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The break point in the pressure–density curve of magnesia prepared by the sea water magnesia process

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Uniaxial compacting behaviour of MgO powders calcined at a temperature between 900 and 1200 °C in air was investigated; the break point which appeared in the pressure–density curve of MgO powder was effective in elucidating the agglomeration state in the powder. The packing density of MgO powder as a function of calcination temperature was measured before and after milling operations. The plots of relative density versus logarithmic pressure also exhibited a break point indicating the pressure at which the contact points in porous agglomerates began to be destroyed. The agglomerate strength of MgO powders calcined at low and high temperatures (900 and 1200 °C) only were measured. The microstructural differences between agglomerates in MgO powder and the surface of a compressed powder (applied pressure 150 MPa) were examined by scanning electron microscopy.

1. Introduction

Ceramic powders are often heated before the moulding and sintering operations to remove the volatile impurities which impede densification during sintering; such preheating may be carried out not only to obtain optimum conditions for satisfying both sinterability and compactability, but also to minimize firing shrinkage. Agglomeration in the powder improves packing properties in the die and, therefore, can increase the green density; however, unless the agglomerates break down or readily deform during compaction, the sintered compact will show a low density and an inhomogeneous microstructure.

During the calcination of ceramic powders, i.e. magnesia (MgO) produced from sea water, various types of agglomeration may form, which affects the properties after the starting materials are treated thermally. In most cases, the ceramic powder is granulated to increase its flowability to lead to closer packing in the die. To evaluate the compactability of the ceramic powder, a standard test [1] is carried out to compress the powder at a fixed pressure and to determine the green density and the compaction ratio.

The use of pressure density or compaction curves has been widespread in the study of metal powders [2–5], pharmaceutical powders [6, 7] and ceramic powders [8]. Bruch [8] was one of the first to use curves to explain the consolidation of ceramic powders. He demonstrated that the plots of green density against the logarithmic pressing pressure for agglomerated or granulated powder showed the appearance of two straight line segments; the break point in the curve was interpreted as the onset of the collapse of the agglomerates. Compaction studies seem to indicate the presence and relative strength of agglomerates in powders.

2. Experimental procedure

The chemical analysis of magnesia (MgO "Lycal 95/57S" from sea water, A. Bembassat S. A., Spain) used in this experiment is given in Table I. The calcination of each powder was carried out at a temperature between 900 and 1200 °C for 2 h in air; the heating rate was 36 °C min^{-1}. After calcination, the powder was quenched and subsequently dry-milled in a polyethylene ball mill with steel balls (5, 15 and

TABLE I Chemical analysis of the original MgO powder

Chemical compound	(%)
MgO	93.00
Ca	2.25
SiO_2	0.70
Fe_2O_3	0.15
Al_2O_3	0.20
Sulphates as SO_3	1.20
Loss at 950 °C	2.50
Sodium as Na_2O	0.10
Chlorides as NaCl	0.40
Carbonates as CO_2	1.20
Manganese as Mn	165.00 p.p.m.
Copper as Cu	5.00 p.p.m.
Surface area	60 m^2 g^{-1}

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20 mm diameter) as a grinding medium for 1.5 h. The milled and unmilled powders were poured into a cylinder (50 cm^3 capacity); the quotient of the weight and the volume occupied by the powder in the cylinder was defined as the packing density. About 2.5 g powder was uniaxially pressed at 150 MPa into a disc (16 mm diameter and 8 mm height) using a rigid steel die. The die walls were lubricated by zinc stearate. The compaction of each powder was performed using an Instron testing machine at a constant strain rate. The bulk density of the green compact was measured by the geometric method. The shape of agglomerates and the surface of the compact were observed by scanning electron microscopy (SEM) after carbon coating to avoid charging during exposure to the electron beam.

3. Results

Fig. 1 shows the packing densities of milled (1.5 h) and unmilled MgO powders; these powders were calcined at a temperature between 900 and 1200 °C. The packing density of each powder varied according to the calcination temperature. These unmilled MgO powders densified slightly with increasing calcination temperatures. The packing densities of milled MgO powders were higher than those of unmilled MgO powders; a rapid increase in packing density of milled MgO powders was observed above 1050 °C.

Fig. 2 shows scanning electron micrographs of the milled and unmilled MgO powders. The microstructural differences which originated from the calcination temperatures were observed in these photographs. In Fig. 2a, as-received MgO powder is seen to contain a large number of particles with size ~ 5 μm; this size was close to the particle size (~ 4 μm) given by the manufacturer. In Fig. 2e and f, necks were formed between particles; each agglomerate with size ~ 20 μm was observed at these temperatures.

The green density of the compact was directly related to the agglomerate strength. Thus the surfaces of compressed MgO powders calcined at various temperatures were also observed by SEM. Fig. 3 shows typical microstructures of the surfaces of the uniaxially compressed powders. The observed surfaces of compressed powders corresponded to the upper surface of the compact, i.e. the surface in contact with the punch; although these microstructures are not representative of green compacts, they do represent the state of porosity. As can be observed in Fig. 3e, the pores in the compressed powder calcined at 1200 °C showed a more inhomogeneous distribution than those in the compressed powder calcined at 900 °C (Fig. 3a). In this micrograph the pores were small and spherical, whereas those in Fig. 3d and e were large, interconnected and crack-like.

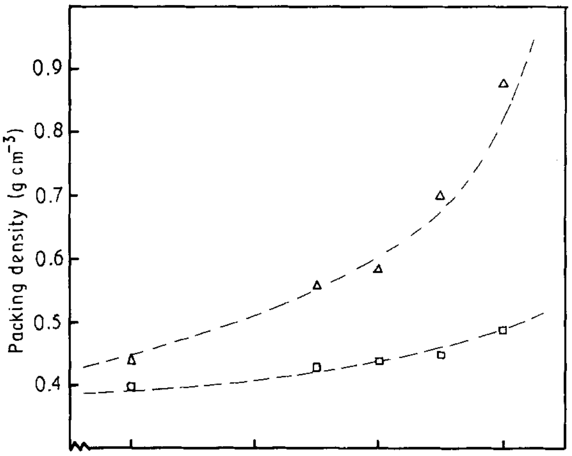

Figure 1 Effect of calcination temperature on packing density of MgO powder (calcination time 2 h, atmosphere air, milling time 1.5 h). (□) Calcined and unmilled, (△) calcined and milled.

In order to evaluate the strength of agglomerates formed during calcination, plots of density against pressure may give semiquantitative information on the properties of the agglomerates [9, 10].

The compaction pressures of MgO powders calcined at low and high temperatures (900 and 1200 °C) are given in Fig. 4. The individual datum points of pressure versus density in Fig. 4 may be calculated from those of the load–displacement curve. Although the curve was approximately continuous, the calculated straight-line segments were obtained from the linear portions of the curves. Note that the results in Fig. 4 were obtained after the original curves [11] were drawn by adjusting the elastic deformation effect of the punch. According to this figure, the break points in the 900 and 1200 °C curves are approximately 25 and 30 MPa, respectively.

4. Discussion

The milled powder has a low packing density at low calcination temperature (i.e. 900 °C), which is believed to be caused by its fine particle size and the presence of porous agglomerates. Nevertheless, at elevated temperatures (1100, 1150, and 1200 °C) the packing density of the calcined and then milled powder increased with increasing calcination temperature, which may be attributed to the presence of (1) numerous dense agglomerates formed by sintering, and (2) the hard agglomerates being difficult to crush even by the grinding operation shown in Fig. 2e; these agglomerates are formed by the active mass transfer between particles at high calcination temperatures. According to Paramanand and Ramakrishnan [12], the high green density of MgO compact shows that the applied load may transmit the large agglomerates rather than the smaller agglomerates. However, it is also possible that in agglomerates formed at low calcination temperatures (where a number of contact points may be present among the agglomerates), the rearrangement of these agglomerates does not occur easily by particle–particle friction. By considering the Griffith principle [13], it is easier to fracture larger particles than smaller ones. The fragmented particles lead to easy void formation between unfractured large particles. In contrast, the smaller particles require higher fracturing pressures; therefore, they are difficult to rearrange in the compact, resulting in low green density. The state, distribution and size of pores are affected by the size, shape and surface area of particles or

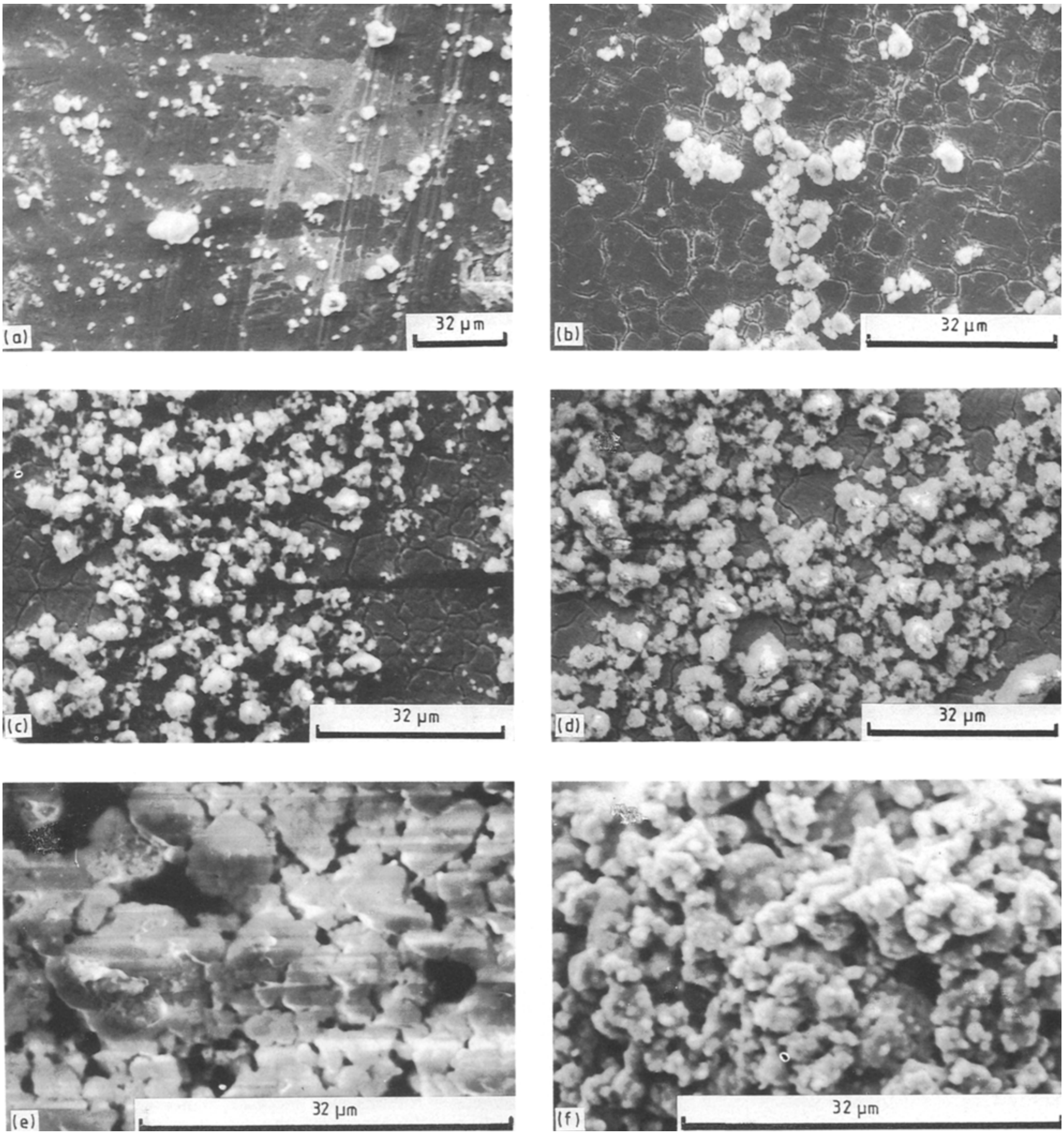

Figure 2 Scanning electron micrographs of MgO powders calcined for 2 h in air and then dry-milled for 1.5 h. (a) As-received, (b) 900 °C, (c) 1050 °C, (d) 1100 °C, (e) 1150 °C, and (f) 1200 °C.

agglomerates in the powder. In other words, the difference in compactability between MgO powders may be due to the difference in size and shape of the particles. The time spent for the milling operation was probably not the optimum, because Fig. 3d and e show the presence of agglomerates even after uniaxial compression; thus these agglomerates may not be destroyed by either milling operation or compaction at the experimental pressures.

Pressure–density curves may be useful for the characterization of ceramic powder. It is possible to interpret the mechanical properties of agglomerates from the compaction process. Whether the break point appears at low or high pressure depends on the powder properties. Niesz *et al.* [9] analysed the compaction curves on a more fundamental basis through the breakdown of the aggregated alumina powders during compaction. They assumed that the semilogarithmic relationship between the mechanical strength, σ, of brittle materials and density [14] is analogous to that for a granulated powder

$$\sigma = \sigma_0 e^{-bp} \qquad (1)$$

where σ_0 is the strength of the non-porous body, b an empirical constant and p the pore fraction. From this relationship it is shown that the pressed density is proportional to the logarithmic applied pressure. Consequently, when the density is plotted against the

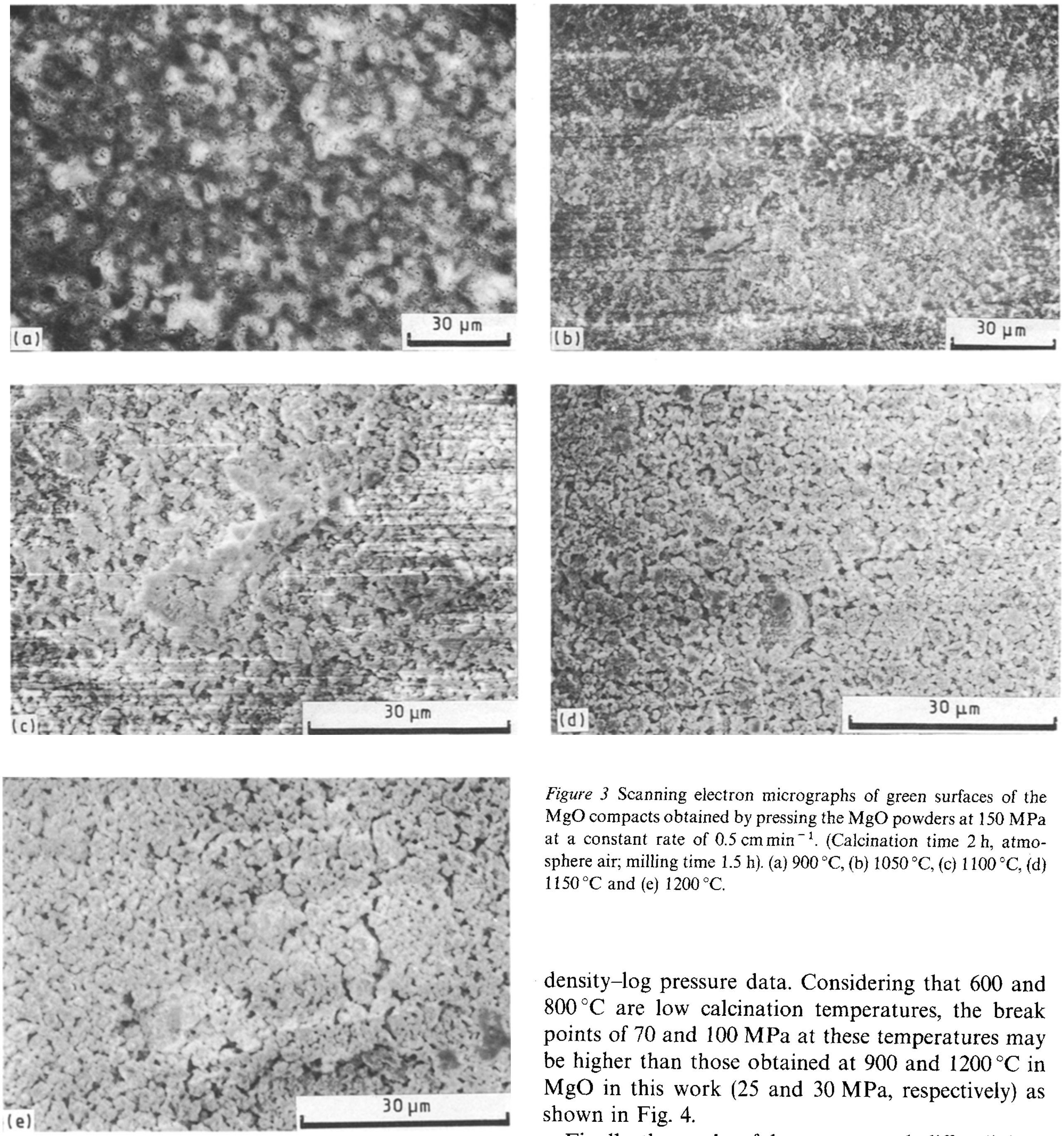

Figure 3 Scanning electron micrographs of green surfaces of the MgO compacts obtained by pressing the MgO powders at 150 MPa at a constant rate of 0.5 cm min^{-1}. (Calcination time 2 h, atmosphere air; milling time 1.5 h). (a) 900 °C, (b) 1050 °C, (c) 1100 °C, (d) 1150 °C and (e) 1200 °C.

logarithmic pressing pressure, a linear relationship is observed. Messing *et al.* [10] plotted density against pressure for three kinds of alumina powders (as-received, aggregated and ungranulated) and found that there are two break points in each curve.

Itatani *et al.* [15, 16] plotted the density versus log pressure for MgO powder obtained by calcining $Mg(OH)_2$ at different temperatures. They obtained two straight lines, intersecting at around 70 MPa for MgO powders calcined at 600 °C. The relative densities of MgO powders calcined at 900 °C and 1200 °C densified exponentially with increasing applied pressures, i.e. the presence of agglomerates cannot be detected in the experimental pressure range. Comparing the results of the present work and those of Itatani *et al.*, a disagreement is seen from the viewpoint of the break point values obtained from the density–log pressure data. Considering that 600 and 800 °C are low calcination temperatures, the break points of 70 and 100 MPa at these temperatures may be higher than those obtained at 900 and 1200 °C in MgO in this work (25 and 30 MPa, respectively) as shown in Fig. 4.

Finally, the results of the present work differ slightly from those obtained by Naujokat *et al.* [17] (break point less than 15 MPa for MgO powder from sea water calcined at 1000 °C for 2 h in air) and are remarkably different from the data in Fig. 5, as discussed later.

Accordingly, the density versus pressure plots described above show that a primary rearrangement occurs below the pressure corresponding to the break point where the agglomerates are fractured; a secondary rearrangement of fragments may lead to dominant densification of fragments. This behaviour has been reported elsewhere [18, 19]. Smith [20] proposed the use of the following empirical density–pressure relationship

$$C_f = (\rho - \rho_0)P^{1/3} \qquad (2)$$

where C_f, is a constant called the "compressibility factor", ρ is the density of the compact (g cm^{-3}), ρ_0 is the apparent density of the powder (g cm^{-3}) and P is the applied pressure (MPa).

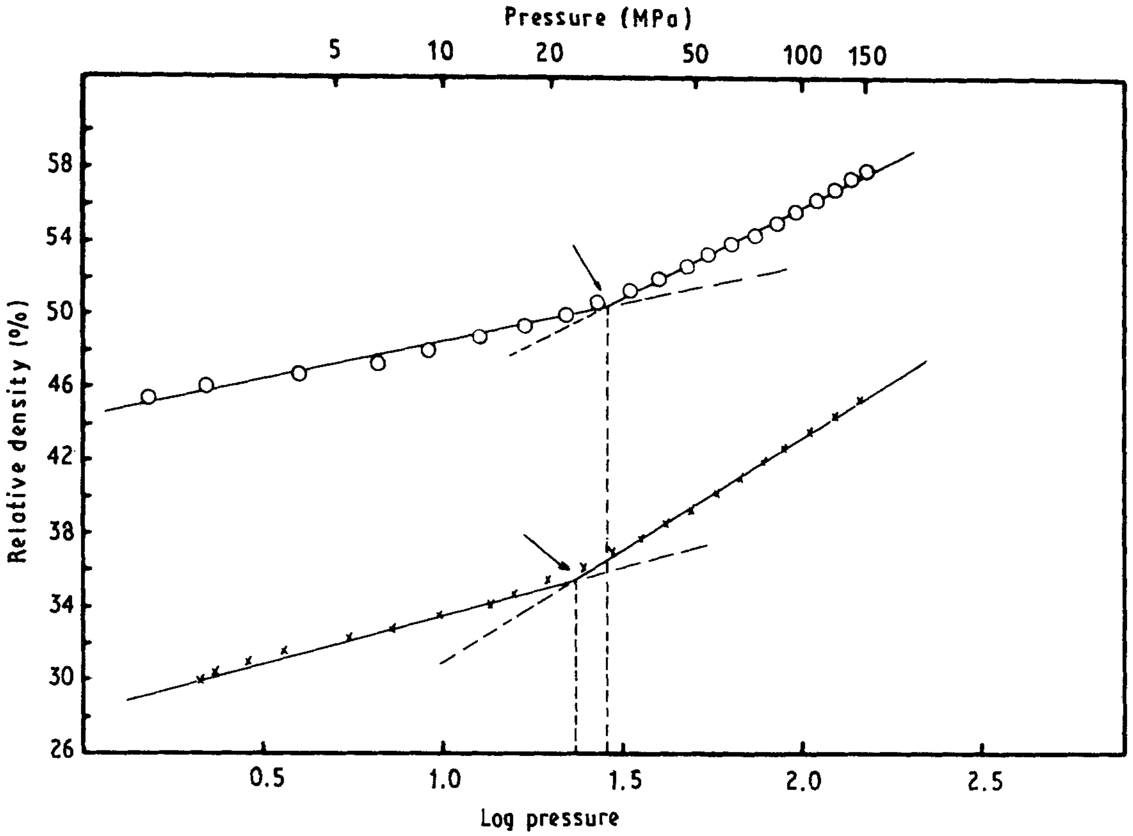

Figure 4 Relationship between relative density and log applied pressure of MgO powder calcined for 2 h and then milled for 1.5 h. Arrows indicate the break points as follows: 25 MPa for (×) 900 °C and 30 MPa for (○) 1200 °C. Pressing rate = 0.5 cm min^{-1}.

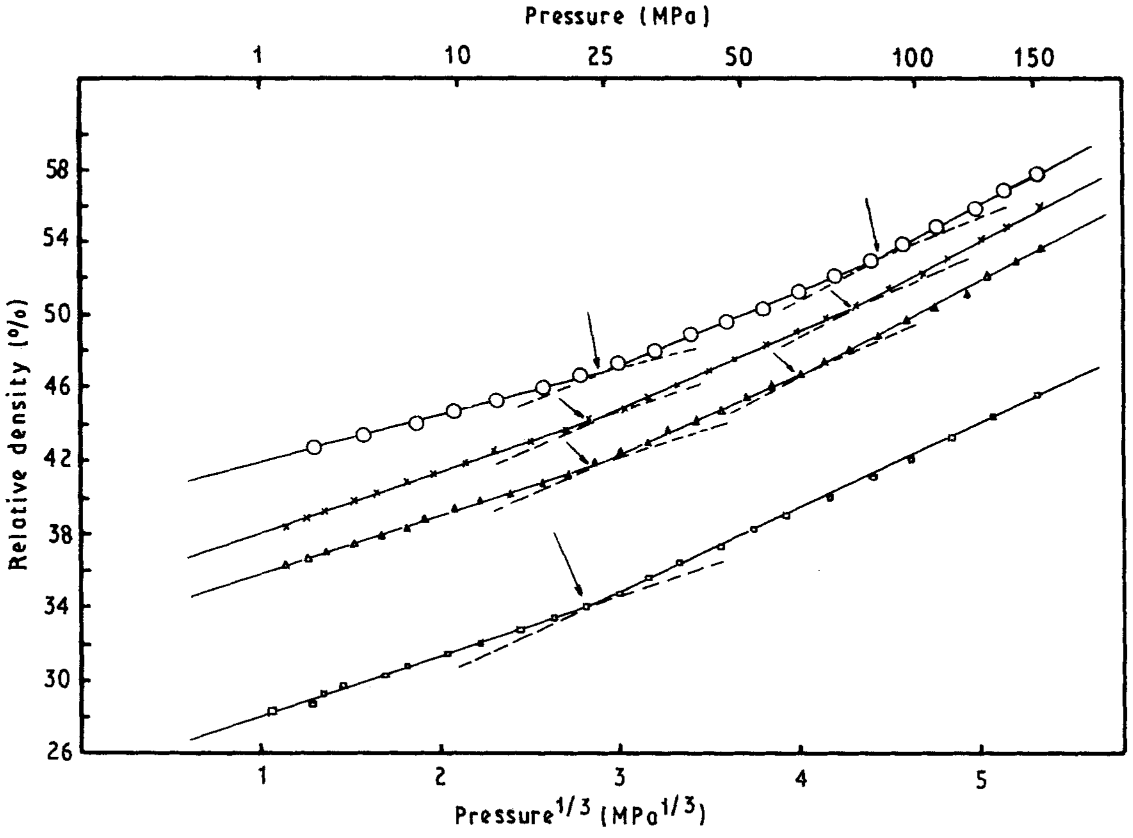

Figure 5 Relationship between relative density and cube root of applied pressure of MgO powder calcined for 2 h and then milled for 1.5 h. Arrows indicate the break points as follows: 24 MPa for (□) 900 °C, 24 and 65 MPa for (△) 1100 °C, 24 and 84 MPa for (×) 1150 °C, and 25 and 91 MPa for (○) 1200 °C. Pressing rate = 0.5 cm min^{-1}.

Fig. 5 shows the plots of relative density versus cube root of the applied pressure for the MgO powders calcined at 900, 1100, 1150 and 1200 °C. It is clearly observed from these plots for MgO powders at a low calcination temperature (900 °C) that two straight-line segments appear with a break point at 24 MPa, which is in accordance with the value of 25 MPa showed in Fig. 4. It is noteworthy that three straight-line segments were found in the other curves (i.e. 1100, 1150 and 1200 °C). The former break points in the three curves are ~ 24 MPa. Likewise, the first break point in the curve at 1200 °C is in agreement with the value at 1200 °C in Fig. 4. Nonetheless, a later break point occurs between 65 and 91 MPa. It seems that a second fracture of the agglomerates can occur at high calcination temperatures; according to the microstructure of green surfaces, some agglomerates still exist which retain their morphology even after compaction at 150 MPa.

The plots in Fig. 5 can be more reliable for evaluating the strength of agglomerates, because in the plots of density versus log pressure frequently used for analysing the compaction phenomena, straight-line approximations and extrapolations will lead to serious errors when straight lines are not clearly distinguishable.

In addition, it is believed that the break points in Fig. 4 are somewhat low for the MgO powder calcined at high temperature, if we consider that sintering occurs at these calcination temperatures as shown in Fig. 2e and f. It is likely that high pressures are required to fracture the agglomerates and to lead to the continuous sliding and rearrangement.

The fact that a second break point does not appear in the curve corresponding to 900 °C (in Fig. 5) suggests the disappearance of hard agglomerates; this assumption may be supported by Fig. 3a which shows that almost all the agglomerates disappear from the powder. However, the agglomerates also have a wide distribution of strengths over which they require broad range of pressures in which to break. Therefore, 150 MPa applied pressure may be insufficient to destroy all the agglomerates present in the calcined and milled powder.

5. Conclusions

The calcination process of MgO powder obtained from sea water was carried out from 900–1200 °C. The following conclusions were drawn.

1. High calcination temperatures frequently promote sufficient diffusion of matter into the neck regions between individual particles to create strong interparticle bonds.
2. Calcination of the MgO powder at still higher temperatures induces the formation of higher density particles. These particles have good packing properties but the initial pores will be large on compacting.
3. High compaction pressures or prolongated milling times are necessary to destroy the residual agglomerates in the powder.
4. Relative density versus pressure plots of MgO powders calcined at 900 and 1200 °C showed two straight-line segments with break points at 25 and 30 MPa, respectively. Moreover, density–pressure$^{1/3}$ plots showed three straight-line segments, i.e. calcination temperature 1100 °C, 24 and 65 MPa; 1150 °C, 24 and 84 MPa; and 1200 °C, 25 and 91 MPa. The break points which appear at ~ 24 MPa at 900 °C may be indicative of the disappearance of the agglomeration state when approaching this break point during uniaxial compaction. According to these plots, a different mechanism controls during the compaction operation. The fact that the break point at 900 °C is approximately the same (i.e. 24 MPa) suggests that the softer agglomerates in the calcined powder begin to be crushed during compaction at the break pressure mentioned above.

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