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Effect of particle packing on extrusion behavior of pastes

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Two powders with different average particle sizes and size distributions were blended in various proportions. The influence of powder mixing on extrusion behavior of pastes containing a water-based binder has been examined. The bimodal mixed stainless steel powder exhibits a low extrusion pressure, small amount of binder and high green density when the mixing fractions of large and small particles are approximately equal. With regard to the mixing of zirconia and stainless steel powders, a similar result has been found, but the mixing fraction of powder corresponding to the optimal packing is shifted to stainless steel-side. In order to improve the extrudability of pastes, it is effective to mix two powders with a large difference in particle size. © *2000 Kluwer Academic Publishers*

1. Introduction

Extrusion is a suitable plastic forming method for fabricating a variety of shapes with constant cross section, not only for flat shapes, but also for structural shapes, such as I-sections, channels, pipes and tubes [1]. In particular, the extrusion of viscous pastes containing a particulate or powder and liquid phase (mainly binder) has become increasingly important because of the advantages of formation of products at low temperature and pressure [2]. At present, paste extrusion as an important near net shape forming process is used in many industrial fields, such as ceramics, chemical, food and pharmaceutical [3].

For paste extrusion, it is desirable to minimize the amount of binder required to achieve suitable rheological characteristics, reduce extrusion pressure and improve the green density of an extrudate. Benbow *et al.* [4] have pointed out that the flow properties of pastes are closely related to those of their constituent binder. Binder is a very important component as a rheology modifier and plays the key role in paste extrusion. Extrusion becomes possible only if sufficient binder has been added to overcome the interparticle friction between the powder particles and the friction forces between the die walls and the powder [5]. However, binder is a temporary vehicle used for packing powder into a desired shape and then retaining the shape of an extrudate without distortion after extrusion. Since binder has to be removed prior to densification, a larger amount of binder results in a longer debinding step with possible flaw formation and larger sintering shrinkage. On the other hand, a decrease in extrusion pressure is of benefit to dies and extruder, more importantly, it would be helpful to avoid or reduce liquid migration [6], phase separation or drainage phenomenon [7] under pressure. Moreover, a high green density is desired in order to obtain a higher sintered density [8] and to minimize sintering shrinkage [9].

Numerous investigations have concerned the influence of particle size distribution on packing configuration and green density in dry powder beds [10–22]. By distributing small particles into the interstices between large particles in an appropriate proportion and particle size ratio, the porosity is reduced and dense packing is obtained. Some observations have been made in packed beds containing liquid phase, such as slip casting [23–25]. Benbow and Bridgwater [26] have described the importance of particle size distribution to properties of dried and fired extrudates, and Blackburn and Bohm [5, 27] have examined the effect of powder packing on paste extrusion parameters.

In the present work, the influence of bimodal particle size distribution on extrusion pressure, amount of binder required and green density of extrudates has been mainly investigated. In addition to mixing the same kind of powders (such as stainless steel powders) with different particle sizes, the mixing effect of different kinds of powders (stainless steel and zirconia powders) was also examined. Two extrusion methods, conventional axisymmetric rod extrusion and multi-billet extrusion which has been developed to fabricate composite pipes [28–30], were used. The purpose of this investigation was to improve the extrudability of pastes, including reducing extrusion pressure, minimizing amount of binder and raising green density by means of mixing two powders with different average particle sizes and size distributions in various proportions.

2. Experimental procedure

A commercially available zirconia powder with an average particle size of 0.7 μm (Wako Pure Chem., Osaka, Japan) was used. Three kinds of water atomized 304L stainless steel powders were obtained from Nippon Atomized Metal Powders, Tokyo, Japan, and their average particle sizes were 5, 9 and 36 μm , which are denoted as SUS(A), SUS(B) and SUS(C), respectively. The particle size distributions of the raw powders and some blends are shown in Fig. 1. The size distributions of the raw powders were measured using a laser- scattering size distribution analyzer (LA-910, Horiba, Tokyo), while those of the blends were calculated from the original particle size distribution data and mixing fractions of two or three powders in the blends. An aqueous solution of water-soluble polymer, hydroxypropyl methylcellulose (HPMC, Shin-Etsu Chem., Tokyo) was used as a binder. The HPMC content in the binder was 15–21 vol%.

The raw powders and powdered HPMC were premixed for 20 min in an electric mortar mixer (ANM1000, Nippon Ceram. Sci., Tokyo), and then distilled water was added and further mixed until homogeneous pastes were obtained (about 30 min). In order to dissolve HPMC in water completely, the mixed pastes were wrapped in plastic bags and stored under saturated humidity below 10°C for 24 h.

The extrusion experiments were performed in two ways: conventional rod extrusion and multi-billet extrusion (MBE) methods. In the rod extrusion, a die with a hole diameter of 4.7 mm (corresponding extrusion ratio $R = 10$), semi-angle of 90° (flat die) and length of the die land of 10 mm was used. The MBE process is based upon co-extruding different kinds of particulate pastes, joining them in chambers and finally obtaining a desired extrudate by means of dies. It can be used to form multilayer composite pipes, and the details have been described in the previous paper [30]. In this investigation, only single layer pipes (equivalent to the inner layers of two-layer pipes) were extruded by the MBE process. Two billets located in different container holes were extruded simultaneously and flowed into an inner chamber, where the pastes were joined and then a pipe was formed and flowed out from the exit of the inner die with the help of a mandrel. The wall thickness of pipes was 1.2 mm, which corresponds to an extrusion ratio of $R = 8.7$. The extrusion experiments were carried out at room temperature without lubrication of the dies, and a constant extrusion speed (ram speed) of 0.167 mm·s^{-1} was used throughout. The green density was calculated from the weight and dimensions of an extrudate after drying at room temperature for 48 h.

3. Results and discussion

3.1. Effect of particle packing on extrusion pressure

Fig. 2 shows the variation of extrusion pressure with content of binder for forming the stainless steel pastes by the rod extrusion method. It can be seen that the pressure is very small regardless of the types of powders at a binder content of about 57.5%. With a decrease in binder content, the pressure gradually rises. The increasing rate of the pressure depends on the particle size and its distribution. Where the binder content is greater than 49%, the pressure for extruding the SUS(A) pastes is lower than that for extruding the SUS(C) pastes. This could be due to a wider particle size distribution of the SUS(A) powder (Fig. 1). When the binder content is below 49%, however, the pressure for the SUS(A) pastes becomes larger, and it rises rapidly with decreasing binder content. This results from a larger specific surface area for the smaller sized SUS(A) powder, which gives rise to an increase in interparticle

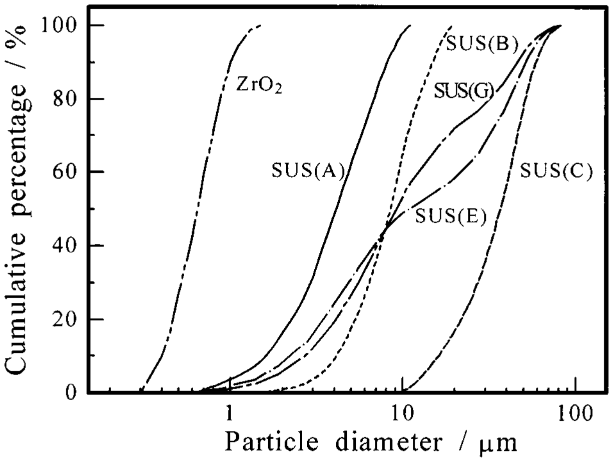

Figure 1 Particle size distributions of zirconia and stainless steel powders. SUS(E) and SUS(G) are binary (SUS(A) and SUS(C)) and ternary (SUS(A), SUS(B) and SUS(C)) mixtures respectively with equal mixing proportions.

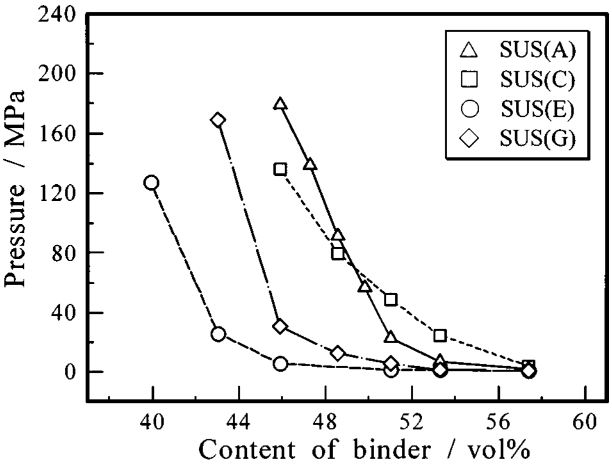

Figure 2 Variation of extrusion pressure with binder content for extrusion of the stainless steel pastes by the rod extrusion method. Extrusion ratio $R = 10$.

frictions. With regard to the mixed powders, SUS(E) and SUS(G) (obtained from mixing the SUS(A) and SUS(C), and SUS(A), SUS(B) and SUS(C) respectively in equal mixing proportions), the extrusion pressures are lower than those of the SUS(A) and SUS(C) powders for the same binder contents. Furthermore, the binder content at which the pressure starts to rise rapidly with decreasing binder content is shifted to a lower one. This is because the mixed powders possess wider particle size distributions and denser packing (will be described in Section 3.3), thus the slip and rearrangement of particles, which are necessary in extrusion process, occur easily. By comparing the two mixed powders SUS(E) and SUS(G), it is found that the binary mixed SUS(E) has a lower pressure level than the ternary mixed SUS(G). As expected, this is the result of a compositional deviation of the SUS(G) powder with respect to optimal trimodal packing. As seen in Fig. 1, although SUS(E) and SUS(G) powders possess the same range of particle sizes, their particle size distributions are different. There exist more intermediate particles in the SUS(G) powder, hence resulting in the difference in extrusion pressure.

The dependence of extrusion pressure on binder content for extrusion of pipes by the MBE process is given in Fig. 3. The variations of the curves are similar to those in Fig. 2. But the pressure values for forming pipes are larger than those for forming rods under the condition of the same binder contents, even though the extrusion ratio of the former (8.7) is less than that of the latter (10). This is caused by a stronger restraint to paste flow and larger shear surface areas (e.g., dead zone interfaces, surfaces of tools with which pastes are contacted) in the MBE process. It is found from Fig. 3 that the mixing proportion of large and small powders in the bimodal mixed powder SUS(A + C) produces a significant influence on the extrusion pressure. The pressure level at $V_f = 0.5$ (V_f: mixing fraction of fine powder) is lower than that at $V_f = 0.3$. Furthermore, the difference in pressure is gradually increased as binder content is reduced. The relationship between extrusion pressure and mixing fraction of fine powder for extrusion of pipes is presented in Fig. 4. It is shown that the extrusion pressure depends on the mixing proportion of large and small powders, even for the same binder content. The pressure change with fraction of fine powder is particularly apparent for the pastes with a lower binder content. For example, for the pastes with a binder content of 46%, the pressure at $V_f = 0.8$ is about ten times of that at $V_f = 0.5$. Moreover, when the fraction of fine powder is raised to $V_f = 1$, the pressure is too large to be able to extrude soundly because of occurrence of a drainage phenomenon [7] (that is, the binder is separated from pastes or water is separated from the binder) under large pressure. It can be seen that the pressure reaches a minimum value near $V_f = 0.5$ (i.e., the mixing fractions of large and small powders are almost the same). It suggests that the adjustment of particle size distribution by mixing powders with different average particle sizes has an important effect on the decrease in extrusion pressure during paste extrusion.

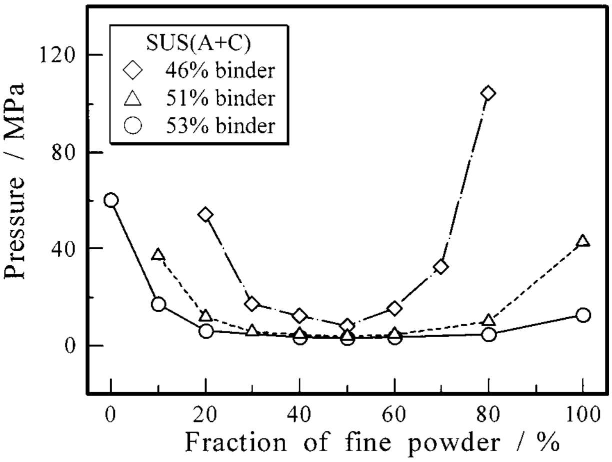

Figure 4 Relationship between extrusion pressure and mixing fraction of fine powder for extrusion of the mixed powders of SUS(A) and SUS(C), extruded by the multi-billet extrusion process.

With regard to the mixed powder consisting of the ZrO_2 and SUS(C), the change in extrusion pressure is shown in Fig. 5 as a function of the mixing fraction of fine powder V_f (ZrO_2 powder here). For the same binder

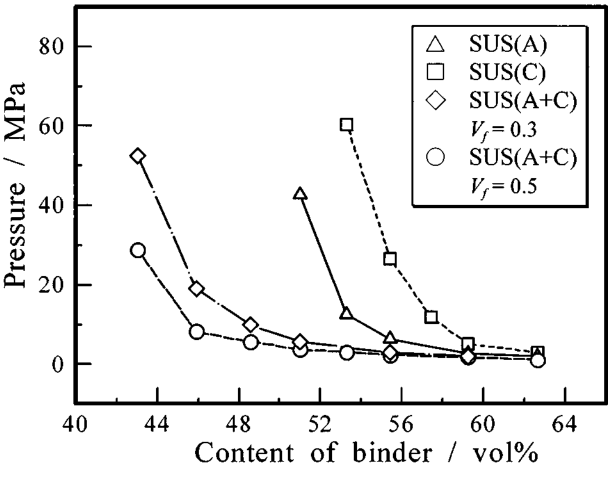

Figure 3 Dependence of extrusion pressure on binder content for extrusion of pipes by the multi-billet extrusion process. $R = 8.7$. V_f: mixing fraction of fine powder.

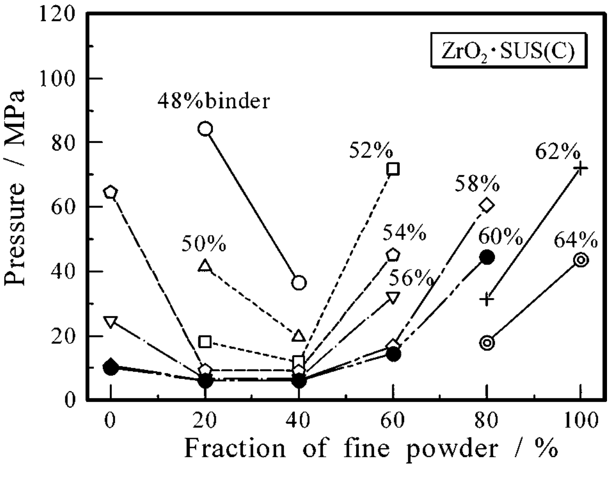

Figure 5 Change in extrusion pressure as a function of the mixing fraction of ZrO_2 powder. The ZrO_2·SUS(C) pastes containing different amounts of binder were extruded by the multi-billet extrusion method.

content, the pressure rises as V_f increases in the range of $V_f > 0.4$. It is reversed at $V_f < 0.4$, and thus the pressure reaches the lowest value at $V_f = 0.4$. This result indicates that the composition where the lowest pressure occurs is shifted to coarser component (i.e., stainless steel-side), in comparison with the binary mixture of stainless steel powders. This is attributed to a larger particle size difference between two components in ZrO_2·SUS(C) than in SUS(A + C), and it will be discussed in Section 3.4. Besides, just as the blends of the SUS powders, the effect of V_f on the extrusion pressure of the ZrO_2·SUS(C) powder becomes less when more binder is added.

3.2. Binder content necessary for extruding soundly

In order to provide pastes adequate rheological characteristics so as to allow plastic forming during extrusion, it is necessary to add sufficient binder to powders. Fig. 6 illustrates a comparison of the minimum amounts of binder required to achieve sound extrudates for five kinds of stainless steel powders. In the case of either rod extrusion or MBE, the necessary binder content lowers slightly with decreasing average particle size of powder. Nevertheless, it is noted that the binder contents required for extruding the mixed powders SUS(G) and SUS(E) are greatly reduced in comparison with the singular powders. In particular, the binary mixed powder SUS(E) exhibits a lower binder content than the ternary mixed powder SUS(G) as a result of the difference in particle size distribution or packing configuration of particles.

As stated above, paste flow takes place during extrusion on condition that the paste has adequate viscosity or rheology. With an increase in packing density, a lower viscosity is achieved for a given solids loading or binder content in the paste [31]. This suggests that less binder is required for extruding at a given viscosity. Consequently, the decrease in binder content due to powder mixing is believed to be the result of improvement of packing density (see Section 3.3). On the other hand, from the view point of plastic forming, the small particles existing in interstices between large particles is also advantageous to slip and shear of particles during extrusion, hence improving the extrudability of pastes.

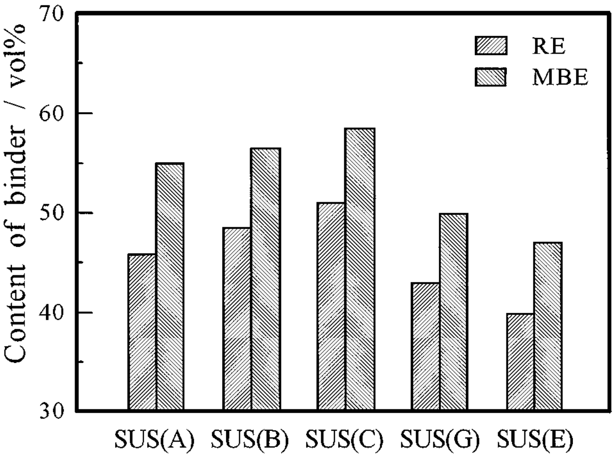

Figure 6 Comparison of the minimum amounts of binder required to extrude soundly. RE: rod extrusion, and MBE: multi-billet extrusion.

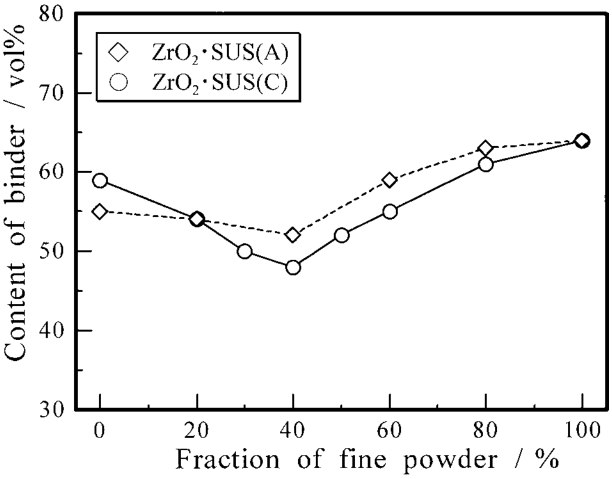

Figure 7 The minimum amount of binder necessary to form sound pipes. The binder content reaches a lowest value near $V_f = 0.4$.

As shown in Fig. 6, the binder content required for the MBE is higher than that for the rod extrusion no matter which SUS powders are used. This arises from the differences in paste flow and stress distribution, which depend on the deformation or flow conditions decided by extrusion methods. In addition, in terms of the forming principle of the MBE, in an extruded pipe there are two joined sections where pastes have to flow to and join soundly. Accordingly, a better paste flowability is necessary for forming pipes by the MBE process than for forming rods by the conventional axisymmetric extrusion method.

Fig. 7 gives the relationship between the minimum amount of binder needed to extrude soundly and the mixing fraction of fine ZrO_2 powder for extrusion of pipes when the ZrO_2·SUS(A) and ZrO_2·SUS(C) powders are used. In both cases, the binder content reaches a minimum near $V_f = 0.4$. This is in good agreement with the pressure change shown in Fig. 5. When small sized ZrO_2 particles are added to the matrix of SUS powders and fill the interstices between the SUS particles, a denser packing results in a decrease of binder content. At $V_f > 0.4$, however, it is necessary to add more binder to powders as V_f rises. This arises from a larger specific surface area in the ZrO_2 powder. Furthermore, the difference in binder content between ZrO_2·SUS(A) and ZrO_2·SUS(C) powders in the range of $V_f > 0.2$ is also related to the specific surface areas of the powders. But an exception at $V_f < 0.2$ is the consequence of poor binding between large SUS(C) particles, because of the larger average particle size and interstices when the SUS(C) powder is used as a matrix. This indicates that more binder is necessary for the ZrO_2·SUS(C) powders at $V_f < 0.2$ in order to obtain sound extrudates.

3.3. Green density of extrudates

Fig. 8 shows the green density variation of extrudates with composition for three kinds of mixed powders: SUS(A + B), SUS(A + C) and SUS(B + C). The extrudates prepared from mixed powders display higher

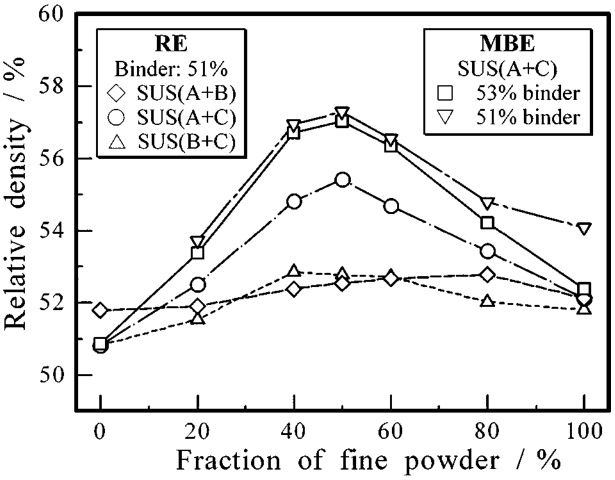

Figure 8 Green density variation of extrudates with composition for the binary mixed stainless steel powders, formed by the rod extrusion (RE) and multi-billet extrusion (MBE) methods.

green densities compared to those from singular powders. This arises from denser packing because of broadening the particle size distributions of powders. It is shown that the increase in density due to powder mixing depends to a large extent on the particle size ratio (D_L/D_S) between large and small powders. Concerning the extrudates obtained by the rod extrusion method, there is less effect for mixing SUS(A) with SUS(B) because the particle size ratio of the two constituent powders is very small ($D_L/D_S = 1.8$). However, the SUS(A + C) powder where the D_L/D_S value is large (7.2) gives a significant packing benefit, and the relative densities of extrudates are significantly increased. When the mixing fraction of fine powder is near 0.5, the green density reaches a maximum value. For the pipes formed by the MBE process, they show a result similar to the rods. Nevertheless, for pastes with the same binder content, there is a higher density for the extrudates formed by the MBE process than for those by the rod extrusion method. This appears to be attributed to a larger extrusion pressure in the MBE process as described before, and further work will be required.

Fig. 9 shows the relative density as a function of binder content for the $ZrO_2 \cdot$SUS(C) mixed powder. The densities of extrudates decrease nearly linearly with increasing binder content for all mixed powders with different mixing proportions. It is seen that the relative density tends to be the highest at compositions of $V_f = 0.4$. Except for $V_f = 0.4$, the green density level of extrudates decreases with an increase in mixing fraction of finer ZrO_2 powder, even though the density is related to binder content. This is the result of a much smaller average particle size (larger specific surface area) and rougher surfaces of particles for the ZrO_2 powder, which significantly influence the particle packing.

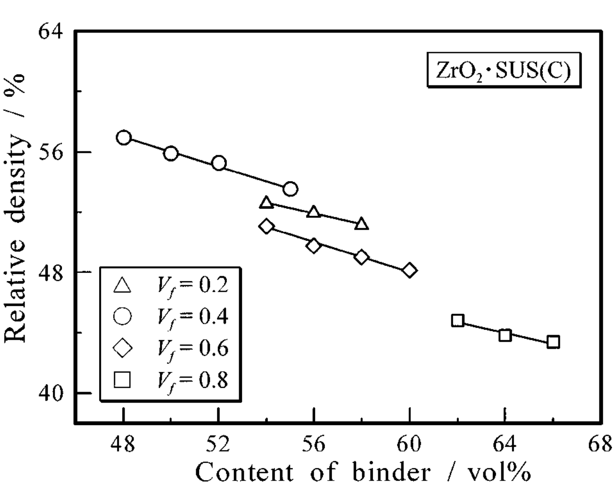

Figure 9 Variation of relative densities of $ZrO_2 \cdot$SUS(C) pipes with binder content.

3.4. Comparison with Furnas's binary packing model

From the foregoing results, it has been found that the bimodal mixed stainless steel powder containing approximately the same proportion of large and small particles ($V_f = 0.5$) exhibits the smallest extrusion pressure and minimum amount of binder in both rod extrusion and MBE process. In addition, the extrudate has the highest green density. Similar results were observed in the mixed powder composed of zirconia and stainless steel particles, but the mixing fraction of the fine powder corresponding to the densest packing was shifted to $V_f = 0.4$. These coincide with the observations on extrusion of alumina pastes reported by Benbow *et al.* [26] and Blackburn *et al.* [5]. Benbow *et al.* [26] found that a minimum liquid content to saturate powder and maximum density of dried extrudate were achieved in the region of 0.4–0.5 fine component.

For a binary mixing system of large and small particles, several models [10–14, 18] have been developed to describe the relationship between particle size distribution and packing characteristics. Among these models, the Furnas model [10, 12] has been successfully applied to a system consisting of two sizes of spherical particles. When the smaller particles of the two particle sizes fill exactly the interstices created by the larger particles, an optimum packing is realized. Fig. 10 illustrates a comparison between the predicted green density and the

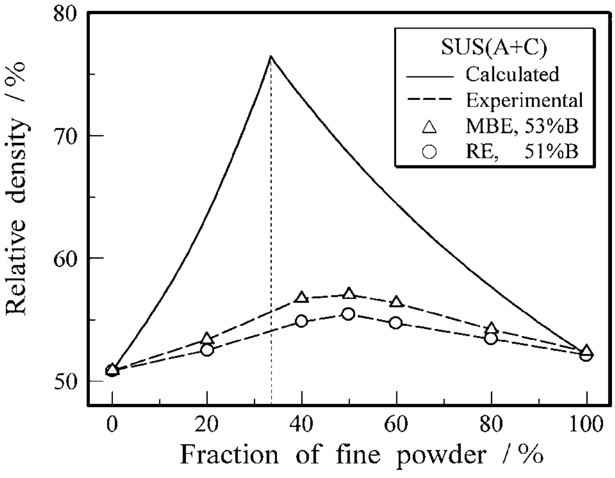

Figure 10 Comparison between the predicted green density according to the Furnas model and the experimental values for binary mixtures of SUS(A) and SUS(C) powders.

experimental values for binary mixtures of the SUS(A) and SUS(C) powders. According to the Furnas model, a relative density of 76.5%, which is much higher than the experimental values, occurs at $V_f = 0.335$. It is evident that the large discrepancy between the calculated and experimental densities is mainly related to packing configuration of mixed powders. The packing configuration has a significant influence not only on the packing density, but also on the composition where the densest packing occurs. It is considered that the difference in packing configuration between the packing beds in the present investigation and the Furnas model is concerned with some factors as follows.

(a) The particle size ratio is far smaller than that of the Furnas model (essentially infinite). For example, $D_L/D_S = 1.8$, 4, 7.2, and 51.4 for SUS(A + B), SUS(B + C), SUS(A + C) and ZrO_2·SUS(C) powders, respectively. Many studies [11, 14, 22] have shown that packing density of mixed powder lowers when the particle size ratio decreases. Furthermore, German [32] has suggested that a small particle size ratio results in shift of the composition corresponding to an optimal packing toward small particle axis. Hence, small particle size ratio is perhaps one of the important factors moving the composition of the optimal packing from $V_f = 0.335$ predicted by the Furnas model to $V_f = 0.4$–0.5 of this investigation. Moreover, it is just the particle size difference that the composition is shifted from $V_f = 0.4$ for ZrO_2·SUS(C) to $V_f = 0.5$ for SUS(A + C), because the former has a larger particle size ratio (51.4) than the latter (7.2).

(b) Powder system alone was taken into account in Furnas's model. In this investigation, however, the presence of large amounts of binder may cause the change in packing configuration because of particle-particle interactions. It has been found that interparticle forces have a significant effect on particle packing in slurry or suspension [33, 34]. In the case of the powder-binder system examined in the current work, capillary forces generated by liquid bridges are believed to be the main component of interparticle forces [35]. Schubert [36] has pointed out that capillary forces can play an important role or may even be decisive for the flow behavior of fine bulk materials and the agglomeration of granular materials. Consequently, it is believed that capillary forces and viscous action of binder in the powder-binder system may exert some influence on particle packing.

(c) Packing behavior of powder beds is often dealt with under the same conditions such as a certain pressure [11, 19, 22]. In paste extrusion process, the binary mixtures with various mixing proportions display different extrusion pressures even for pastes with the same binder content (Figs 4 and 5).

(d) The powders used here have irregular shapes and continuous particle size distribution. Moreover, the zirconia particles present rough surfaces, which influence slip and shear between particles during extrusion.

4. Conclusions

The change in particle size distribution or packing configuration by mixing large and small powders has an important effect on the extrusion behavior of pastes. The effect of powder mixing depends to a large extent on the mixing proportion and particle size ratio between large and small powders. The bimodal mixed stainless steel powder exhibits a low extrusion pressure, small amount of binder and high green density when the mixing fractions of large and small particles are approximately equal. A similar result has also been observed in the mixed powder composed of zirconia and stainless steel powders, but the mixing fraction of the smaller zirconia powder corresponding to the optimal packing is shifted to 0.4. It is shown a larger difference between the experimental value and predicted density by the Furnas model due to the difference in packing configuration. On the other hand, in the multi-billet extrusion process, a higher extrusion pressure, larger amount of binder or better paste flowability are necessary compared to the conventional axisymmetric rod extrusion method, which results from the differences in deformation or flow conditions of pastes. Furthermore, a higher green density can be achieved in the multi-billet extrusion than in the rod extrusion.

References

1. C. ALDEA, S. MARIKUNTE and S. P. SHAH, *Adv. Cem. Based Mater.* **8** (1998) 47.
2. H. BOHM and S. BLACKBURNS, *Brit. Ceram. Trans.* **93** (1994) 169.
3. Y. CHEN, A. BURBIDGE and J. BRIDGWATER, *J. Am. Ceram. Soc.* **80** (1997) 1841.
4. J. J. BENBOW, S. BLACKBURNS and H. MILLS, *J. Mater. Sci.* **33** (1998) 5827.
5. S. BLACKBURNS and H. BOHM, *Chem. Eng. Res. & Design, Trans. IChemE* **71** (1993) 250.
6. A. S. BURBIDGE, J. BRIDGWATER and Z. SARACEVIC, *ibid.* **73** (1995) 810.
7. Z. CHEN, K. IKEDA, T. MURAKAMI and T. TAKEDA, *J. Mater. Sci.* **35** (2000) 2517.
8. J. ZHENG and J. S. REED, *J. Am. Ceram. Soc.* **72** (1989) 810.
9. J. A. MANGELS and R. M. WILLIAMS, *Am. Ceram. Soc. Bull.* **62** (1983) 601.
10. C. C. FURNAS, *U. S. Bur. Mines Rep. Invest.* No. 2894 (1928).
11. A. E. R. WESTMAN and H. R. HUGILL, *J. Am. Ceram. Soc.* **13** (1930) 767.
12. C. C. FURNAS, *Ind. Eng. Chem.* **23** (1931) 1052.
13. H. E. WHITE and S. F. WALTON, *J. Am. Ceram. Soc.* **20** (1937) 155.
14. R. K. McGEARY, *ibid.* **44** (1961) 513.
15. R. L. COBLE, *ibid.* **56** (1973) 461.
16. G. L. MESSING and G. Y. ONODA JR., *ibid.* **61** (1978) 1.
17. *Idem., ibid.* **61** (1978) 363.
18. R. F. FEDORS and R. F. LANDEL, *Powder Technol.* **23** (1979) 225.
19. J. P. SMITH and G. L. MESSING, *J. Am. Ceram. Soc.* **67** (1984) 238.
20. F. ZOK, F. F. LANGE and J. R. PORTER, *ibid.* **74** (1991) 1880.
21. R. M. GERMAN, *Metall. Trans. A* **23** (1992) 1455.
22. J. ZHENG, W. B. CARLSON and J. S. REED, *J. Am. Ceram. Soc.* **78** (1995) 2527.
23. P. A. SMITH and R. A. HABER, *ibid.* **75** (1992) 290.
24. S. TARUTA, N. TAKUSAGAWA, K. OKADA and N. OTSUKA, *J. Ceram. Soc. Jpn.* **104** (1996) 47.
25. G. TARI, J. M. F. FERREIRA, A. T. FONSECA and O. LYCKFELDT, *J. Euro. Ceram. Soc.* **18** (1998) 249.
26. J. J. BENBOW and J. BRIDGWATER, *Chem. Eng. Sci.* **42** (1987) 753.
27. S. BLACKBURNS and H. BOHM, *J. Mater. Sci.* **29** (1994) 4157.
28. Z. CHEN, J.-X. XIE, T. MURAKAMI and K. IKEDA, *J. Jpn. Soc. Technol. Plast.* **36** (1995) 1003.

29. Z. CHEN, T. MURAKAMI and K. IKEDA, *ibid.* **37** (1996) 1328.
30. Z. CHEN, K. IKEDA, T. MURAKAMI and T. TAKEDA, *J. Am. Ceram. Soc.* **83** (2000) 1081.
31. R. M. GERMAN, in "Reviews in Particulate Materials, Vol. 1," edited by A. Bose, A. Lawley and R. M. German (Metal Powder Industries Federation, Princeton, New Jersey, 1993) p. 109.
32. *Idem*., in "Particle Packing Characteristics" (Metal Powder Industries Federation, Princeton, New Jersey, 1989) p. 144.
33. D. I. LEE, *J. Paint Technol.* **42** (1970) 579.
34. B. V. VELAMAKANNI and F. F. LANGE, *J. Am. Ceram. Soc.* **74** (1991) 166.
35. M. C. COELHO and N. HARNBY, *Powder Technol.* **20** (1978) 201.
36. H. SCHUBERT, *ibid.* **37** (1984) 105.

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