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A colloidal method for manganese oxide addition to alumina powder and investigation of properties

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Various methods can be applied to introduce additives to ceramic materials. Of these methods, mechanical mixing may not always be suitable to obtain a uniform distribution of the small quantities of additive within the structure, requiring colloidal methods to be applied for the purpose. The addition of manganese oxide to alumina powder has been studied using a colloidal method. The effect of the manganese addition on alumina microstructure and the later stages of the densification behaviour was investigated, together with the hardness and mechanical strength. No evidence of secondary phase formation was detected between the manganese cation and alumina powder for up to 0.5 wt % manganese addition, suggesting that manganese is in solid solution with alumina. The microstructural evidence presented suggests that small quantities of a manganese addition to alumina enhance the densification process through the formation of fast diffusion paths within the crystalline structure, similar to the effect of TiO_2 addition.

1. Introduction

Additives are commonly being used in the processing of traditional and advanced ceramic materials for the purpose of changing the microstructure, resulting in changes in mechanical and physical properties. For example, ZnO is doped with several different oxides to increase or decrease the grain size in order to modify the electrical properties of varistors. Furthermore, alumina has been doped with a variety of oxides to enhance the hardness and toughness of the material.

A variety of oxides such as TiO_2, SiO_2, Cr_2O_3, Fe_2O_3, MnO and MgO are the types of additives commonly used in structural alumina ceramics to enhance sintering and to modify the microstructure and mechanical properties. Fe_2O_3 and TiO_2 additives were found to enhance sintering, together with grain growth, while CaO and SiO_2 additives were found to be detrimental to the densification process, although they yielded fine-grain microstructures [1]. Simple binary compositions which form low-temperature melting glass compositions, such as those in the $MnO–TiO_2$ system [2], and complex compositions in the $CuO–TiO_2–B_2O_3–MgO$ system [3], were shown to lower the alumina sintering temperature while resulting in duplex microstructures.

The effect of MnO on the initial sintering of alumina has been studied previously [4, 5]. However, the full densification regime and detailed microstructural examination have not yet been investigated. According to the results of early studies based on shrinkage data, the sintering rate accelerated until the impurity concentration exceeded a certain impurity level, typically 0.3% MnO. It is first proposed that the addition of MnO in any of the proportions of 0.1–1.0% MnO, caused a change in the diffusion mechanism to bulk diffusion from grain-boundary diffusion, as was also observed for the pure alumina. Later, it was suggested that a change in mechanism from volume to grain-boundary diffusion occurred after about 4% linear shrinkage for samples having concentrations up to 0.3% MnO.

When a small amount of material is intended to be mixed with another major component, there is usually a problem of insufficient mixing. The wet ball milling technique is commonly used to enhance the quality and homogeneity of mixing. Although the wet ball milling technique is sufficient for most of the cases, it may have its limitations when doping with a minor amount of submicron particles. Doping of alumina with less than 1% additive is difficult to achieve when oxides are directly mixed, requiring colloidal methods to be employed. If the desired dopant could be added to alumina in the form of a salt solution, more homogeneous microstructures and properties could be obtained. The desired ceramic cation containing salts such as nitrates, sulphates and acetates can be used for obtaining a homogeneous mixture. In this study, a colloidal method for the addition of manganese-oxide in the form of manganese acetate, $Mn(CH_3COO)_2 \cdot 4H_2O$, to alumina was investigated. The effect of small amounts of manganese cation addition on the sintering behaviour of alumina, its microstructural development and mechanical properties was also investigated.

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2. Experimental procedure

An additive that can easily be dissolved in water, forming its ions, to yield a homogeneous dispersion is the first criterion for a proper additive material because water is the most economical and commonly used solvent in alumina processing. Furthermore, the additive should also display easy decomposition properties and have no residual mass left after the decomposition process. Therefore, manganese acetate, $Mn(CH_3COO)_2 \cdot 4H_2O)$, which is soluble in water, methanol, ethanol, and dehydrates at 80–130 °C [6], was selected as the organic additive. It was intended to prepare a 50 vol % alumina suspension in acetate–water solution; thus, prior to mixing, the required amounts of manganese acetate, determined from the stoichiometric calculation, were added to water to yield 0.1%, 0.3% and 0.5% MnO_2 on AlCOA A-16SG grade alumina powder which has an average particle size of 0.38 μm and a specific surface area of 9 $m^2 g^{-1}$.

The most stable suspensions for commercial alumina powders occur at pH = 2 [7] where the particle to particle repulsion is very strong, not allowing any agglomeration among the alumina particles. When the manganese acetate is added to the water by magnetic stirring, the pH of the solution drops to 4, but later continuously increases to the zero point charge value of alumina as the alumina powder is added to the solution. Formic acid is found to be a suitable pH stabilizer for the water–acetate system. Therefore, as alumina powder is gradually added to the water–acetate solution, the steadily increasing pH was kept to around 2, by the addition of formic acid. Continuous magnetic stirring was applied to suspensions during the mixing step. The 50 vol % alumina suspension prepared was then dried at 90 °C for 12 h to remove all of the liquid. It is suggested that during the drying stage, manganese cations are precipitated on alumina particles in a well-dispersed state.

The dry pressing technique was selected as the forming process for the dried powders. 20 cm diameter and 0.3 cm thick tablets were pressed under 100 MPa pressing stress and the same size tablets were also prepared from undoped alumina powder for comparison purposes. Samples of both doped and undoped powders were sintered at 1550, 1600, 1650 °C for 1 h under normal furnace atmosphere conditions. Sintering temperatures were reached using a heating rate of 5 °C min^{-1}.

After sintering, sample densities and porosities were determined by the boiling water technique. The average mechanical strength of the samples was calculated using the failure loads of samples determined using a ball-on-ring test apparatus [8]. The average microhardness of the samples was determined on polished surfaces of samples under 500 g load after a minimum of 15 independent measurements. Scanning electron microscope (SEM) investigations with electron microprobe analysis were carried out on polished and thermally etched samples.

3. Results and discussion

AlCOA A-16SG powder can easily be sintered to 97% theoretical density after sintering at 1540 °C for 1 h [9]. This study carried out on undoped similar alumina powder, also confirms the above result after sintering at 1550 °C for 1 h. Table I gives the results of densification for undoped and manganese-doped alumina samples sintered at different temperatures. While the full density can be achieved for undoped alumina at higher sintering temperatures, there is always a small amount of porosity in manganese-doped samples. The higher the amount of manganese doping, the higher the relative amount of porosity for the same sintering temperature, owing to the presence of a large number of closed pores trapped within the grains as shown in Fig. 1.

TABLE I Sintering shrinkage, per cent theoretical density and porosity of undoped and manganese-doped calcined aluminas

Sintering temperature (°C)	Shrinkage (%)	Theoretical density (%)	Porosity (%)
Undoped alumina			
1550	15.94	97.5	2.4
1600	16.50	99.5	0.5
1650	16.55	100.0	0.0
0.1 % Manganese-doped alumina			
1550	15.87	98.0	2.0
1600	16.22	99.0	1.0
1650	16.48	99.2	0.8
0.3% Manganese-doped alumina			
1550	15.83	98.0	2.0
1600	15.86	98.5	1.5
1650	16.00	99.2	0.8
0.5% Manganese-doped alumina			
1550	15.85	98.2	1.8
1600	15.96	98.0	2.0
1650	15.95	98.5	1.5

Sintering at higher temperatures resulted in a relatively homogeneous grain-growth process for undoped alumina, with only a few pores trapped between the grains. The average grain size increased from 1.38 μm to 3.05 μm after sintering at 1650 °C for 1 h (Fig. 2). Similar grain-growth phenomena, but inhomogeneously, were observed in manganese-doped samples at a more intensive level. Fig. 1 shows scanning electron micrographs of 0.5 % manganese-doped samples after the 1550 and 1650 °C sintering process. Compared to the undoped samples of Fig. 2, these samples have large-sized grains, as large as 25 and 120 μm for 1550 and 1650 °C, sintering, respectively. The average grain sizes of the two samples shown in Fig. 1, were found to be 9.5 and 30 μm as determined with the line intercept count method [10].

Although, the role of manganese addition in the sintering of alumina has been studied before [4, 5], no detailed study of the microstructural and mechanical properties has been carried out. The shrinkage data were evaluated to show that bulk and boundary diffusion are both effective in the initial stage of sintering up to 4 % shrinkage [5]. No comments were made concerning the later stage of sintering. It was also recently proposed that manganese oxide addition to alumina resulted in the formation of a secondary phase between the grains [11]. A eutectic composition is present on the MnO-rich side of binary MnO–Al_2O_3 system at 1520 °C [12]. This may suggest the formation of a fragmentary liquid phase during the sintering process carried out above 1550 °C. However, micrographs shown in Figs. 1 and 3 do not indicate the presence of any secondary phase formation between the grains within the limits of this study up to 0.5% manganese additions, contrary to the proposed claims of liquid formation [4]. It appears from all the micrographs that the grain-growth process in the later stages of sintering is enhanced via another process other than the formation of a liquid phase. In fact, manganese, like iron, displays a variable valency, so that a complex series of oxides and hydroxides exists. The ready valency change of manganese also leads to many defect structures and non-stoichiometric compounds. Therefore, it may be suggested that different manganese cations with different valency states can substitute the aluminium cation sites within the crystalline structure, resulting in either vacancy formation or an extra electron. This type of phenomenon was shown to exist during sintering in the case of TiO_2 doping to alumina powder by activating the volume diffusion rate of species [13]. The sintering rate is proportional to the vacancy concentration that forms as Ti^{3+} and Ti^{4+} enter Al_2O_3 substitutionally, and when the charge neutrality is achieved by the presence of other divalent cations in the powder. An energy dispersive X-ray analysis that was carried out on polished and thermally etched samples in the SEM, indicated that manganese was well distributed throughout the grains, and no segregation of manganese was detected at the grain boundaries. Therefore, it may be proposed that manganese cations substitute the aluminium sites, resulting in fast diffusion paths within the single grains during the sintering process. As a result of the fast diffusion paths formed, the process of excessive grain growth is enhanced when the amount of manganese addition is increased from 0.1% to 0.5%, as shown in Fig. 3.

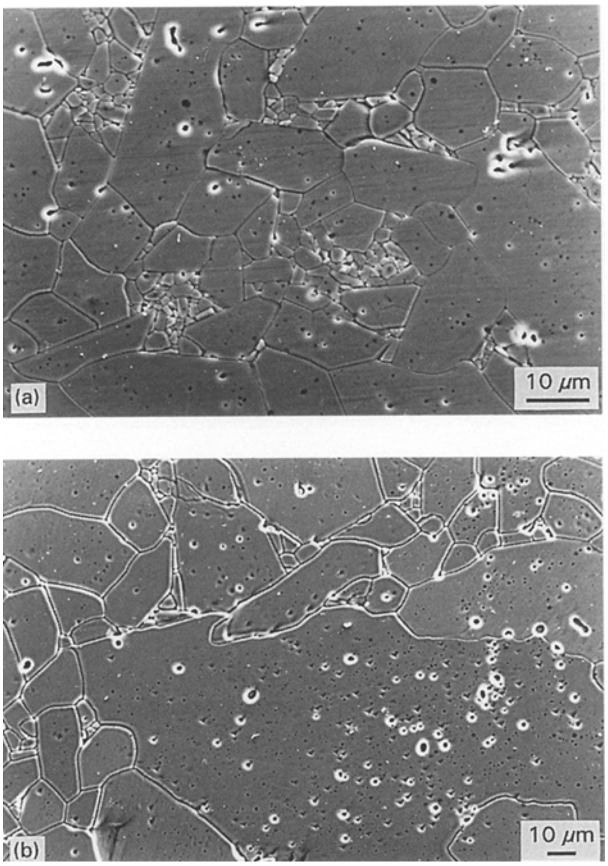

Figure 1 Scanning electron micrographs of 0.5% manganese-doped alumina: (a) after sintering at 1550 °C, (b) after sintering at 1650 °C.

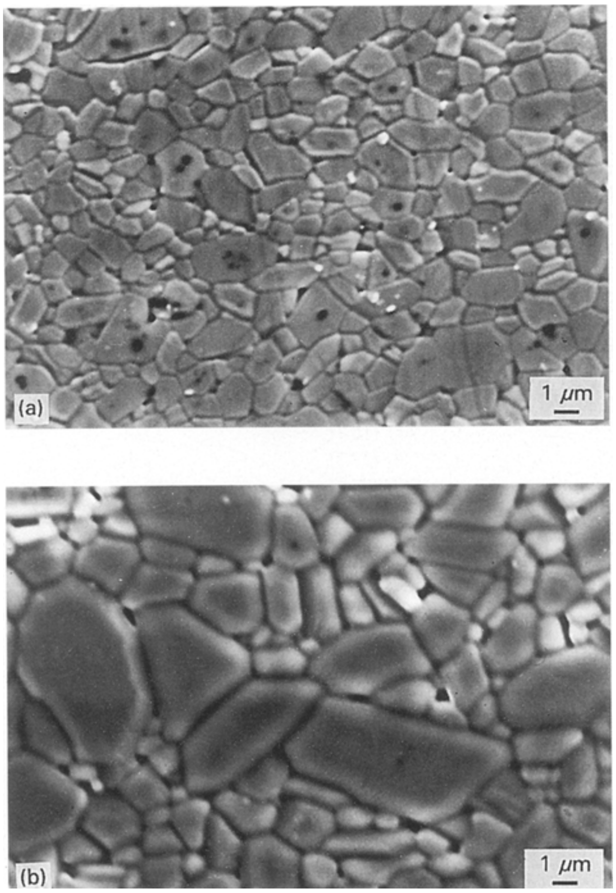

Figure 2 Scanning electron micrographs of undoped alumina samples: (a) after sintering at 1550 °C, (b) after sintering at 1650 °C.

Microhardness measurements and the strength of the samples are presented in Table II as a function of sintering temperature and dopant amount. It can be deduced from this table that there is a slight increase in microhardness values as the sintering temperature is increased, regardless of the dopant portion. On the other hand, manganese doping to alumina causes a slight decrease in hardness relative to undoped samples.

Based on the results presented in Table II it will be difficult to derive some definitive information regarding the role of the manganese addition for the strength of alumina. Although a trend of some strength reduction is present in samples sintered at 1550 and 1600 °C, higher strength values obtained for samples sintered at 1650 °C require some caution in relation to this statement. On the other hand, the relatively low standard deviation and high Weibull modules of those samples which contain more than 0.3% manganese doping, indicate the formation of more reliable microstructures from the mechanical strength point of view. Therefore, it may safely be said that the addition of

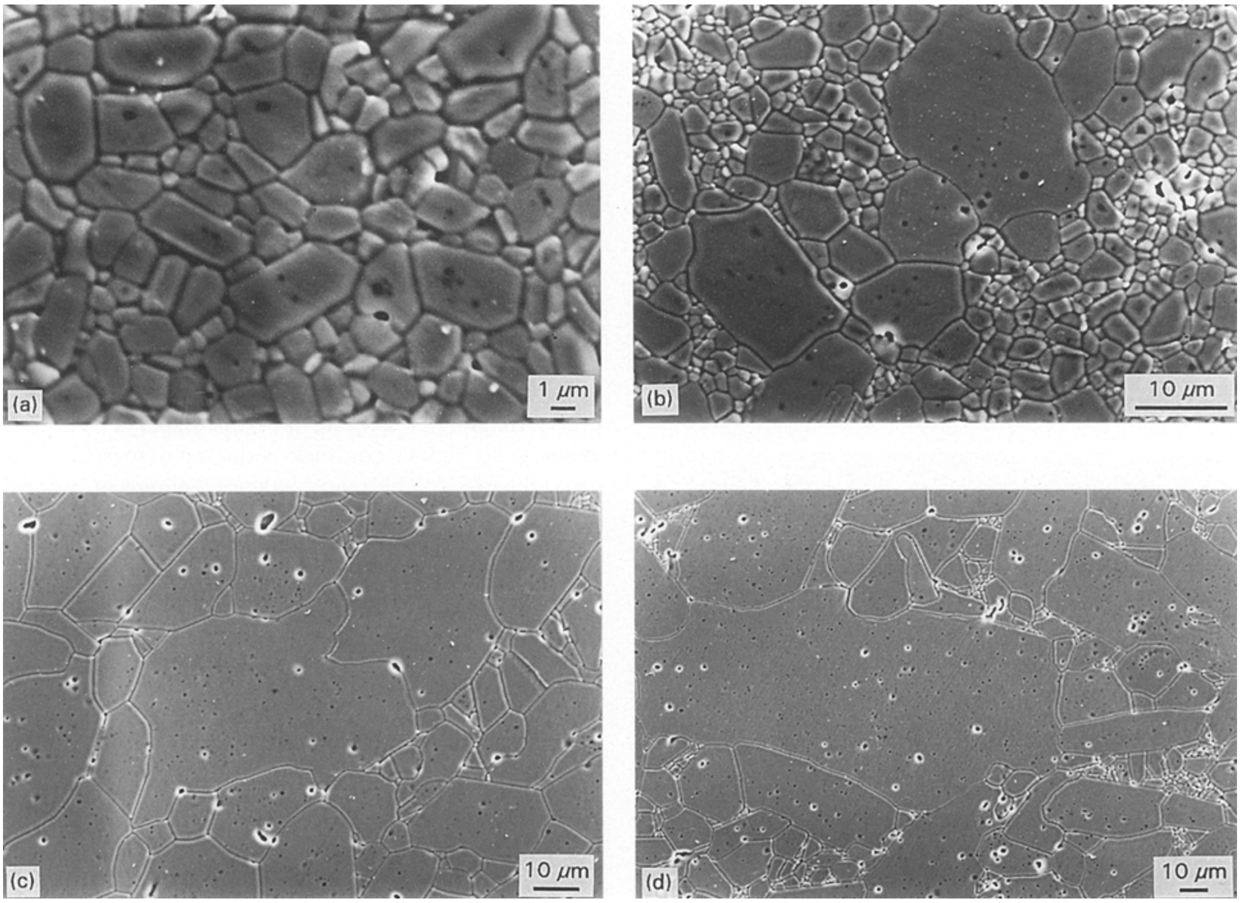

Figure 3 Grain-growth process in samples sintered at 1600 °C as a function of manganese addition: (a) undoped alumina, (b) 0.1% manganese, (c) 0.3% manganese (d) 0.5% manganese additions.

TABLE II The average microhardness and strength of manganese-doped and undoped alumina samples sintered at different temperatures

	Temperature (°C)	Microhardness (S.D.) (MPa)	Strength (S.D.) (MPa)	Weibull modulus
Undoped alumina	1550	18.98 (0.64)	344 (76.9)	4.65
	1600	19.41 (0.58)	363 (53.2)	6.94
	1650	20.29 (0.85)	334 (71.7)	4.84
Manganese doped alumina				
0.1%	1550	18.94 (0.44)	299 (45.4)	6.95
	1600	19.36 (0.38)	318 (37.6)	8.34
	1650	20.15 (0.63)	296 (49.4)	6.41
0.3%				
	1550	18.33 (0.72)	239 (21.8)	11.60
	1600	18.86 (0.67)	203 (16.7)	12.96
	1650	19.56 (0.55)	380 (27.7)	14.94
0.5%	1550	18.30 (0.79)	200 (24.0)	19.01
	1600	18.80 (0.35)	190 (20.3)	10.07
	1650	19.53 (0.42)	353 (29.1)	13.07

manganese to alumina causes the consistent flaws that are responsible for the fracture of samples.

4. Conclusions

The colloidal approach is an effective method to obtain a homogeneous distribution of additives, especially when small quantities of additives are concerned. Doping of alumina with very small quantities of manganese by means of the colloidal approach yield an excessive grain growth phenomenon during sintering of alumina compacts. No evidence was found for liquid phase nor secondary phase formation within the limits of the dopant level studied. Therefore, it is postulated that the grain-growth process is due to the formation of fast volume diffusion paths within the grains because manganese can occur in different valency states, similar to iron and titanium. It is also thought that while the undoped samples can be sintered to full density at 1650 °C, doped samples can only be sintered to 98%–99% theoretical density owing to the presence of closed pores trapped within the grains. A slight decrease in hardness was recorded as the amount of manganese doping increased. It is hard to suggest any correlation with respect to the function of manganese on materials strength; however, it can safely be proposed that manganese addition to pure alumina yields structurally more reliable structures, based on the high Weibull modulus and low standard deviation of fracture strength measured for doped samples.

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