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Densification of Alumina at 1250°C with MnO_2 and TiO_2 Additives

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Abstract: The effects of MnO_2 and TiO_2 additions in 3 wt% MnO_2 + (0·5, 1·5, 3·0) wt% TiO_2 additive combinations on the sintering of α-Al_2O_3 have been investigated. The microstructural development along with the microhardness has been characterized. The Al_2O_3 + 3 wt% MnO_2 + 0·5 wt% TiO_2 system resulted in high densification (98% of the theoretical density) giving a uniform grained microstructure and yielding a hardness value of 23·14 GPa at a sintering temperature as low as 1250°C.

1 INTRODUCTION

Sintering of alumina ceramics at relatively low temperatures to obtain dense and fine grained microstructures with sufficient mechanical properties is one of the targets of technological investigations.

The investigations of the influence of MnO_2 and TiO_2 on the sintering behavior of alumina started many years ago. Earlier investigations on the sintering of TiO_2 doped Al_2O_3 showed that there was no indication of a solid solution of TiO_2 in Al_2O_3 when sintered in air.[1] The densification was due to the enhanced grain growth along the grain boundaries. The sintering rate of alumina gradually increased when titania was added up to a certain percent, beyond which the rate leveled off or decreased at a rate due to the formation of a second phase which was found to inhibit the densification.[2] In another study,[3] precipitation in rod or needle-like shapes was observed at the triple junctions, at the grain boundaries and within the matrix, which resulted in increased hardness. In another study, it was shown that the addition of TiO_2 promoted aluminium ion diffusion by a vacancy diffusion mechanism.[4]

The influence of MnO_2 was found to be similar to the effect of TiO_2. The sintering rate increases to a maximum level and then decreases as the Mn concentration exceeds the 0·3 wt% level due to the formation of a second phase. It was proposed that the addition of MnO_2 led to a change in the diffusion mechanism from a grain boundary process to a bulk diffusion process.[5,6]

In this study, the effects of TiO_2 and MnO_2 and the combination of TiO_2 and MnO_2 addition on the sintering characteristics and on the mechanical properties of alumina were investigated.

2 EXPERIMENTAL PROCEDURE

Alcoa A16 SG alumina powder with an average partical size of 0·37 μm and reagent grade $Mn(CH_3COO)_2 \cdot 4H_2O$ and TiC_3 were used as the starting materials. Alumina suspensions of 50 vol% Al_2O_3 were prepared in water solutions of manganese (2) acetate and titanium (3) chloride at pH 2 adjusted with HCl, and slowly added into the solution while stirring and ultrasonicating to break up the agglomerates. The obtained suspensions were dried at 110°C. During this operation the suspensions were mixed regularly to prevent sedimentation. The dried powders were then calcined at 600°C for one hour in order to obtain additive oxides and pressed to disk shaped samples. These pressed samples were sintered to 1250, 1350, 1450 and 1550°C for one hour, employing 10°C/min as the heating and cooling rates. The compositions of the samples are given in Table 1.

The sintered densities of the samples were measured by the water immersion technique. Vickers

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microhardness was measured on the polished samples using a Leitz Mini Load Hardness Tester at a load of 300 g and an average of 10 indentations per specimen. The results are given in Table 2. The polished samples were thermally etched at 100°C below the sintering temperature. They were then coated firstly with carbon (~250 Å) and later with gold (~300 Å) for the SEM study, equipped with the Energy Dispersive X-Ray Spectrometer (EDS) facility (Figs 1–3).

Table 1. Compositions of the Al_2O_3 samples

No.	% MnO_2 added	% TiO_2 added
0	—	—
1	3·0	—
2	—	3·0
3	3·0	0·5
4	3·0	1·5
5	3·0	3·0

3 RESULTS AND DISCUSSION

The densities of the undoped samples decreased from 68 to 95% of the theoretical density with the increased sintering temperatures employed in this

Table 2. Theoretical densities π (%) and Vickers microhardness V_H (GPa) of the samples

No.	1550°C π	1550°C V_H	1450°C π	1450°C V_H	1350°C π	1350°C V_H	1250°C π	12540°C V_H
0	95·0	22·55 ±1·92	89·9	20·59 ±1·27	77·1	18·24 ±1·57	68·7	—
1	98·7	24·81 ±2·68	96·2	21·47 ±2·11	86·3	19·22 ±2·04	73·0	—
2	97·5	23·14 ±3·68	95·2	21·77 ±1·40	95·0	23·43 ±3·01	81·1	—
3	98·5	18·23 ±1·82	98·5	19·51 ±1·37	98·2	23·82 ±2·21	98·2	23·14 ±1·47
4	95·9	24·81 ±2·47	98·2	22·26 ±2·36	98·2	21·86 ±1·46	94·4	22·06 ±0·93
5	95·2	26·77 ±2·07	95·0	20·39 ±2·06	98·5	22·35 ±2·01	98·2	21·57 ±2·50

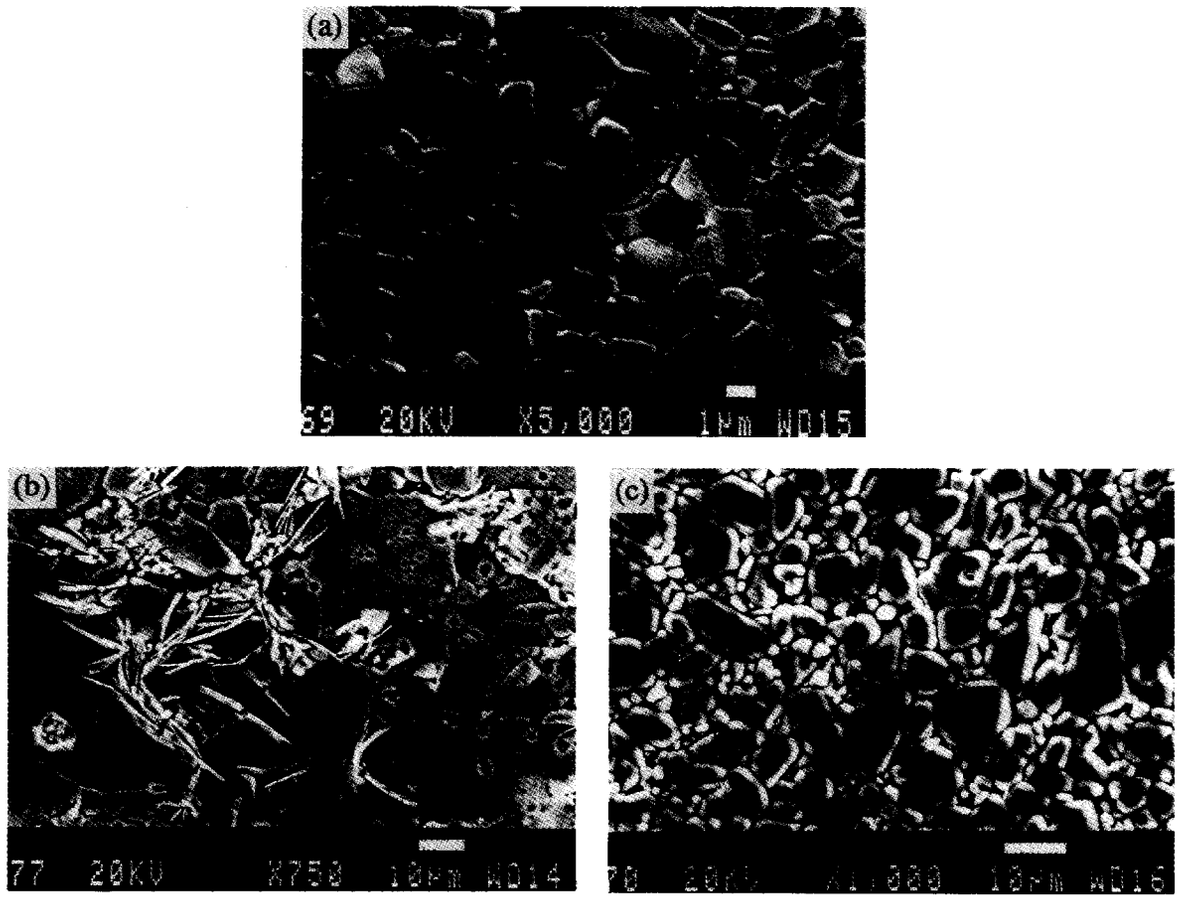

Fig. 1. SEM micrographs of (a) undoped, (b) Mn-doped and (c) Ti-doped alumina, sintered at 1550°C.

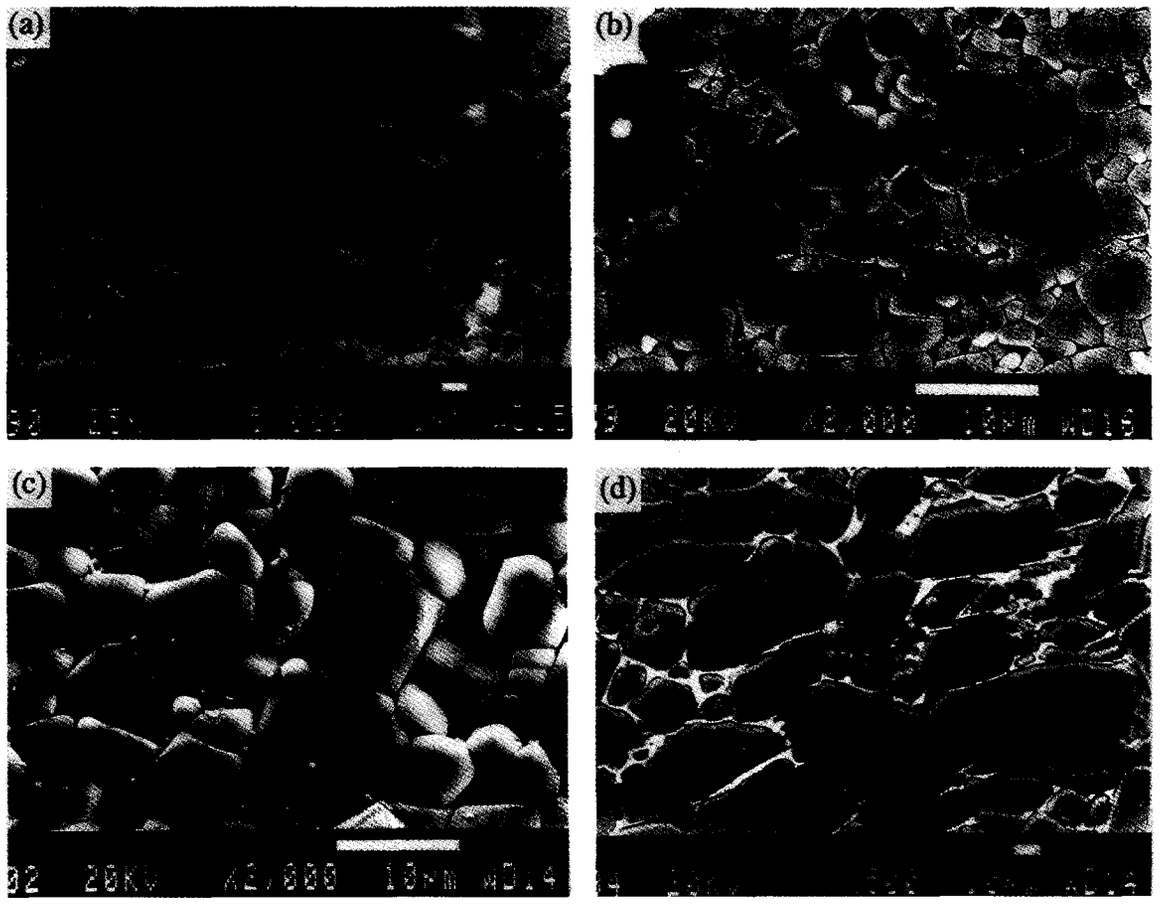

Fig. 2. The microstructures of Al_2O_3 + 3 wt% MnO_2 + 1·5 wt% TiO_2 samples sintered at (a) 1250°C, (b) 1350°C, (c) 1450°C and (d) 1550°C.

study. The densities of the 3 wt% MnO_2 doped alumina increased from 73 to 98·7% of the TD. This shows that MnO_2 results in a favorable effect in the densification process. The 3 wt% TiO_2 doped samples also showed a similar effect, but at lower sintering temperatures, therefore TiO_2 addition was more effective than MnO_2 addition.The densities of the MnO_2 and TiO_2 doped alumina samples ranged approximately between 95 and 98% of the TD. However the 0·5 wt% TiO_2 and 3 wt% MnO_2 doped samples have showed ~98·5% densification level in all sintering conditions employed. The densification of the alumina decreased with the increasing amount of the TiO_2 additive and sintering temperature, due to the formation of a second solid phase and liquid phase. Therefore, the

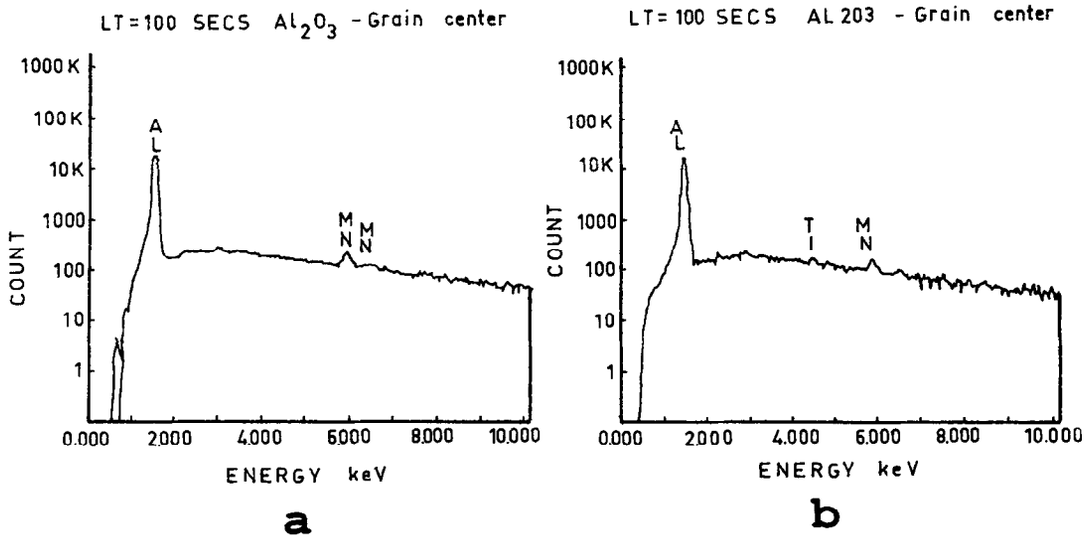

Fig. 3. EDX-point analysis of (a) 3 wt% MnO_2 and (b) 3 wt% MnO_2 + 3 wt% TiO_2, added to Al_2O_3.

addition level of 0·5 wt% TiO_2 to the 3 wt% MnO_2 doped alumina was found to be sufficient to achieve the 98·2% TD value at 1250°C. The microhardness values showed high standard deviation because of the different levels of porosity, grain size and secondary phase distribution in the samples. The hardness increased with increasing sintering temperature in the pure alumina and MnO_2 and TiO_2 doped samples. Overall, the TiO_2 + MnO_2 doped alumina samples gave higher hardness values at the same sintering temperature due to precipitation hardening. Similar results were also observed in other ternary systems.[7]

According to the SEM micrographs of the samples (shown in Figs 1 and 2), the effect of the single additions was more evident on grain growth when compared with the undoped samples (Fig. 1). In the samples having 3 wt% MnO_2 and 3 wt% TiO_2, the grain size increased up to 13 and 7 μm, respectively, with increased sintering temperature. The EDX-point analysis from the centers of large grains (Fig. 3) indicates that MnO_2 formed a solid solution with alumina. MnO_2 doped samples gave exaggerated grain growth with a high amount of closed pores when sintered at 1550°C. The draining of the second phase and needle-like appearance of the phases at the grain boundaries indicate that precipitation occurred at this temperature. An observation of the formation of a second phase between the grains was reported in the case of the 0·5–1·5 wt% MnO_2 doped alumina which was attributed to the limited solid solubility of MnO_2.[8]

In the TiO_2 doped samples, the segregation of TiO_2 was also observed at the grain boundaries of Al_2O_3, giving various morphologies at different sintering temperatures. This segregation resulted in porosity between the small and large grains. As shown in Fig. 2(d) the excess addition of TiO_2 to the Al_2O_3 + 3 wt% MnO_2 system increased the formation of the second phase or the glassy phase, which resulted in the increment of intergranular pores. The formation of the needle-like second phase was also observed in the 3wt% MnO_2 + 0·5 wt% TiO_2 samples sintered at 1450°C and 1550°C. When TiO_2 was increased up to 1·5 wt% the grains became rounded and a large number of pores were formed during sintering at 1350°C and 1450°C.

The microstructure of the 3 wt% MnO_2 + 3 wt% TiO_2 doped alumina showed an exaggerated grain growth having glassy phase pockets along grain boundaries and also in grain junctions.

4 CONCLUSIONS

The sintering rate of alumina powder compacts increased when 0·5–1·5 wt% titania was added to the Al_2O_3 + 3 wt% MnO_2 system, which promoted grain growth and lowered the sintering temperature. A high densification, up to 98·2% TD, was achieved at 1250°C resulting in a microhardness value of 23·14 GPa.

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