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Use of coupling agents as a route to improvement of the compressibility of fine zirconia and alumina powders

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In order to improve the compressibility of fine zirconia and alumina powders, powders were surface-treated with aluminate, silane and titanate coupling agents. The surface modification reduced both powder/powder friction and powder/die-wall friction, which increased the density of the compacts. At 2% additions, the effectiveness of the coupling agents on density increase was in the order, silane > titanate > aluminate. In zirconia systems with different titanate concentrations it was found the optimum amount of coupling agent could be approximated by the amount required for monolayer coverage on the powder surface.

1. Introduction

In die-pressing of powders, high powder/powder friction and powder/die-wall friction will result in low and non-uniform density of the pressed bodies [1–3]. Usually, the effects of friction become increasingly serious as the size of powders is decreased. Lubricants used for reduction of friction are classified into two types: i.e. internal lubricants for reducing powder/powder friction, and external lubricants for reducing powder/wall friction [4].

The molecules of coupling agents have two functional groups; generally, one will react with inorganic materials, and the other will prefer to react with organic materials [5]. In ceramic fabrication, coupling agents have been used to improve the rheological properties of the ceramic compound for injection moulding [6–8]. Ceramic oxides treated with coupling agents transform from hydrophilic to hydrophobic. The phenomenon helps to protect the fine particles from agglomeration due to atmospheric moisture. Moreover, it is probable that the organofunctional end of the agent adsorbed on the particle surfaces affects powder/powder and powder/wall friction directly. In the current study, it has been shown that coupling agents have dual functionality in the reduction of friction, which aids in promoting the compressibility of fine zirconia and alumina powders.

2. Experimental procedure

Partially stabilized zirconia (PSZ) (Y31710, Osaka Cement Co. Ltd, Osaka, Japan) and alumina (AL-160SG-3, Showa Denko, K. K, Tokyo, Japan) powders were used. The densities of PSZ and alumina were 6021 and 3920 kg m^{-3}, and the specific surface areas 12.3 and 6.0 m^2 g^{-1}, respectively. The coupling agents used were aluminate (acetoalkoxy aluminium diisopropylate, AL-M, Ajinomoto Co. Ltd, Tokyo, Japan), silane (*n*-octadecyl trimethoxy silane, AX43-065, Toray Silicone Co. Ltd, Tokyo, Japan), and titanate (isopropyl triisostearoyl titanate, KR-TTS, Ajinomoto Co. Ltd). The densities of aluminate, silane and titanate were 950, 980 and 940 kg m^{-3}, respectively, at room temperature.

The PSZ and alumina powders were ball-milled for 1 h in toluene containing the dissolved coupling agent. The amount of coupling agent was 2% by weight of ceramic powder. PSZ powders with 0.5%, 1%, and 5% titanate were prepared separately. Powders ball-milled without coupling-agent additions (0%) were used as reference powders. The mixed slurries were decanted, and this was followed by vacuum evaporation. After pulverizing the dried cakes to under 250 μm, the powders were further dried for 2 days in an electric oven at 110°C, and cooled over silica gel.

Compaction of disc specimens was carried out on a universal dynamic tester (Model 1350, Instron Corp., Canton, MA, USA), using a cylindrical hardened-steel die with 20 mm inner diameter. Five discs were single-side pressed for all powders at compaction pressures of 10, 20, 50, 100 and 200 MPa. The pressure transmission ratios were measured at 200 MPa. As will be described later, this ratio depends on the height, H, and diameter, D, of the powder bed. The dimension H/D was adjusted to 0.5 ± 0.01 at the measuring pressure by controlling the powder weight. The adsorbed coupling agents increase the apparent powder

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weights. However, the adsorbed amounts are smaller than the added amounts because hydrolysis of the coupling agent occurs. The adsorbed weights were evaluated by thermogravimetry (TG) in static air from room temperature to 900 °C. The bulk density of the compact was calculated by weighing a disc and subtracting the ignition loss after ejection from the die. The tensile strength was obtained from diametral compression test. No forming agent except the coupling agent was added during preparation of the powders. Thus, complicated fracture patterns occurred in the discs pressed at high pressure owing to lamination. The discs pressed at low pressures of 10 and 50 MPa were used in the strength tests.

3. Results and discussion

Surface treatment with 2% coupling agent addition improved the compressibility of PSZ powders as shown in Fig. 1, the effectiveness on density increase being in the order, silane > titanate > aluminate. Silane addition increased the density of the compact at 200 MPa by 11% compared to that of the untreated powder (0%). In terms of pressing pressure, 200 MPa was required to attain 49% density for the untreated powder, but only 15, 45 and 80 MPa, respectively, for the silane, titanate, and aluminate-treated powders. The effect of titanate concentration on compact density is shown in Fig. 2. Compact density increased with increasing titanate additions up to 2%. However, the increase between 2% and 5% was much smaller than that between 1% and 2%. Subsidiary experiments revealed that a monolayer adsorption on the surface of the PSZ powder could be realized at 2% titanate addition [9]. The pseudo S-shaped curve of compact density versus titanate addition may reflect surface coverage by the titanate molecules.

Fig. 3 shows the relation between the diametral tensile strength and density of the compacts. Obviously, the strength increases with increasing density. Quite different compressibility between treated and untreated powders (Fig. 1) made it impossible to achieve the same compact density for all powders within the experimental pressure range. Even so, it can be easily recognized through extrapolation of the density–pressure curves that compact strength at the same density will be in the order, untreated > aluminate > titanate > silane. The effect of titanate amounts on compact strength is shown in Fig. 4. The strength decreased considerably with increasing titanate additions up to 2%. However, the curves for 5% and 2% titanate additions overlap, and the apparent difference of strength between 2% and 5% can be attributed to the difference in compact density. Compact strength at a constant density is proportional to the adhesive force between the particles [10]; i.e. the decrease in strength corresponds to a decrease in particle adhesive force. Comparisons between Figs 1 and 3, and Figs 2 and 4 indicate that the improvement in compressibility is connected with the decrease of adhesive force between particles.

Fig. 5 shows the effect of titanate additions on pressure transmission through PSZ powder beds. The transmission ratio increases with increasing titanate additions. Compared to the changes of density (Fig. 2) and strength (Fig. 4) with titanate additions, the change of transmission ratio is not so marked between 1% and 2%, but relatively great between 2% and 5%. At 2% additions of the coupling agents, the transmission ratio was in the order, titanate (89.3%) > aluminate (79.5%) > silane (75.3%) > untreated (67.3%).

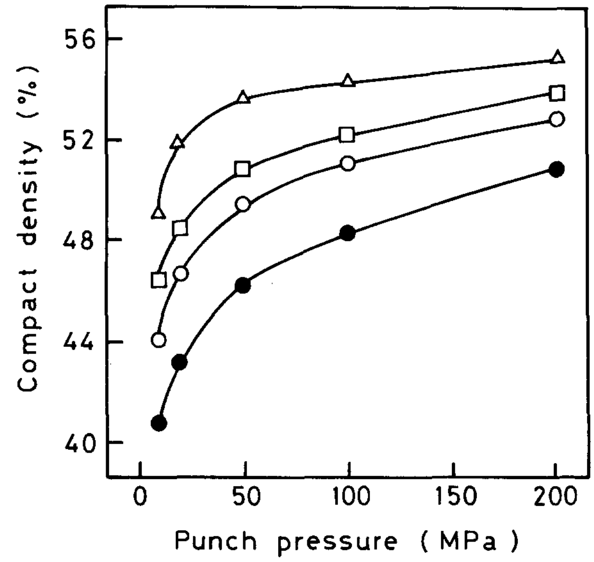

Figure 1 Effect of coupling agents on the compaction diagram of zirconia powders: (●) no addition, (○) 2% aluminate, (□) 2% titanate, (△) 2% silane.

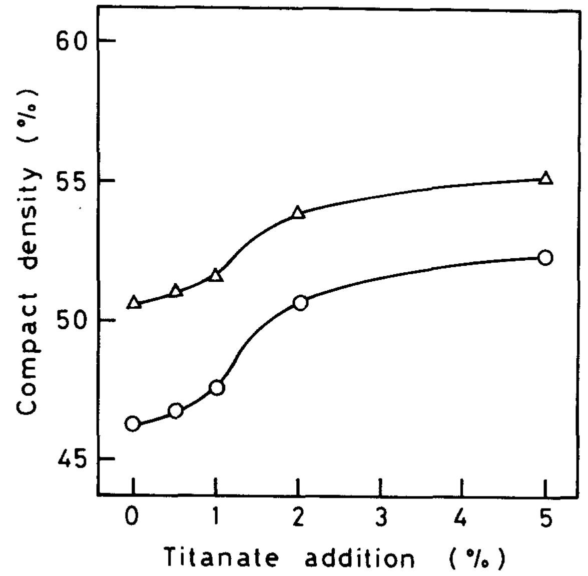

Figure 2 Compact density of zirconia powders as a function of titanate addition: (○) 50 MPa, (△) 200 MPa.

The pressure-transmission ratio can be expressed [11] as

$$\frac{P_L}{P_H} = \exp\left[\frac{-4(\tan\phi_W)KH}{D}\right] \qquad (1)$$

where P_H is the applied pressure on a movable upper punch, P_L the received pressure on a fixed lower

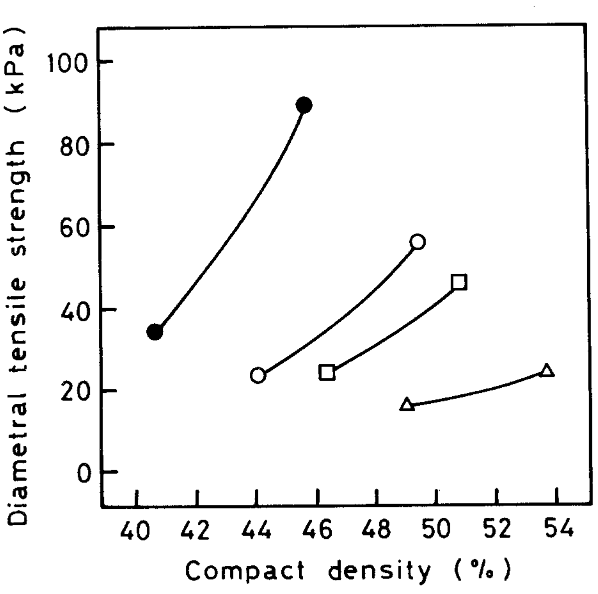

Figure 3 Relation between diametral tensile strength and compact density of zirconia powders: (●) no addition, (○) 2% aluminate, (□) 2% titanate, (△) 2% silane.

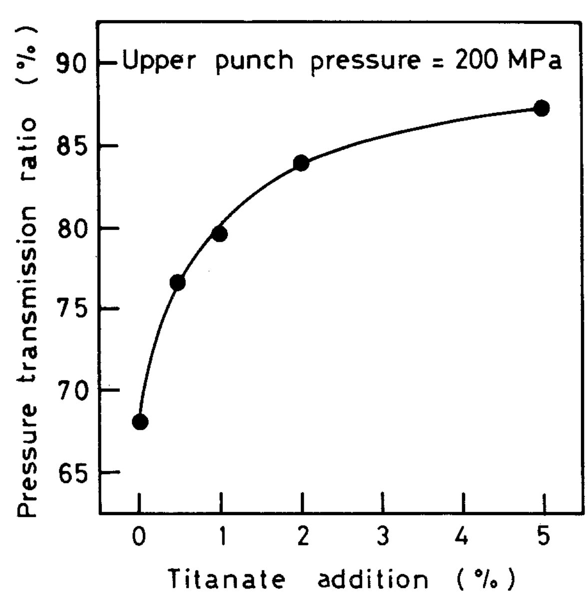

Figure 5 Pressure transmission through a bed of zirconia powders as a function of titanate addition.

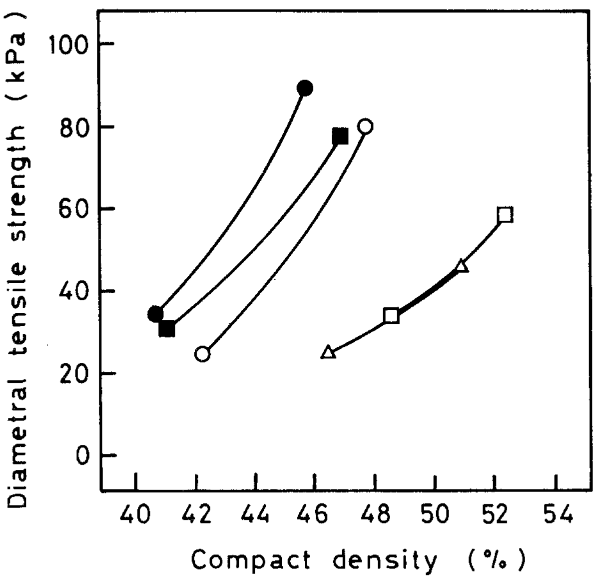

Figure 4 Curves of diametral tensile strength versus compact density of zirconia powders, illustrating the effect of titanate addition: (●) no addition, (■) 0.5%, (○) 1%, (△) 2%, (□) 5%.

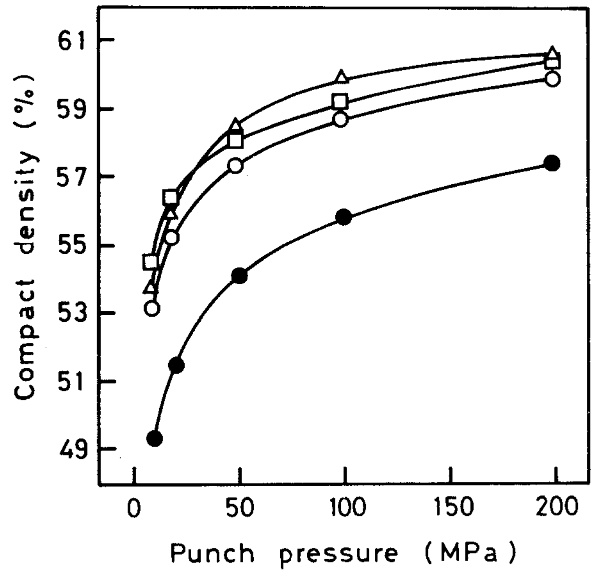

Figure 6 Effect of coupling agents on the compact density of alumina powders: (●) no addition, (○) 2% aluminate, (□) 2% titanate, (△) 2% silane.

punch, D the compact diameter, H the compact height, and ϕ_W the powder/wall friction angle. K is Rankine's coefficient, and can be expressed as a function of powder/powder friction angle, ϕ_p [12]

$$K = \frac{1 - \sin\phi_p}{1 + \sin\phi_p} \qquad (2)$$

Equations 1 and 2 predict that the transmission ratio depends on both ϕ_p and ϕ_W. If the other parameters except ϕ_p are constant, the ratio will decrease with decreasing ϕ_p (although it seems contradictory). While the decrease of interaction force between particles (Figs 3 and 4) must imply a decrease of ϕ_p, the surface treatment increases the transmission ratio. This suggests that the coupling agents adsorbed on the surface of particles also reduce ϕ_W. In the system treated with different titanate additions, the compaction density increases slightly between 2% and 5% (Fig. 2) although the particle interaction force changes little (Fig. 4). Therefore, it can be considered that the increase of transmission ratio (Fig. 5) caused the slight increase of density. In other words, the extra titanate amount over the monolayer coverage will contribute not to a decrease of powder/powder friction but to a decrease of powder/wall friction. It might be concluded that the surface treatment with coupling agents improves the compressibility of the PSZ powders through the reduction of both ϕ_p and ϕ_W.

From the molecular structure of three coupling agents, i.e. silane ($(C_{18}H_{37})$–Si–$(OCH_3)_3$, mol. wt = 370), titanate ($(CO_2C_{17}H_{35})_3$–Ti–(OC_3H_7), mol. wt = 957), and aluminate ($(COCH_3CHCO_2C_{18}H_{37})$–

$Al\text{-}(OC_3H_7)_2$, mol, wt = 485), 2% silane is almost equivalent to that of 5% titanate in view of the mole concentration. The compact densities of PSZ powders treated with 5% titanate are 52% at 50 MPa and 55% at 200 MPa, respectively (Fig. 2). These values are almost consistent with those of PSZ powders treated with 2% silane (Fig. 1). Molecular weight may be the major factor influencing the effectiveness of silane and titanate on compressibility. Nevertheless, although the molecular weight of aluminate is only half that of titanate, the aluminate could not improve the compressibility so much as titanate. Mixing tests with water showed that PSZ powders treated with 2% silane and with 2% titanate floated on the water, whereas those powders treated with 2% aluminate yielded an imperfectly mixed slurry. The fundamental requirements for the boundary lubricants working as surface films on particles are that the molecules can be bonded stiffly to the surface of particles, and that the interaction between the molecules is high enough for oriented adsorption [13]. These molecules can be considered to have almost the same organofunctional group lengths, i.e. about 18 times as long as the distance of C–C bonding. Therefore, the differences in the effectiveness of the aluminate and titanate may arise from the structural difference of their organofunctional groups, and from the different bonding ability with the PSZ powders.

It is reasonable to expect that the coupling agents can be widely applied to other oxides. In fact, the compressibility of alumina powder was improved by surface modification in a manner similar to that of PSZ (Fig. 6). At low pressures of 10 and 20 MPa, the compact density is slightly higher in the titanate system than in the silane system. This may be attributed to the existence of unstable agglomerates which are inevitably created through the processes of slurry mixing, drying, crushing and sieving. These agglomerates are not so hard, but their effects on the compressibility cannot be avoided at low compaction pressures.

4. Conclusion

The effects of aluminate, silane and titanate coupling agents on the compressibility of fine zirconia and alumina powders were investigated experimentally. All coupling agents increased the compact density and the pressure-transmission ratio, but decreased the compact strength. It has been shown that reduction of both powder/powder friction and powder/wall friction contributes to such improvement of compressibility. Coupling agents can be used as effective lubricants for compaction of fine ceramic powders, particularly oxides. Compatibility with other forming additives such as binders and plasticizers should be further examined prior to application to industrial dry pressing.

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