JOURNAL OF MATERIALS SCIENCE 30 (1995) 1357–1360

Direct observation of non-uniform distribution of PVA binder in alumina green body

Y. ZHANG, N. UCHIDA, K. UEMATSU
Department of Chemistry, Nagaoka University of Technology, Kamitomioka 1603–1, Nagaoka, Niigata, Japan

To study the effect of binder distribution in a powder granule on the internal structure of the compacts, the internal structure of green bodies with various PVA contents was examined by a liquid immersion technique and SEM. By the liquid immersion technique, a dark three-dimensional network was found in the as-compacted green bodies, but disappeared after binder removal. This result shows that the structure corresponds to binder-rich surface layer of the spray-dried granule. Detailed examination on green bodies after the binder removal showed that the low density region was present at the boundaries of granules and was related to the binder-rich region. The voids between granules increase with increasing the PVA content.

1. Introduction

A large processing void behaves as a fracture origin [1–2] and has been long recognized as one of the critical problems for manufacturing ceramics with high strength and reliability. The detection of the large processing voids [3, 4] and the understanding of their behaviour in the densification process were very important and were both successfully accomplished in recent papers [5–8]. A novel and simple technique was used to examine internal structures of porous materials such as green and partially sintered bodies [9–11]. In the method, the specimen was made transparent with an immersion liquid for the transmission optical microscopic examination. Examination of the bulk specimen showed the features of extremely large agglomerates and large processing voids at the granule boundaries. However, specimens in these studies were examined after binder removal.

The origin of the large processing voids can be ascribed to the hard surface layer which is formed by the surface segregation of binder [12]. But there has rarely been direct evidence to prove this due to a lack of an adequate characterization method. Therefore we only have very limited understanding of the features of such a binder layer and the effect of it on the formation of the large processing voids. Electron probe X-ray microanalysis (EPMA) is usually used to examine component distribution in ceramics, but is not suitable for examining organic binder distribution in a granule, because it is difficult for EPMA to examine the carbon element and its resolving power is not high enough. In this paper, the liquid immersion technique is applied to examine the presence of non-uniform distribution of binder in the green body compacted with alumina-PVA powder. The formation of large processing voids in green bodies will be discussed.

2. Experimental procedure

Both high purity alumina powder (AL160SG-2, Syowakeikinnzoku, Japan) and PVA binder (105, Kurare, Japan) for the experiments were of commercial grade. Binder aqueous solution of various concentrations (1.6, 2.24, 3.85 wt.%) was prepared by dissolving PVA in distilled water. Alumina powder (100 g) was added to the solution (165 g) and mixed with an attrition mill for 1 h. The slurry was spray-dried in a commercial equipment with the inlet and outlet air temperatures being 200 and 95 °C, respectively. The spray-dried granules with moisture content 0.5 wt.% were uniaxially pressed into pellets (12 mm × 4 mm diameter) at 10 MPa and subsequently isostatically pressed at 100 MPa to prepare green bodies. To burn out the binder, the green bodies were heated to 700 °C at 3 °C min^{-1} in air. Internal structures of green bodies before and after binder removal were examined with the liquid immersion technique. The green bodies to be examined were thinned to about 0.2 mm with a grinding paper, and the thinned specimens were immersed in a liquid. Micrographs were taken with an optical microscope (Optiphot, Nikon, Japan) in the transmission mode. Methylene iodide ($n = 1.74$) and 1-bromonaphthalene ($n = 1.69$) were used as the immersion liquids for the observations before and after binder removal, respectively. The fracture surfaces of green bodies before and after binder removal were also examined by scanning electron microscopy (SEM) (JSM-T100, Jeol, Japan).

3. Results

Fig. 1 shows the transmission optical micrographs of green bodies with various PVA contents before binder removal. Methylene iodide was used as the immersion liquid. A dark network structure was found in all

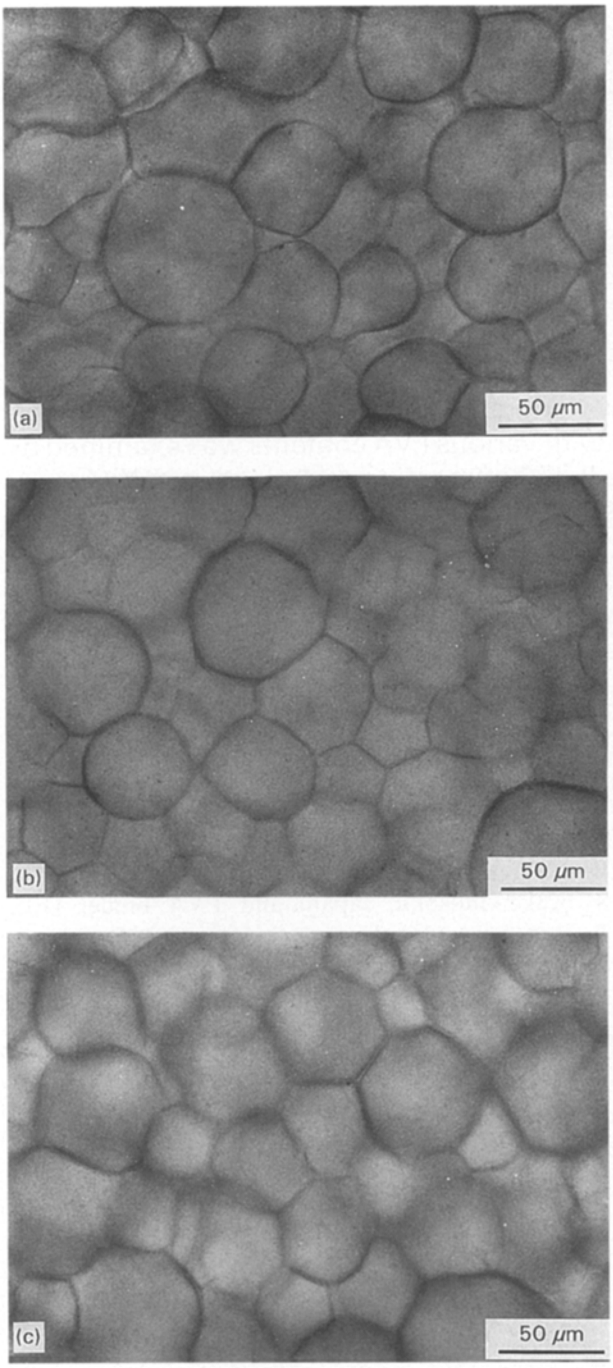

Figure 1 Optical micrographs of as-pressed compacts with various PVA contents. (a) 3.85 wt.%; (b) 2.24 wt.%; (c) 1.6 wt.%.

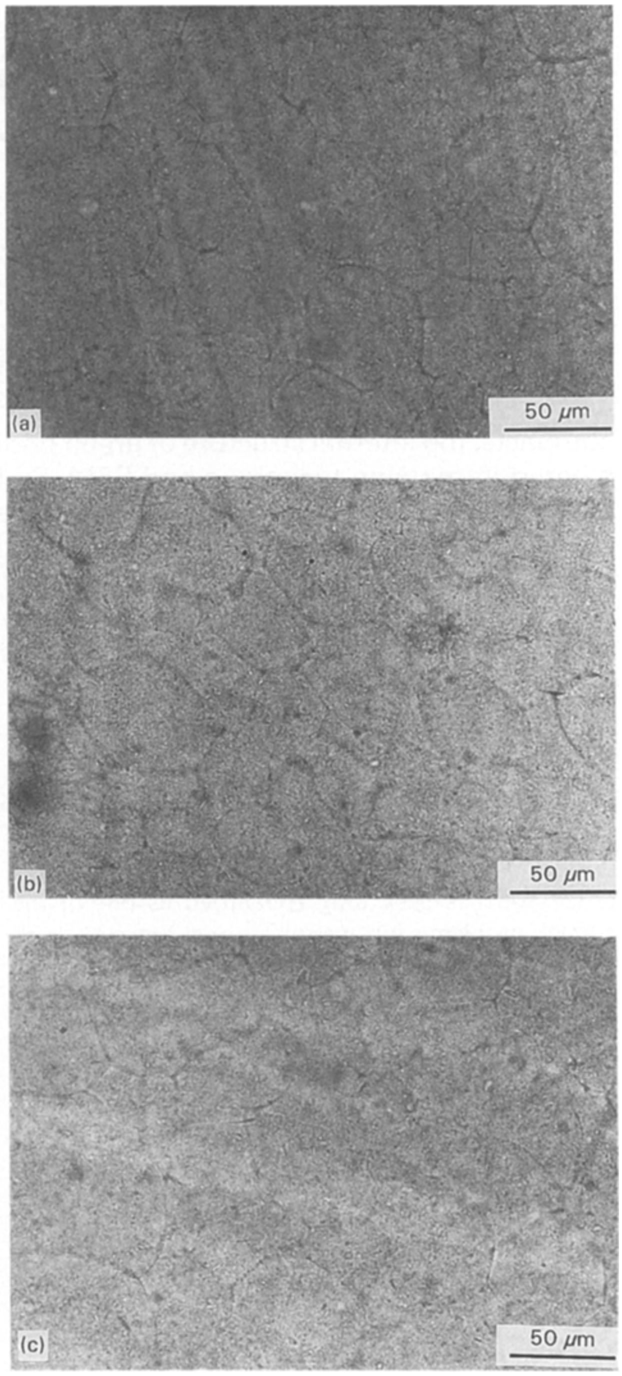

Figure 2 Optical micrographs of the compacts with various PVA contents. (a) 3.85 wt.%; (b) 2.24 wt.%; (c) 1.6 wt.%; after binder removal.

samples, and was remarkable with the increase of PVA content. After the binder removal, the network structure disappeared, and the specimen became more transparent and featureless. The result shows that the dark network corresponds to the surface segregation of PVA in the spray-dried granules. The higher PVA content, the more remarkable the segregation. PVA distribution in green bodies can be examined by this technique.

To characterize the detailed internal structure of green body after binder removal, 1-bromonaphthalene was used as immersion liquid. It provided a larger mismatch of refractive index with alumina and was better suited to revealing small features than methylene iodide. The results are shown in Fig. 2. A faint network structure was again found. This network structure must be the successive array of voids or/and the low density region, and it became faint as PVA content increases.

Fig. 3 shows the SEM micrographs of the fracture surfaces of green bodies before binder removal. In all specimens, the granules with non-spherical shape were clearly observed. The granules were deformed but were not crushed into small pieces in the compaction process. The micrographs also show voids between granules, especially at the junctions of three granules, and cracks on the surface of granules. Transgranular fracture increased with decreasing PVA content. In the

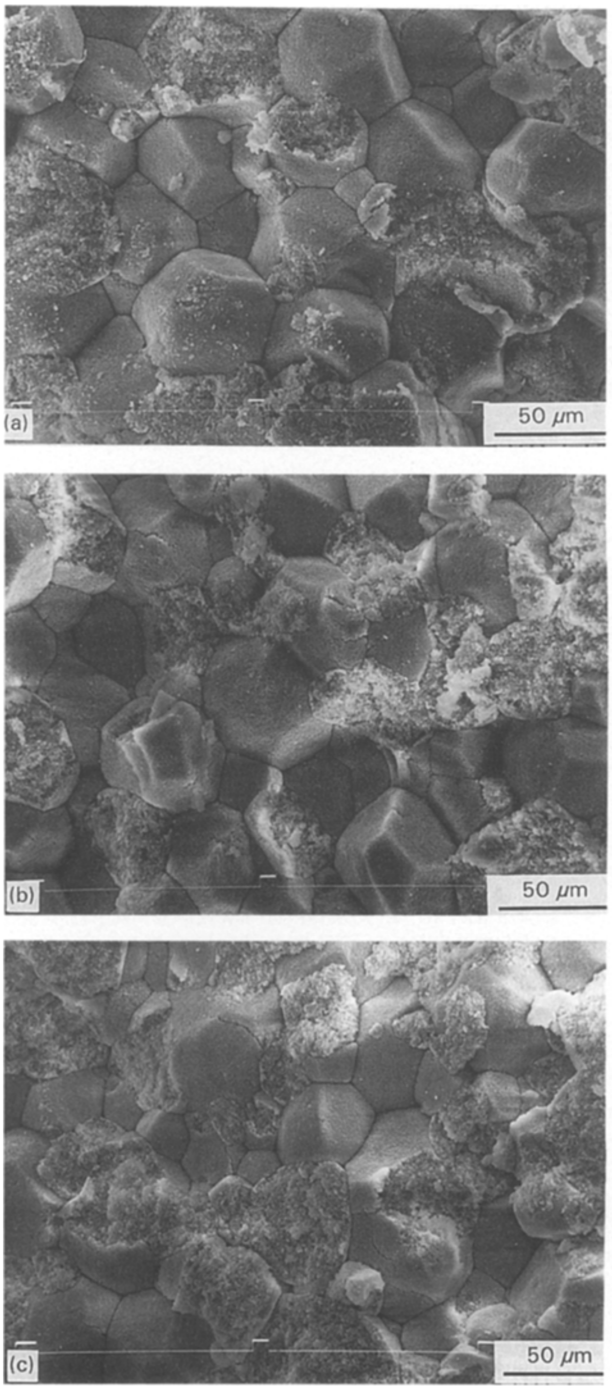

Figure 3 SEM micrographs of fracture surfaces of as-pressed compacts with various PVA contents. (a) 3.85 wt.%; (b) 2.24 wt.%; (c) 1.6 wt.%.

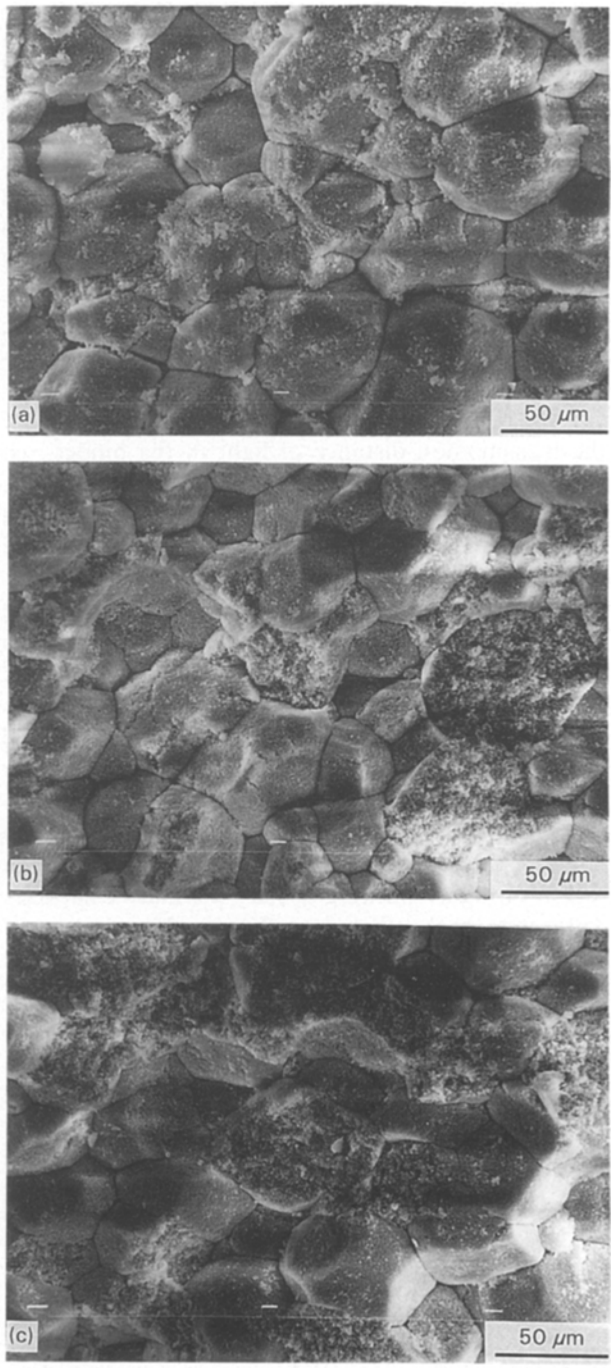

Figure 4 SEM micrographs of fracture surfaces of the compacts with various PVA contents. (a) 3.85 wt.%; (b) 2.24 wt.%; (c) 1.6 wt.%; after binder removal.

specimens after binder removal (as shown in Fig. 4) the fracture occurred almost along the granule boundaries, except in the specimens with low PVA content. The result shows that bonding between granules becomes weaker after binder removal.

4. Discussion

The results of this study clearly show the presence of a binder-rich layer in the surface region of spray-dried granules. This layer results in the network structure of a binder-rich region in the green bodies. The hard granule is difficult to deform and break down, thus the region of low packing density is formed between the granules. The non-uniform packing density affects the densification of the green body [13–15] and forms large processing voids in the sintered ceramics [16–18]. The elimination of non-uniform distribution of binder in powder granules is thus very important in improving the uniformity of ceramics.

The liquid immersion technique has been found to be a powerful tool for examining the internal structure of porous materials [9–11]. The present study demonstrates that this method can also be used to characterize the distribution of the additive which has a different refractive index from the matrix. The distribution can be shown up with an immersion liquid which has a refractive index similar to that of the matrix particles but different from that of the additive. For example, methylene iodide ($n = 1.74$) is suitable in the system of alumina-PVA; the refractive indices for alumina and PVA are 1.77 and about 1.5, respectively. In this case, the reflection of light does not take place at the interface between the matrix particle and the immersion liquid, but does so at the interface between PVA and the matrix particle or the immersion liquid. The more PVA in a region, the weaker the transmitted light. Therefore, if the distribution of PVA is non-uniform, a contrast in the transmitted light appears; the binder-rich region looks darker.

If the binder is rich in the surface region of a sphere the transmission distance of light in the binder-rich region varies with the radial position of the granule. The transmission distance in the surface region is longer in the edge area of the granule than in the centre, therefore the edge of the granule looks dark.

The immersion liquid technique can also examine the packing density of a green body with a suitable immersion liquid. If the difference in refractive index between matrix particle and immersion liquid is too small for light to reflect, the detailed features of the compact can hardly be shown up. If an immersion liquid with a suitable mismatch of reflective index with alumina is used, a certain reflection takes place on the interface of alumina and the immersion liquid. In the region of higher packing density the matrix particles connect to each other, and thereby the numbers of interfaces between the particle and immersion liquid is less than that in the region of low compaction density. Therefore light reflects more markedly in the low density region, and the region looks darker.

The results observed with the immersion liquid technique and SEM showed that the low density region was formed between the granules. The formation mechanism may be that the voids between granules remain after compaction because the granules with the crust of high binder content are too hard to deform enough, and that the matrix particles in the high binder content surface region of the granule cannot rearrange easily to raise packing density. The higher PVA content, the more PVA segregates to the surface of the granule, and the harder the granule becomes. Therefore, the more voids remain and the fracture occurs almost along the granule boundaries. The granules with low PVA content are easy to deform, and the voids between the granules can be removed, thus the binding between the granules is stronger, and the transgranular fracture exists even after binder removal.

To make the formation mechanism of the low density network clear, a lot of research is still needed, but it is known from the present study that the formation of the network is related to the non-uniform distribution of binder in the granules, and the immersion technique is an effective method for characterizing the distribution of the additives and the homogeneity of packing density in porous materials.

References

1. A. G. EVANS, *J. Am. Ceram. Soc.* **65** (1982) 127.
2. F. F. LANGE, *ibid.* **72** (1989) 3.
3. K. UEMATSU, M. MIYASHITA, J.-Y. KIM, Z. KATO, and N. UCHIDA, *ibid.* **74** (1991) 2170.
4. J.-Y. KIM, M. MIYASHITA, M. INOUE, N. UCHIDA, K. SAITO and K. UEMATSU, *J. Mater. Sci.* **27** (1992) 587.
5. K. UEMATSU, M. MIYASHITA, J.-Y. KIM and N. UCHIDA, *J. Am. Ceram. Soc.* **75** (1992) 1016.
6. M. MIYASHIA, J.-Y. KIM, Z. KATO, N. UCHIDA and K. UEMATSU, *J. Ceram. Soc. Japan* **100** (1992) 1357.
7. J.-Y. KIM, M. MIYASHITA, N. UCHIDA and K. UEMATSU, *J. Mater. Sci.* 27 (1992) 6609.
8. K. UEMATSU, M. SEKIGUCHI, J.-Y. KIM, K. SAITO, Y. MUTOH, M. INOUE, Y. FUJINO and A. MIYAMOTO, *ibid.* **28** (1993) 1788.
9. K. UEMATSU, J.-Y. KIM, Z. KATO, N. UCHIDA and K. SAITO, *J. Ceram. Soc. Japan,* **98** (1990) 515.
10. K. UEMATSU, J.-Y. KIM, M. MIYASHITA, N. UCHIDA and K. SAITO, *J. Am. Ceram. Soc.* **73** (1990) 2555.
11. J.-Y. KIM, M. INOUE, Z. KATO, N. UCHIDA, K. SAITO, and K. UEMATSU, *J. Mater. Sci.* **26** (1991) 2215.
12. S. L. LUKASIEWICZ, *J. Am. Ceram. Soc.* **72** (1989) 617.
13. J. ZHENG and J. S. REED, *ibid.* **72** (1989) 810.
14. A. ROOSEN and H. K. BOWEN, *ibid.* **71** (1988) 970.
15. F. F. LANGE *ibid.* **67** (1984) 83.
16. W. D. KINGERY and B. FRANCOIS, "Sintering and Related Phenomena" (Gordon and Breach, New York, 1976).
17. B. J. KELLETT and F. F. LANGE, *J. Am. Ceram. Soc.* **72** (1989) 725.
18. S. FUKAI, N. UCHIDA, Z. KATO and K. UEMATSU, in "Pressure Effects on Materials Processing and Design", MRS Symposium Proceedings vol. 251, edited by K. Ishizaki, E. Hodge and M. Concannon, (MRS, 1992) p. 21.

Received 6 September 1993
and accepted 8 September 1994