JOURNAL OF MATERIALS SCIENCE 29 (1994) 121–124

Sintering characteristics of microfine zirconia powder

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In this paper the sintering characteristics of yttria-doped zirconia microfine powder are investigated by measuring shrinkage and shrinkage rate curves of powder compacts. The experimental results show that there is a transition point in the shrinkage–temperature curves and two peaks appear in the shrinkage rate–temperature curves. These results provide further support for the idea that the sintering of microfine zirconia powders is a two-stage process. In the first stage, sintering of the powder compact is mainly dominated by inner-sintering in agglomerates and in the second stage, sintering will occur among densified agglomerates. The microstructure of agglomerates during sintering is also studied by TEM and provides evidence that the transition point in the shrinkage–temperature curve is the end of the first sintering stage. Furthermore, the relationships between sintering characteristics and powder parameters are investigated. It is found that the shrinkage rate in the first stage is related to the primary grain size of the powder, and in the second stage it is related to agglomerate size. The effect of agglomerates on the sinterability of microfine ZrO_2 powder can be directly evaluated by the difference of shrinkage rate between the two sintering stages. Experiments also show that the shrinkage rate can be influenced by heating rate. A rapid heating rate would result in difficulties in the second sintering stage.

1. Introduction

Zirconia ceramics with excellent mechanical properties have been of interest to ceramic scientists in the last decade [1, 2]. Zirconia ceramics such as TZP, which has a toughness of up to 18 $\text{MPa m}^{1/2}$ [3], can only be prepared from microfine zirconia powder. But owing to the agglomeration of powder, using microfine zirconia powder does not certainly mean that the powder compact can be easily sintered to high density at a relatively low temperature as expected [4]. Studies show that an inhomogeneous microstructure is formed either in powder compacts or in sintered ceramics when hard agglomerates exist in the powder [5, 6]. Usually it is necessary to increase the sintering temperature to achieve high density, and as a result, poor microstructures may be formed owing to grain growth and non-uniform distribution of pores [7, 8]. For this reason, many studies have been made to reduce or eliminate agglomeration of microfine powders [9–11]: for instance, using alkoxide precursors to prepare microfine powder, which has better sinterability by forming soft agglomerate [10], helps to improve sinterability.

The effects of agglomerates on powder behaviour, like compaction behaviour and sinterability, are dependent on the structure of the agglomerates. Experiments show that the compaction behaviour of microfine powder is related to its sinterability [12]. If the agglomerates can be broken in compaction, it will not affect the sinterability of the microfine powder. Van de Graaff [13] studied the compaction behaviour of microfine zirconia powder prepared by different routes and found that agglomeration can be evaluated by the hardness of the agglomerate. Some agglomerates can be broken by a relatively low compaction pressure, i.e. the soft agglomerates; and some cannot be broken, i.e. the hard agglomerates. If agglomerates can be broken in compaction, there will be a transition in the compaction curves as shown in Fig. 1. The compaction pressure at which the agglomerates are broken can be defined as the hardness of the agglomerates. These experiments provided a way to differentiate the soft and hard agglomerates.

Differentiating hard agglomerate from soft agglomerate is only one step in understanding the effect of agglomerates on the sinterability of a powder. Rhodes [14] investigated the relationship between sinterability and agglomerate size and showed that the sinterability can be improved by reducing agglomerate size. Dynys and Halloran [15] studied the microstructure of ZrO_2–Al_2O_3 ceramics and concluded that hard agglomerates will result in inhomogeneous microstructure in the powder compact and a decrease in shrinkage rate during isothermal initial-stage sintering. Lange [5, 7] investigated the sintering behaviour of microfine ZrO_2 powder by measuring the pore distribution of a powder compact during sintering, and applied pore coordination number

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theory [16] to explain the effect of agglomerates on sinterability and related microstructure. According to his explanation, the driving force for densification is related to the pore coordination number: the pore coordination number within agglomerates is low and is easily eliminated during sintering, while the pore coordination number between agglomerates is related to the size and morphology of agglomerates. Some pores with a high pore coordination number cannot be eliminated even at high temperature. However, these works seem to be qualitative analyses of the effect of agglomerates on the sinterability of microfine powder, and they have not established the relationship between sinterability or sintering characteristics and the parameters of microfine powder. In this paper, we try to provide a method to directly investigate the sintering characteristics of microfine zirconia powder, and expect to establish the relationship between sintering characteristics and powder parameters.

2. Experimental procedure

The microfine zirconia powder investigated in this paper was prepared by the sol–gel method. It contained 3.0 mol % yttria. Powder A and Powder B were prepared in different process conditions and were different in powder characteristics. The powders were first mixed with 0.5 wt % organic binder and then isostatic pressed into bars at 250 MPa. The bars were cut into cylinders with diameter 7 mm and length 15 mm. The shrinkage curves of powder compacts were measured in a thermal expansion analyser from room temperature to 1450 °C at a selected heating rate. A computer was connected with this thermal expansion analyser and the differential of the shrinkage curve plotted as a shrinkage rate curve. The BET specific area was measured by the nitrogen absorption method and the agglomerate size distributions were determined by the light-dispersion method. The morphology and microstructure of powder before and after sintering at selected temperatures were observed by an EM400 transmission electron microscope.

3. Results and discussion

3.1. Densification process of microfine zirconia powders

In experiments, we first measured the shrinkage and shrinkage rate curves of two microfine zirconia powder compacts, A and B. Fig. 2 shows the shrinkage and shrinkage rates of these two powder compacts against sintering temperature. It can be seen that there is a transition appearing at elevated temperature in the shrinkage curve, which can be considered to be a dividing point for two densification processes, and this transition is more obvious in curve A than in curve B. The shrinkage rate curves consist of two peaks. Two peaks in the shrinkage curve certainly mean that this densification is a two-stage process. Many papers [5–8] have investigated the sintering of microfine ZrO_2 powders by measuring the pore distribution or observing the microstructure of the powder compact, and have concluded that the sintering of agglomerated microfine powder should be a two-stage process. This experiment provides a direct observation on this phenomenon.

We also can see that the transition in shrinkage curves is related to the two peaks in the shrinkage rate curves. The transition appears in the range between these two peaks and becomes more obvious when there is a difference of intensity between these two peaks. If we define a transition point T_t in the shrinkage curve, then the temperature of this point can be determined by relating it to the lowest point between two peaks in the shrinkage rate curve. The definition of this point can be considered as the end of the first sintering stage and the beginning of the second stage. Shi and Yen [8] observed the sintering of agglomerated microfine ZrO_2 powder by measuring the pore distribution of the powder compact and found that this inner-sintering ended at elevated temperature. In Fig. 2, we obtain the temperature of the transition point as 1050 and 1175 °C for powders A and B, respectively. To test this definition, we observed the microstructure of powder A before sintering and after sintering at the transition temperature (1050 °C). Fig. 3 is the morphology of powder A calcined at 650 °C. We can see agglomerates which consist of small grains, and pores can clearly be seen. Fig. 4 show the microstructure of the same powder sintered at 1050 °C. The agglomerates can also be seen clearly, but have now been fully sintered, only pores between agglomerates being left.

From these experiments and analyses, we can conclude that there are two main characteristics of the

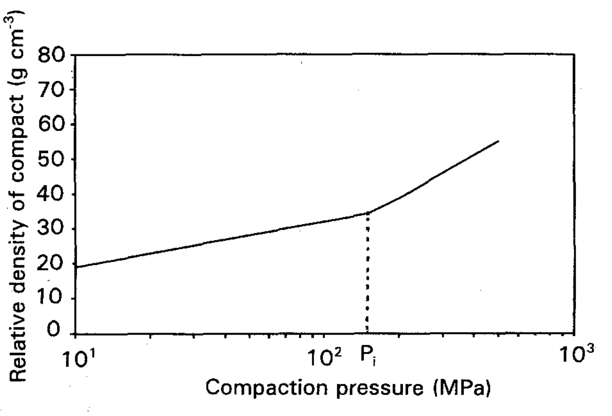

Figure 1 Relative density of microfine ZrO_2 powder compact versus compaction pressure [13].

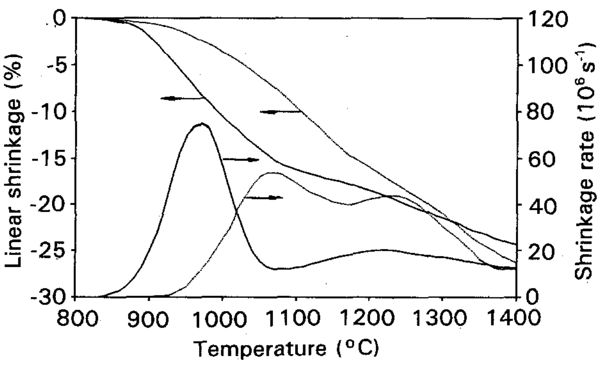

Figure 2 Linear shrinkage and shrinkage rate versus sintering temperature for microfine ZrO_2 powders: (—) sample A, (· · ·) sample B.

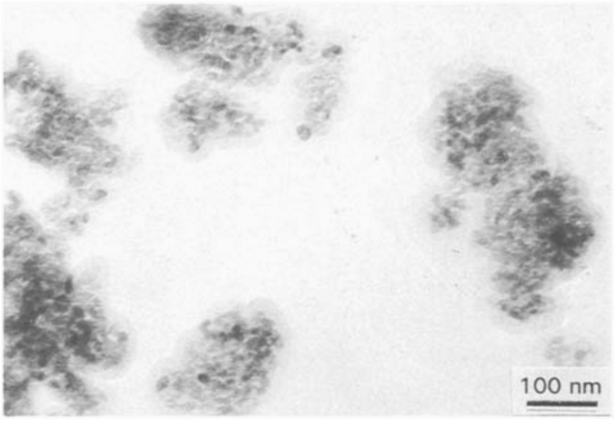

Figure 3 Morphology of microfine ZrO_2 powder calcined at 650 °C.

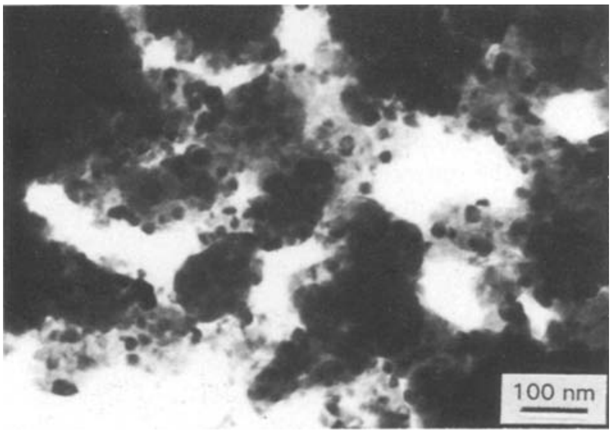

Figure 4 Microstructure of microfine ZrO_2 powder sintered at 1050 °C.

TABLE I BET specific surface area and primary grain size of microfine ZrO_2 powder

Sample	BET specific surface area ($m^2\ g^{-1}$)	Primary grain size (μm)
A	72.1	0.014
B	31.5	0.03

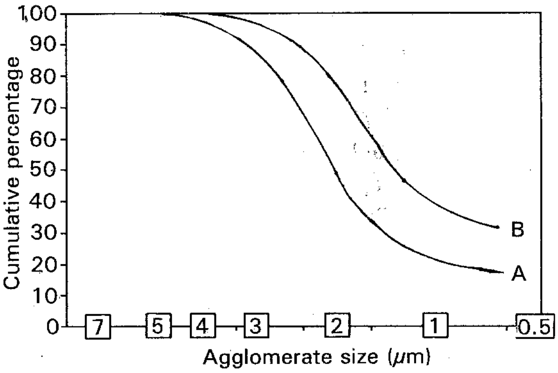

Figure 5 Agglomerate size distributions of powders A and B.

sintering process of microfine ZrO_2 powder, i.e. a transition point in the shrinkage curve and different shrinkage rates in different sintering stages.

3.2. Relationship between sintering characteristics and powder parameters

In Fig. 2 we can see that the transition temperature and shrinkage rate are different for powder A and powder B. The shrinkage rate of compact A in the first sintering stage is higher than that of compact B, and in the second sintering stage it is lower than that of compact B. We also can see that the temperature of the transition point in curve A is lower than that in curve B. If we related these characteristics to the powder parameters, we could find the relationship between them. The main parameters of microfine powder which usually concern us are the BET specific surface area and the agglomerate size distribution. Table I gives the BET specific surface area of powder A and powder B. The calculated grain size of the powders is also listed. Fig. 5 shows the agglomerate size distribution of the powders. We can see that the primary grain size of powder A is smaller than that of powder B, but its agglomerate size is larger than that of powder B. If we compare these results with the results obtained from Fig. 2, the relationship between sintering characteristics and powder parameters can be found: the smaller the primary grain size of the powder, the higher the shrinkage rate in the first sintering stage; the smaller the agglomerate size of powder, the higher the shrinkage rate in the second sintering stage, i.e. the shrinkage rates in the first and second sintering stage are related to the primary grain size and agglomerate size, respectively. These results suggest that in agglomerated microfine powders, higher BET specific surface areas do not certainly mean a good sinterability. The sinterability should be related to both primary grain size and agglomerate size.

In previous discussion, we considered the transition point as the end of the first sintering stage. Since the sintering rate in the first sintering stage is related to the primary grain size of the powder, it is easily seen that the smaller the grain size, the lower the ending temperature of first sintering stage, i.e. the lower the temperature of the transition point. This exactly reflects the situation in curve A and curve B in Fig. 2.

For relating the shrinkage rate of the powder compact in the first and second sintering stages to the grain size and agglomerate size of the powder, respectively, if we consider that the agglomeration of microfine ZrO_2 powder can be expressed by the difference between grain size and agglomerate size, then it should also be expressed by the difference in shrinkage curves between the first and second sintering stages. This means that the effect of agglomerates on the sinterability of microfine ZrO_2 powder can be evaluated by this difference in shrinkage rate. We can define A_c as the agglomeration coefficient of microfine ZrO_2 powder. Then A_c can be simply expressed by the equation

$$A_c = \frac{S_1 - S_2}{S_1}$$

where S_1 and S_2 are the maximum shrinkage rates in the first and second sintering stage, respectively. The higher the value of A_c, the more serious the effect of agglomeration on the sinterability of microfine ZrO_2 powder.

3.3. Effect of heating rate on sintering of microfine ZrO_2 powder

In experiments, we also found that the density of sintered ZrO_2 ceramics is affected by the heating rate. This result is also reported in other papers [1] and a slow heating rate is preferable for sintering a microfine ZrO_2 powder compact to high density. Fig. 6 shows the shrinkage curves of compact B at different heating rates. It can be seen that the heating rate has an obvious effect on shrinkage in both first and second sintering stages, and this effect becomes more obvious in the second stage. However, the transition-point temperature remains nearly unchanged with increase of heating rate.

The structure of agglomerated microfine powder compacts during sintering is schematically illustrated in Fig. 7. The compact consists of small packing units (agglomerates). For agglomerates first sintered and densified at a rapid rate, as we observed before, a tensile stress should be produced between sintered agglomerates and cause them to break away from the surrounding matrix, leaving gaps between them [5]. This should result in difficulty in sintering in the second stage. An increased heating rate might increase the tensile stress between agglomerates and cause agglomerates to break away more easily, just as the quenching of ceramics in water results in thermal stress and microcracking, and would certainly cause more difficulties in sintering in the second stage.

The fact that the temperature of the transition point is nearly unchanged with increase of heating rate means that the first stage of sintering should not be affected by heating rate for inner-sintering in agglomerates. The decrease of shrinkage rate might be the result of agglomerates breaking away from the surrounding matrix, and would equal a slight dilatation of the powder compact.

4. Conclusions

1. The linear shrinkage and shrinkage rate curves can effectively evaluate the whole sintering process of microfine ZrO_2 powder. The results show that the sintering of microfine powder compacts can be divided into two stages.

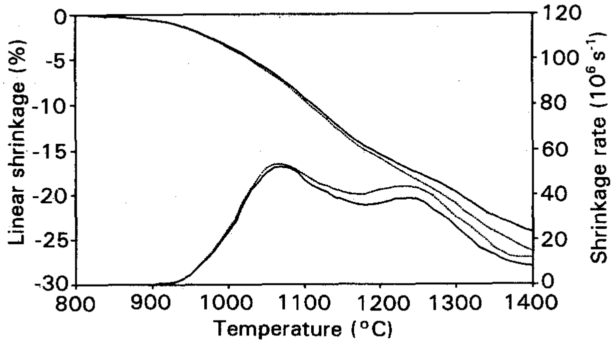

Figure 6 Linear shrinkage and shrinkage rate curves of powder compact B at different heating rates: (· · ·) 1 °C min^{-1}, (—) 5 °C min^{-1}.

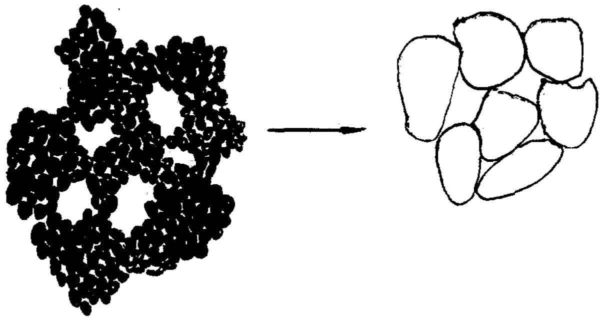

Figure 7 Schematic illustration of structure of agglomerated powder compact.

2. In the sintering of microfine ZrO_2 powder compacts, the shrinkage rate will be different in different sintering stages: in the first stage the shrinkage rate is determined by the primary grain size of the powder, and in the second stage it is related to agglomerate size; the difference of shrinkage rate between the two stages can effectively evaluate the effect of agglomerates on the sinterability of the powder.

3. A transition point in the sintering of microfine ZrO_2 powder has been defined. The definition of this point is the end of the first sintering stage, and this is only related to the primary grain size of the powder.

4. In sintering, the heating rate can affect the densification of the powder compact. The reason for this is that a rapid heating rate will result in tensile stress between early-sintered agglomerates and the surroundings, and cause them to break away from the surrounding matrix more easily.

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Received 20 July 1992
and accepted 16 March 1993