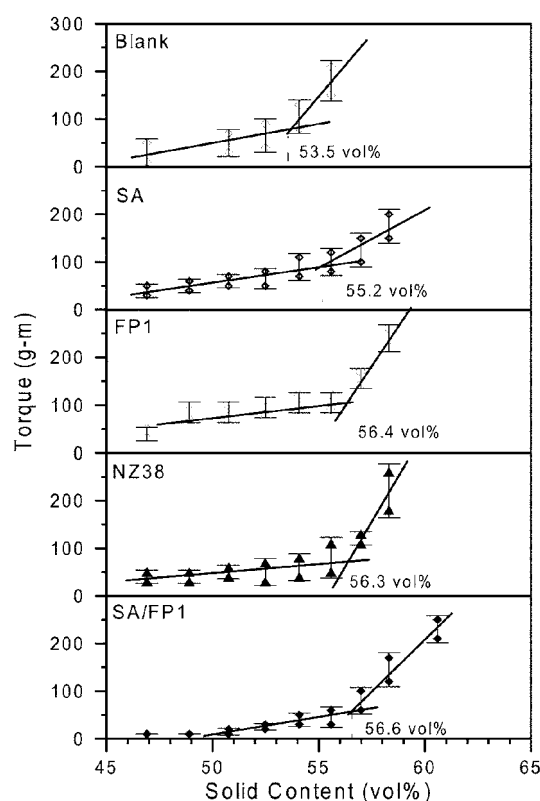


Fig. 5. Torque as a function of solid content of the MH formulations with surfactant either blank, SA, FP1, NZ38, or SA/FP1.

solid state to a melted state whilst mixing with the powder. The first peak is called the loading peak when the powder and binder are mixed to produce a granular state. The second peak is called the fusion peak when the binder is wetted and coated on the powder to get a dough state. The feedstock with SA surfactant needs 20 min to get to the fusion peak and produces a consistent dough in 5 min. The SA/FP1 feedstock takes 12 min to achieve fusion and produce a dough state in 3 min. These results imply that FP1 can quickly wet powder.

Cheremisinoff [16] reported that a resin or polymer having insufficient lubricity is characterized by a high loading peak and a short fusion time. By contrast, a compound with excessive lubrication will produce slippage and a long fusion time. The torque at the loading peak and the fusion time with SA feedstock is greater than that of SA/FP1. The results of feedstock with powder are different to those with compounding by a polymer. The SA/FP1 feedstock has a low loading

peak and a shorter fusion time. Besides, the final torque value is lower (120 g-m) for SA/FP1, resulting in a shorter kneading period.

German and Bose [17] predicted an appropriate solid loading by torque rheometer measurement and were able to get reproducible feedstocks for CIM. The effects of powder loading in the feedstocks on the final torque value are shown in Fig. 5. The critical solid loading of Mg-PSZ feedstock containing no surfactant is 53.5 vol%. As SA is added, a well lubricating property is usually observed in powder feedstocks. However, the critical solid loading of the SA-feedstock is less than 56 vol%. The critical solid loading which contained surfactant either FP1, NZ38, or SA/FP1 is >56 vol%. These results imply that the feedstock with FP1 or NZ38 surfactant may have a better dispersive effect.

According to German's suggestion [18], a solid loading of 54 vol%, about 2.5 vol% less than the critical loading of feedstocks, was selected for the following kneading process. The time needed to achieve a consistent dough after adding all the ingredients is shown in Table 1, which shows that the shortest of 3 min is measured for the feedstock with FP1/SA surfactant. The time needed for kneading of the other PSZ feedstocks is more than 10 min. The most likely explanation for this is that the feedstock of FP1/SA has the best wetting effect compared with the other surfactants in the same kneading process.

Rheology Properties of Feedstocks

It is accepted that a minimum viscosity of a feedstock also shows a better dispersive effect. Lin and German [18] reported that a feedstock with a low apparent viscosity and a low flow yield stress was preferred for the prevention of molding failures of alumina parts. A well-dispersed condition of the powder

Table 1. Time needed for kneading to get consistent dough (ref. Fig. 4)

Surfactant	Time
SA	20 min
FP1/SA	3 min
FP1	14 min
NZ38/SA	16 min
NZ38	20 min

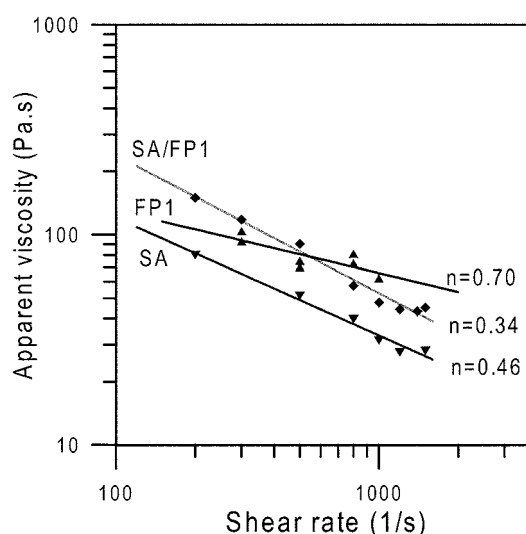


Fig. 6. Relationship of the viscosity of three MH feedstocks to shear rate tested at 170°C.

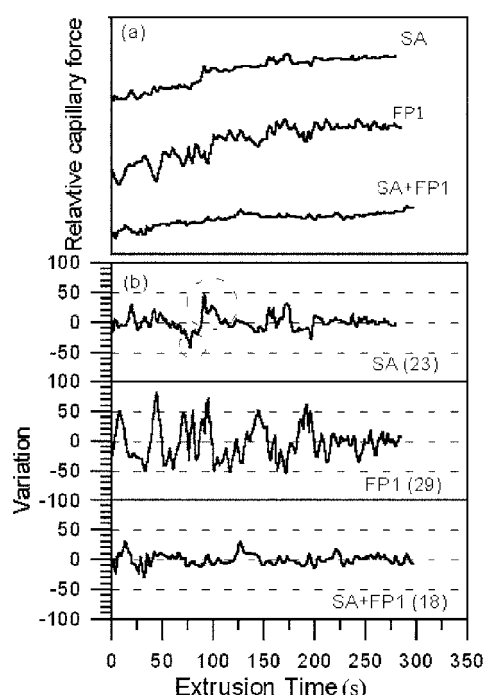


Fig. 7. (a) Capillary force plotted against extrusion time in the feedstocks of SA and FP1/SA, (b) after baseline subtraction.

in the blends results in a low apparent viscosity and consistent rheological properties, which are represented by a flow index n and yield stress. Figure 6 shows the viscosity of different feedstocks as a function of shear rate at 170°C. In the range of 100–1500 s^{-1} , the viscosity of the feedstock with SA reduces to <100 Pa.s. The flow index is 0.46. The viscosity of the feedstock with FP1/SA is higher but the flow index is 0.34 less than that of the feedstock with SA. The viscosity of FP1 is below 100 Pa.s and the flow index is 0.3. The rheological behavior of FP1 feedstock is not really stable. Generally, stearic acid is often referred to as a processing aid or lubricant. When the SA concentration is reduced, the feedstock increases the friction force which results in an increase of viscosity. When FP1 replaces same of the SA, the viscosity rises. This implies that the FP1 is a good dispersant, but not a good lubricant.

German and Bose [17] reported that a homogenous feedstock would have a small variation of capillary pressure versus testing time. If the binders are less homogenous in the feedstock, the rheological behavior of a melted feedstock changes dramatically when the feedstock flows through a capillary. Figure 7 shows the force variation plotted against extrusion time of the feedstocks with SA, FP1 or FP1/SA. The centerline in Fig. 7(a) is fitted by 4th order polynomial equation with the least square derivation as a minimum. The data in Fig. 7(b) is obtained by subtracting the values of the centerline from the experimental data of Fig. 7(a). The standard deviation of the feedstock with SA ($\sigma=23$) is higher than that with SA/FP1 (18) and with FP1 (29). The Variation-of- force vs. time (V-t) curve of a feedstock with FP1/SA is less scattered than that of SA and FP1. These results show that the feedstock with FP1/SA is more homogenous, although the previous viscosity results appear to show that the feedstock with SA shows a lower viscosity than that with FP1/SA. The force-time testing method is sensitive to show the homogeneity of feedstocks.

Sintered Properties

After solvent debinding, thermal debinding and sintering, the dimensional change of IM and sintering samples were measured. Table 2 reveals dimensional and density changes as a function of surfactant types in green and sintering bodies. The dimensional variation of sintered parts at 1600°C and 1700°C is similar. The standard deviation of the dimension of green parts is less than 0.07%. Among these, the NZ38 case has large variations in every processing stage.

Table 3 shows the density of green and sintered bodies which contained different surfactants. The sintered densities of five specimens are all in the range of $99\pm0.2\%$ theoretical density (T.D.). The FP1/SA sample shows a smallest deviation, 0.31% (1600°C) or 0.4% (1700°C) in sintering density than the others.

Figure 8 shows the fracture strength of sintered bodies prepared with different surfactants in sintering conditions of 1600°C/1 hr or 1700°C/1 hr. The average fracture strength is about 230 MPa for SA, FP1/SA and

Table 2. Dimensions and the standard variation of sintered body with different surfactants

Mg-PSZ	Properties	SA	FP1/SA	FP1	NZ38/SA	NZ38
Green body	Length (mm)	49.65±0.01	49.71±0.01	49.72±0.03	49.70±0.02	49.77±0.04
Sintered body at 1600°C/1 hr	Length (mm)	40.78±0.03	40.52±0.02	40.23±0.05	40.51±0.01	40.31±0.05
Sintered body at 1700°C/1 hr	Length (mm)	40.79±0.03	40.24±0.01	40.57±0.02	40.07±0.02	40.43±0.08

Table 3. Density of green and sintering bodies contained different surfactants

Mg-PSZ	SA	FP1/SA	FP1	NZ38/SA	NZ38
Green density (g/cm^3)	3.23	3.12	3.17	3.23	3.32
Sintered density and variation (σ) at 1600°C for 1 hr	5.68±0.55%	5.67±0.31%	5.68±0.75%	5.69±1.2%	5.67±2.6%
Sintered density and variation (σ) at 1700°C for 1 hr	5.68±0.59%	5.68±0.40%	5.68±0.56%	5.69±0.63%	5.68±2.0%

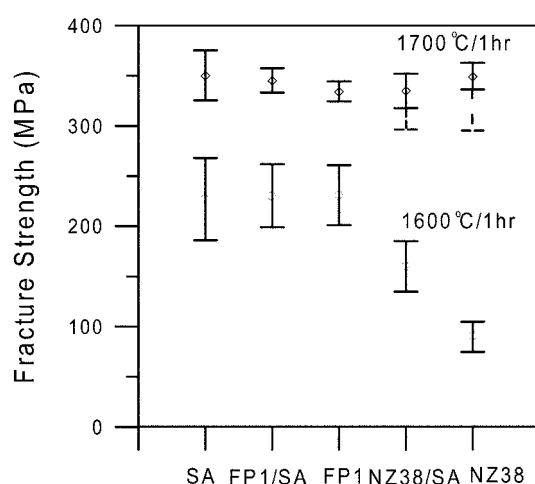


Fig. 8. Fracture strength of Mg-PSZ with specified surfactant by sintering at 1700°C or 1600°C for 1 hr.

FP1 at a sintering temperature 1600°C for 1 hr. FP1/SA shows a smaller variation of fracture strength than the others. Sintered samples of NZ38 and NZ38/SA show an apparently lower fracture strength than the others. The surfaces of sintered parts NZ38 or NZ38/SA contained several fissures which might cause the reduction of the fracture strength. Song and Evan [19] reported that one of the reasons for producing surface fissures was that green parts were held above their softening point in solvent debinding or in annealing. In the present research, green parts containing NZ38 or NZ38/SA hardly show fissures in the stages of solvent and thermal debinding. The possible reasons and stages causing surface fissures are the inhomogeneous phase transformations of ZrO_2 phases due to quicker heating on the surface than the interior of the parts. Therefore, as the sintering rate above 1000°C changes from 10°C/min to 5°C/min the cooling rate for the case of 1700°C/1 h, and the fissure crack within sintered parts with NZ38 or NZ38/SA disappears.

In Fig. 8, the average fracture strength of five samples is about 345 MPa. However, FP1/SA shows a smaller variation of the fracture strength than the others. The sintering parts of NZ38 and NZ38/SA show a greater variation. The reason is possibly due to the difference in the formation of processing defects. The states of porosity and large defects in samples with SA or NZ38 reduce their fracture strength.

Conclusions

The effects of four surfactants for the injection molding of Mg-PSZ feedstocks have been investigated. The results show:

(1) The surfactant FP1 was adsorbed on MgO surfaces and showed a dispersive function for MgO/ ZrO_2 powder by an electrostatic repulsion mechanism. In combination with the effects of dispersion and lubrication through the addition of FP1/SA, we can prepare

a Mg-PSZ feedstock with better molding properties.

(2) The observation of the sedimentation height of suspensions showed a better dispersion effect of ZrO_2 powder with FP1 in wax and heptane systems. From the results of capillary variation-of-force vs. time (V-t), FP1/SA shows a smaller variation than those with SA or FP1.

(3) The dimensional variation of IM parts in the five surfactants showed a significant difference. The sintered samples had a fired density 99% T.D. with a standard deviation of 0.5-3% T.D.

(4) The average fracture strength of the Mg-PSZ sintered at 1700°C for 1 h was 345 MPa. The samples with FP1/SA showed a smaller variation of fracture strength than that of the others.

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