Drainage phenomenon of pastes during extrusion

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The effects of elemental powder characteristics, binder content and its composition, as well as some additives on pressure change and drainage phenomenon of pastes during extrusion have been mainly investigated. The pastes consisted of a powder, zirconia or stainless steel, and a water-based binder, an aqueous solution of water-soluble polymer (hydroxypropyl methylcellulose). The drainage phenomenon has been found in extrusion of the stainless steel pastes with lower binder contents, while the zirconia pastes show a small probability of drainage in the range of the binder contents used in this investigation. It is shown that broadening particle size distribution by mixing powders with different average particle sizes has a significant effect on decreasing extrusion pressure and restraining occurrence of the drainage phenomenon, thus improving the extrudability of pastes. It is effective to increase the binder content in pastes, raise the mixing fraction of HPMC in binder and add plasticizer like glycerol, in order to reduce occurrence of the drainage phenomenon during extrusion of the stainless steel pastes.

1. Introduction

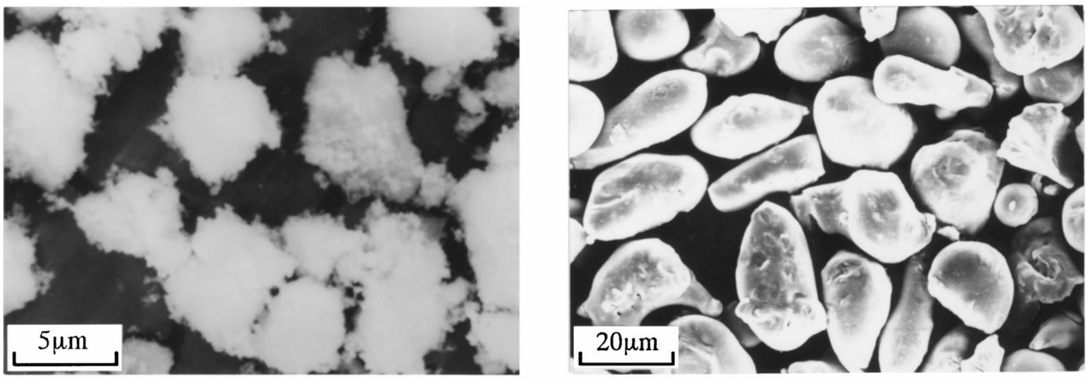
Extrusion has found widespread application in manufacture of elongate products with various cross section shapes, because of its related technical (for example, heavy deformation can be obtained due to high hydrostatic pressure) and economic (capable of manufacturing continuously) advantages. In particular, the extrusion of pastes containing a particulate or powder and liquid phase is an important processing technique in many industrial fields, such as ceramics, chemical, food and pharmaceutical [1]. At present, it has also been used for fabricating metallic [2] and composite materials [3–5].

Since many powders (e.g., ceramics) are nonplastic when mixed with water alone, it is necessary to mix additives, such as binder and plasticizer, into powders, thus providing adequate rheological characteristics so as to allow plastic forming during extrusion and retain the shapes of extrudates after extrusion. In order to avoid long-time debinding operations of extrudates (like debinding of thermoplastic polymeric materials used in powder injection molding frequently), water-based binder systems are often used in extrusion of pastes [6–14]. In the previous papers [5, 15], a new method named "multi-billet extrusion" has been developed to fabricate metal-ceramic composite pipes. This technique is based upon simultaneous extrusion of different kinds of pastes, in which an aqueous solution of water-soluble polymer was used as binder. However, when the binder content is lower, a phase separation may take place under a large extrusion pressure applied during extrusion [15]. In this paper, this phase separation is called "drainage phenomenon", and it implies that the binder is separated from pastes (powder-binder mixtures) or water is separated from the binder in extrusion process.

It is quite evident that it is necessary to reduce or restrain occurrence of the drainage phenomenon during extrusion, so as to ensure normal extrusion operation, the same rheological characteristics of pastes and homogeneity of extrudates. In the work reported here, the effects of powder particle size, size distribution and surface state, binder content and its composition, as well as some additives (plasticizer, lubricant) on the drainage phenomenon have been mainly investigated.

2. Experimental procedure

In the present work, zirconia and stainless steel were used as the examples of ceramic and metal, respectively. The zirconia powders were commercially available high purity powders with average particle sizes



(a) (b)

Figure 1 SEM photographs of (a) ZrO_2(A) (0.7 μm) and (b) SUS(C) (36 μm) powders.

of 0.7 μm (Wako Pure Chem. Co., Osaka, Japan) and 32 μm (Kojundo Chem. Lab. Co., Ltd., Saitama, Japan), which are denoted as ZrO_2(A) and ZrO_2(C) respectively. Two kinds of water atomized 304L stainless steel powders were obtained from Nippon Atomized Metal Powders Co., Tokyo, Japan, and their average particle sizes were 5 μm (SUS(A)) and 36 μm (SUS(C). Fig. 1 shows the scanning electron micrographs of the ZrO_2(A) and SUS(C) powders. The zirconia powder exhibits rough surfaces, and fine particles are agglomerated, while the stainless steel powder possesses smooth surfaces even though the particle shapes are irregular. Moreover, a bimodal mixing powder SUS(A+C) was prepared by mixing the SUS(A) and SUS(C) powders with an equal mixing ratio. As for the binder, an aqueous solution of water-soluble polymer, hydroxypropyl methylcellulose (HPMC, Shin-Etsu Chem. Co., Tokyo) was used. The viscosity of 2%HPMC aqueous solution was 4560 mPa·s at 20°C. The mixing fraction of HPMC in binder was varied in the range of 15–30 wt%. In addition, as an example, small amount of glycerol (plasticizer), stearic acid and oleic acid (lubricant) were involved to improve the plasticity or lubricity of pastes when required.

The raw powders and HPMC were premixed, and then continued to mix after added the other additives if necessary. Distilled water was added to the above mixtures and further mixed until homogeneous pastes were obtained. In order to dissolve HPMC in water completely, the mixed pastes were wrapped in plastic bags and stored in a saturated humidity at temperatures below 10°C, because HPMC is soluble in cold water.

To prepare the billets for extrusion, the pastes were consolidated at a pressure of approximately 5 MPa with a floating die. The extrusion experiments were performed in two ways: conventional rod extrusion and multi-billet extrusion 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 die land of 10 mm was used. The details on the multi-billet extrusion have been described in the previous paper [15]. In this paper, the pipes with a wall thickness of 1.2 mm (extrusion ratio $R = 8.7$) were formed by the multi-billet extrusion method. The extrusion load and stroke were measured using a load cell and a displacement gauge respectively, and the pressure vs. stroke curves were continuously recorded by a computer. The extrusion experiments were carried out at room temperature without lubrication of dies, and a constant extrusion speed of 10 mm·min^{-1} was used throughout.

3. Results and discussion
3.1. Effect of elemental powder characteristics on drainage
Fig. 2 shows the initial porosity in billets, which were consolidated at a pressure of about 5 MPa before extrusion, as a function of the binder content. The porosity in all consolidated billets decreases nearly linearly as the binder content increases. For the same amount of the binder, the porosity in the zirconia billets is higher than that in the stainless steel ones, suggesting that the zirconia powders are more difficult to be densified under the same compacting pressure. Furthermore, the variation of porosity due to different average particle sizes is small for the stainless steel powders, whereas large for the zirconia powders. The fine ZrO_2(A) powder shows a higher porosity than the coarse ZrO_2(C) powder under the condition of the same amount of the binder. These compacting behaviors are related to the particle sizes, size distributions and surface states of the elemental powders, it will be described later.

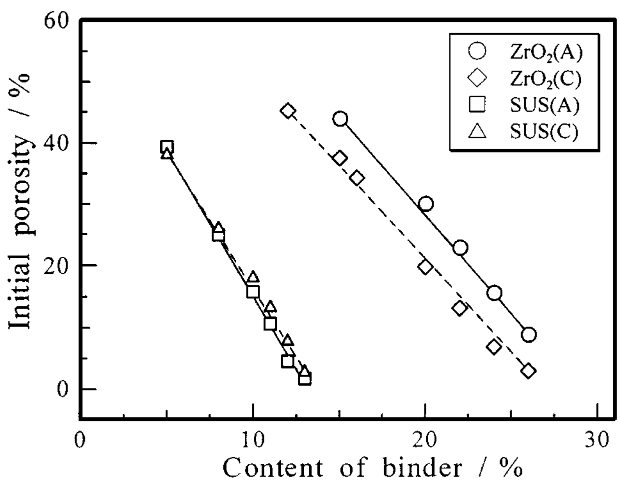


Figure 2 Dependence of the initial porosity in billets on content of the binder. The billets were consolidated at a pressure of about 5 MPa by a floating die pressing method.

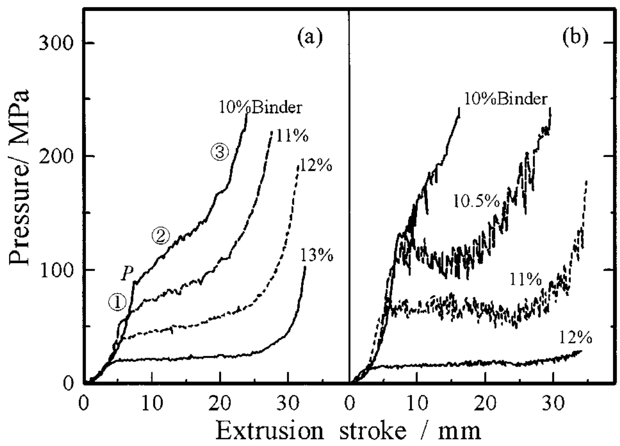


Figure 3 Extrusion pressure vs. stroke curves obtained from forming of the stainless steel pastes by rod extrusion method. Binder composition: HPMC/$H_2O = 15/85$. (a) SUS(C) (36 μm) and (b) SUS(A) (5 μm) powders.

Fig. 3 illustrates the extrusion pressure *vs*. stroke curves for forming of the stainless steel pastes. With regard to the SUS(C) powder with an average particle size of 36 μm, the changes of pressure with stroke are roughly divided into three stages shown in Fig. 3a. The pressure rise in the first stage is concerned with a decrease in porosity existed in billets, and volume reduction of the compressible binder. This is obviously different from extrusion of densified metals, where volumes of billets are kept constant in whole extrusion process. The lower the binder content is, the longer the compacting stage because of higher initial porosity. When some pressure is reached, say point *P* in Fig. 3a, the extrusion starts to occur and the curve enters the second stage. At the binder content of 13%, the change in pressure is considerably small in the second stage. With the decrease in the binder content, the level of extrusion pressure rises. At the same time, the slope of curve, that is, the increase rate of pressure with stroke turns large. Usually, extrusion pressure reduces gradually after the beginning of extrusion, due to a decrease in friction force between billet and container. As shown in Fig. 3a, however, the pressure further rises after extrusion starts. Corresponding to the pressure rise, the drainage phenomenon was confirmed experimentally, and the extent of drainage is increased with decreasing the binder content. Consequently, drainage is considered as the reason for pressure rise.

In general, there is a rise in pressure in final extrusion stage of metals [16]. This is the result of an increase in flowing resistance, because the flow of metals occurs in radial direction towards the entrance of extrusion die when billet becomes into a thin disk (discard). Concerning the extrusion of pastes, the drainage phenomenon is influenced by extrusion pressure to a large extent. The large extrusion pressure arises from drainage easily, conversely, drainage promotes the increase in extrusion pressure as well. This interdependence gives rise to rapid increase of pressure in the third stage. Since the pressure level increases and the extent of drainage becomes large as the binder content is decreased, the rapid pressure rise in the third stage is shifted to smaller strokes, and the range of the second extrusion stage is narrowed. In particular, as seen in Fig. 3a, at the binder content of 10%, the extrusion pressure is increased with stroke uninterruptedly, and remarkable drainage phenomenon takes place. As a result of interdependence between pressure rise and drainage, eventually the paste could not be extruded successfully after a short stroke. In this case, the pressure rise in the third stage is caused mainly by drainage, other than the radial flow of discard.

As for the SUS(A) powder (Fig. 3b), it can be seen that the pressure rise due to drainage in the second stage is restrained when the binder content is 11% and 12%. This indicates that the finer powder with larger specific surface area is helpful to reduce or avoid the drainage phenomenon. However, when the binder content is decreased to 10%, the pressure rises more rapidly than the SUS(C) powder, exhibiting more serious drainage to be brought about. It is resulted from a higher pressure under which extrusion starts at the binder content of 10%, because the SUS(A) powder possesses a larger pressure increase rate with decreasing the binder content than the SUS(C) powder (see Fig. 9). In addition, the pressure vs. stroke curves are characterized by serration for the SUS(A) powder due to bigger interparticle friction.

The extrusion pressure vs. stroke curves for forming of the zirconia pastes are shown in Fig. 4. The variations of pressure with stroke have similar characteristics, although the pressure levels are different, depending on the average particle size and binder content. Unlike the extrusion behavior of the stainless steel powders shown in Fig. 3, a sharp peak exists in each curve, and the pressure rise caused by drainage cannot be found. The pressure initially rises abruptly, then decreases gradually after a sharp peak occurs at some stroke. The larger the binder content is, the lower the peak pressure and the shorter the stroke up to the peak. It is evident that these pressure vs. stroke curves are also different from those of direct extrusion of metals. Generally speaking, during direct extrusion of bulk metals, even if a peak probably occurs when extrusion starts, the peak is relatively dull and the value is also small [16, 17]. Besides, the stroke up to the peak is extremely short.

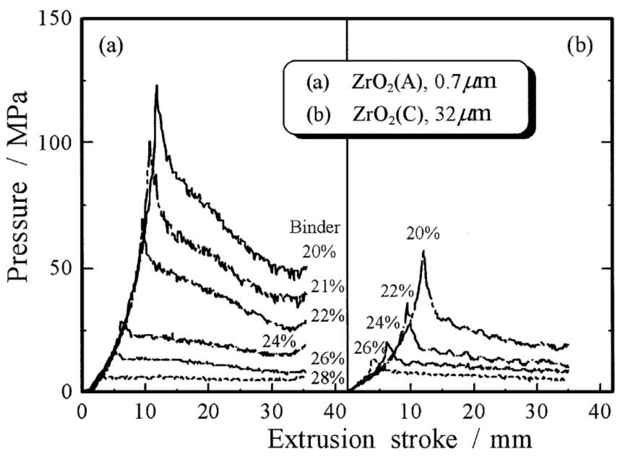


Figure 4 Extrusion pressure vs. stroke curves obtained from forming of the ZrO_2 pastes by rod extrusion method. Binder composition: HPMC/$H_2O = 15/85$.

By comparing the curves of the ZrO_2(A) and ZrO_2(C) powders, it is found that the pressure level of the coarse ZrO_2(C) powder is lower than that of the ZrO_2(A) powder under the same binder content. It arises from the lower flowing resistance in extrusion process of the ZrO_2(C) powder, because of its larger average particle size and wider particle size distribution [5].

It is obvious that the drainage phenomenon is closely related to various interactions between particles as well as between particle and binder, such as, van der Waals, electrostatic, capillary actions and so on. Among these interactions, capillary forces generated by liquid bridges in contact with particles are believed to be the main component of interparticle forces [18]. Furthermore, capillary forces should be a function of powder properties and rheological characteristics of binder. From the results of Figs. 3 and 4, it can be seen that the elemental powder characteristics have an important effect on drainage of pastes during extrusion. The drainage phenomenon is easier to occur for the stainless steel powders than for the ZrO_2 powders in the range of the binder content used. In this investigation, the binder content was decided so as to secure the soundness of extrudates. Since the ZrO_2 powders are characterized by rougher surfaces and hence larger specific surface areas compared to the stainless steel powders, it is required to add more amount of the binder to the ZrO_2 powders to obtain sound extrudates. On the other hand, in addition to particle size and size distribution, particle shape and its surface state exert significant influence on the extrusion behavior of pastes. For example, although the SUS(C) powder has a similar average particle size to the ZrO_2(C) powder, the extrusion behaviors of the both are quite different. Fig. 5 schematically illustrates the filling processes of powders under external pressure. For stainless steel powder, the slip between particles generates easily as a result of smooth surfaces of particles, thereby the pores between particles are easy to be filled under pressure applied. However, ZrO_2 powder is difficult to be filled even under higher pressure due to rough surfaces of particles, and the pressure to which binder is subjected is lower, resulting in small probability of drainage. Moreover, drainage is a time dependent process. Although there exists a sharp and high peak in pressure vs. stroke curve of ZrO_2 paste containing lower amount of the binder, the time passing through the peak is very short, thus reducing the generation of the drainage phenomenon.

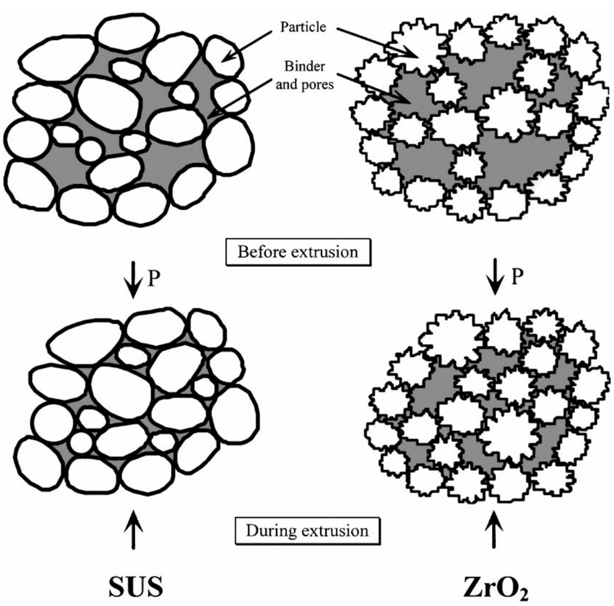


Figure 5 Schematic filling processes of the powder-binder mixtures under external pressure. It is difficult to be filled for ZrO_2 particles due to rough surface.

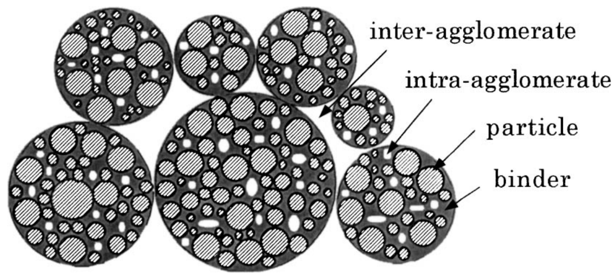


Figure 6 A schematic illustration of inter-agglomerate macropores and intra-agglomerate micropores in a powder-binder mixture.

Schubert [19] has pointed out that capillary forces can play an important role or may even be decisive for the agglomeration of granular materials. When a powder is mixed with viscous binder so that a dense suspension or particulate paste is formed, the agglomeration between particles could occur on account of capillary forces and viscous action of binder, in addition to the agglomeration due to van der Waals force (especially in finer ZrO_2 powder) and electrostatic force. The pores in a particulate paste may be divided into two types: inter-agglomerate and intra-agglomerate. A schematic illustration is given in Fig. 6. The inter-agglomerate pores are larger (macropores) than the intra-agglomerate pores (micropores). In the initial period of compacting, the larger pores of inter-agglomerate are easily filled through the movement, arrangement and some fragmentation of agglomerations. However, the pore sizes of inter-agglomerate are gradually decreased as compacting proceeds. These pores and the smaller pores of intra-agglomerate within agglomerations are difficult to be further filled, and the shearing deformation between particles may be required, hence giving rise to the abrupt increase in pressure in the initial period of extrusion. The shearing deformation necessary for filling the pores becomes large, as the binder content is decreased. Since the magnitude of mechanical forces, for example, friction and interlocking forces, are very much increased by an increase in surface roundness [18], it is difficult to produce shearing deformation and large pressure is required to form shearing surfaces in the ZrO_2 pastes with lower binder contents. Nevertheless, the macroscopic shearing deformation occurs once the shearing surfaces are formed completely, In this way, the stress is released, and the extrusion is performed under a lower pressure, thereby the peak appears in pressure vs. stroke curve.

3.2. Effect of binder composition

As described in the above section, the drainage phenomenon has been observed in extrusion of the stainless

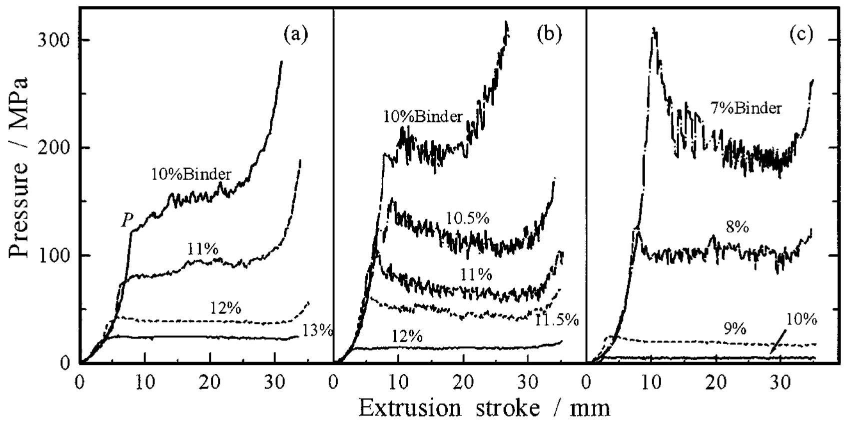


Figure 7 Extrusion pressure vs. stroke curves measured from forming of the stainless steel pastes by rod extrusion method. Binder composition: HPMC/H_2O = 25/75. The powders of (a) SUS(C) (36 μm), (b) SUS(A) (5 μm) and (c) SUS(A+C) were used respectively.

steel pastes with lower binder contents, whereas the zirconia pastes show a small tendency of drainage. Consequently, we only discuss the effects of the binder and other additives on drainage behavior of the stainless steel pastes in this and next sections.

Fig. 7 shows the pressure vs. stroke curves for extrusion of three kinds of stainless steel powders SUS(A), SUS(C) and SUS(A+C), where the mixing fraction of HPMC in binder was raised to 25% from 15% shown in Fig. 3. For the SUS(C) powder (Fig. 7a), when the binder content is 12% and 13%, the extrusion proceeds under nearly constant pressures in stable extrusion period. In comparison with the results of Fig. 3, the pressure rise with stroke becomes slow in the second stage at the binder contents of 11% and 10%, though the pressures are higher at the moment when extrusion starts (such as point P shown in Fig. 7a). Furthermore, the start of rapid increase in pressure generated in the third stage is prolonged to a larger stroke. As a result of these, the extent of drainage is reduced. Similar results can be seen in the fine SUS(A) powder of Fig. 7b. Therefore, it is effective to improve the drainage behavior of pastes by raising the mixing fraction of HPMC in binder, i.e., increasing the viscosity of binder itself.

As seen in Fig. 7a and b, the SUS(A) and SUS(C) powders show high extrusion pressures at the binder content of 10%, accompanied by occurrence of drainage. As for the bimodal mixing powder SUS (A+C) which was prepared by mixing SUS(A) and SUS(C) with an equal proportion, however, its extrusion pressure is so low that the pressure is hardly required at the same binder content (10%), exhibiting an excellent extrudability. Since the mixed powder has a wider particle size distribution, the particle packing is denser, and the rearrangement and slip between particles are easily taken place during extrusion, leading to the decrease in deformation resistance. When the binder content is decreased to 9% and 8%, the drainage phenomenon has not been found and sound extrudates can be obtained. Besides, a sharp peak is detected at the binder content of 7%, which is somewhat like the ZrO_2 powders. In this case, no striking drainage was observed during extrusion, though the extrudate was unsound because of a lower binder content. It is indicated that broadening particle size distribution by mixing powders

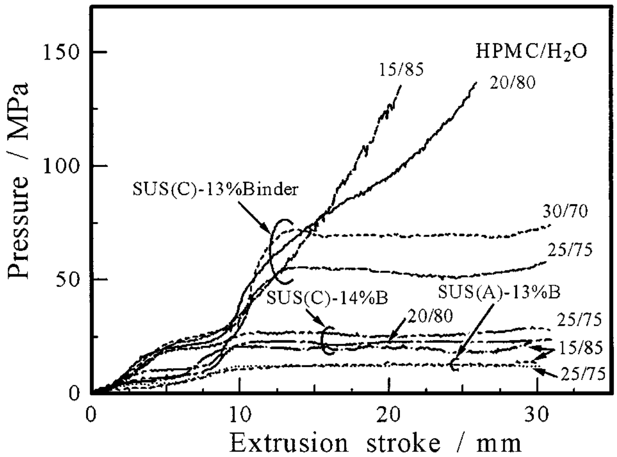


Figure 8 Extrusion pressure vs. stroke curves obtained from forming of pipes by multi-billet extrusion method.

with different average particle sizes has an important effect on decreasing extrusion pressure and restraining occurrence of the drainage phenomenon in extrusion process, hence improving the formability of pastes.

Fig. 8 shows the pressure vs. stroke curves obtained from pipe extrusion by the multi-billet method, when the SUS(A) and SUS(C) powders were used. With regard to the pastes of the SUS(C) powder with a binder content of 13%, the variations of extrusion pressure with stroke are very different, depending on the proportion of HPMC and H_2O in binder. At HPMC/H_2O = 15/85, the pressure rises with stroke in large rates. As a result, the separation between the powder and binder came about, and a normal extrusion process could not be performed. It suggests that the forming of pipe by the multi-billet extrusion method has a similar extrusion behavior to the forming of rod by conventional rod extrusion method. However, it is noted that, in the rod extrusion, no pressure rise due to drainage has been found (Fig. 3) and sound extrudate was obtained in spite of the same composition. It is resulted from different deformation conditions which are decided by the structures of dies in the rod extrusion and multi-billet extrusion methods, even for pastes with the same composition, i.e., the same rheological characteristics. When the mixing fraction of HPMC is increased to 20%, the extent of drainage is reduced and the increase rate of pressure with stroke is decreased, owing to the increase in viscosity of the binder. At the fractions of HPMC $\geq$ 25%, the extrusion pressures are almost definite in the stable extrusion stage, and the drainage phenomenon was not observed in experiments. Nevertheless, the different proportions between HPMC and H_2O bring about changes in magnitude of extrusion pressure. For instance, the pressure at HPMC/H_2O = 25/75 is lower than that at HPMC/H_2O = 30/70, as the former contains more moisture than the latter.

When the binder content is raised to 14%, the pressure levels are greatly decreased, compared to those at the binder content of 13%. Furthermore, the pressure hardly varied with stroke and no drainage phenomenon was observed in the HPMC range of 15–25%, even if the magnitude of pressure depends on the mixing fraction of HPMC in binder. Concerning the SUS(A) pastes containing a binder content of 13%, the pressure is much lower than the SUS(C) pastes with the same binder content, and it looks as if the magnitude of pressure is independent on the binder composition.

The variations of extrusion pressure with binder content for extrusion forming of the three kinds of stainless steel powders are given in Fig. 9. The extrusion pressure is strongly dependent on the binder content in forming of both rod and pipe. Especially in the range of lower binder contents, the pressure falls dramatically with increasing the binder content. It is shown that the pressure change is concerned with the powder characteristics and deformation modes. The SUS(A) and SUS(C) powders exhibit different variation rates of pressure with the change in binder content, and the pressure of the mixed powder SUS(A+C) is the lowest in the range of the binder contents used for extrusion of both rods and pipes. Under the condition of the same powder, there is a difference in extrusion pressure between the rod extrusion and multi-billet extrusion. The pressure for pipe extrusion is higher than that for rod extrusion, although the extrusion ratio (R) of the former (R = 8.7) is smaller than the latter (R = 10). As described previously, the occurrence of the drainage phenomenon during extrusion depends to a large extent on the extrusion pressure. The larger the pressure is, the higher the extent of drainage. It is suggested that the possibility of drainage is larger when pastes are extruded into pipes by the multi-billet extrusion method, compared to the rod extrusion. Hence, it is necessary to add more amount of the binder to powder for fabricating pipes, in order to decrease extrusion pressure, avoid the drainage phenomenon occurring and obtain sound extrudates.

From the results described above, it is concluded, it is an effective way to increase the binder content in pastes, so as to reduce extrusion pressure and restrain drainage during extrusion process. Moreover, an increase in mixing fraction of HPMC in binder is beneficial to reduce drainage because of improvement of viscosity in the binder, even though the extrusion pressure is increased to a certain extent.

3.3. Effect of additives

In order to decrease extrusion pressure and reduce occurrence of the drainage phenomenon, the influence of several additives has been examined. Fig. 10 gives a comparison of the extrusion pressure vs. stroke curves for forming of the pastes of the SUS(A) and SUS(C) powders with and without the additives. In the absence of any additive, there are high pressure levels for extrusion of the SUS(A) and SUS(C) pastes, and the drainage phenomenon is accompanied simultaneously, just as described before. The pressure levels are reduced largely for both the SUS(A) and SUS(C) powders by the additives. Nevertheless, in the case of the SUS(C) powder, the addition of oleic acid leads to an increase in pressure with stroke. Furthermore, the drainage phenomenon was confirmed by experiment. It is considered that oleic acid causes the decrease in viscosity of the binder, which results in occurrence of the drainage phenomenon. In the case of the SUS(A) powder (Fig. 10b), the extent of drainage caused by addition of oleic acid is reduced due to larger specific surface area of the

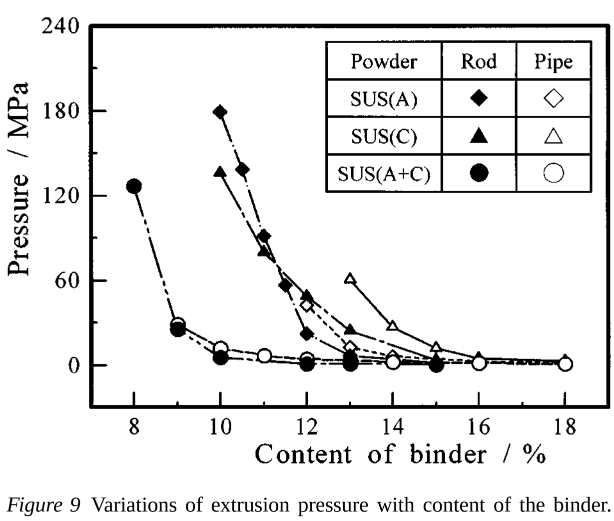


Figure 9 Variations of extrusion pressure with content of the binder. The stainless steel pastes were formed by rod extrusion (R = 10) and multi-billet extrusion (R = 8.7) methods. Binder composition: HPMC/H_2O = 25/75.

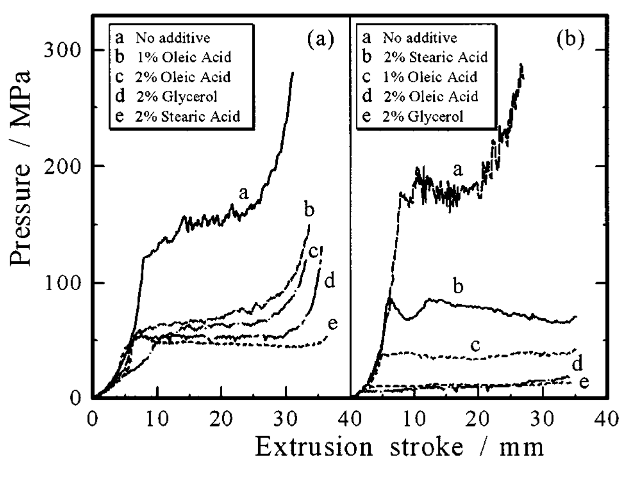


Figure 10 Extrusion pressure vs. stroke curves for forming of the stainless steel pastes with and without additives. The experiments were performed by rod extrusion method. The binder content was 10%, and its composition was HPMC/H_2O = 25/75. (a) SUS(C) and (b) SUS(A) powders.

SUS(A) powder, and the pressure is almost kept constant even at an addition of 1% oleic acid.

On the one hand, an addition of the fatty acid has been effective on lowering extrusion pressure, and on the other hand, has impaired the soundness of extrudates (for example, crack formation in extrudates) [20], especially in forming of the coarse SUS(C) powder. This is the result of insufficient interparticle adhesive forces, which are caused by the chemical adsorption of a fatty acid on particle surfaces, as well as the decrease in viscosity of the binder. Among the three kinds of additives used in this study, only glycerol shows advantageous, not only extrusion pressure is decreased but also sound extrudates could be obtained.

4. Conclusions

The pastes containing a powder, zirconia or stainless steel, and a binder of an aqueous solution of water-soluble polymer (HPMC) were extruded by rod extrusion and multi-billet extrusion methods. The pressure change and drainage phenomenon of pastes during extrusion have been examined. It is found that the elemental powder characteristics have an important effect on drainage of pastes during extrusion. The drainage phenomenon has been obviously observed in extrusion of the stainless steel pastes with lower binder contents, while the zirconia pastes show a small probability of drainage in the range of the binder contents used in this investigation. Broadening particle size distribution by mixing powders with different average particle sizes has a significant effect on decreasing extrusion pressure and restraining occurrence of the drainage phenomenon, thus improving the extrudability of pastes.

In order to reduce extrusion pressure and restrain drainage of the stainless steel pastes, it is effective to increase the binder content in pastes and to add plasticizer like glycerol. Moreover, an increase in mixing fraction of HPMC in binder is beneficial to reduce drainage because of improvement of viscosity in binder, even though the extrusion pressure is raised to a certain extent.

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