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Influence of the Water Content of Milling Medium on the Mechanical Properties of Reaction Bonded Aluminium Oxide (RBAO) Ceramics

J. TEMUUJIN[1,2,3], J. CORONEL[1] and M. SENNA[2]

[1]*Advanced Ceramics Group, Technical University of Hamburg-Harburg, Hamburg, Denickestrasse 15, D-21073 (Germany)*

E-mail: jtemuujin@yahoo.com

[2]*Department of Applied Chemistry, Faculty of Science and Technology, 3-14-1 Hiyoshi, Kohoku-ku, Keio University, Yokohama 223-8522 (Japan)*

[3]*Institute of Chemistry and Chemical Technology, Mongolian Academy of Sciences, Ulaanbaatar 51 (Mongolia)*

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Abstract

Influence of the water content of milling medium on the properties of reaction bonded aluminium oxide powder precursors and their sintered mechanical properties is studied. As a result of interaction between absolute ethanol and aluminium, the water content of the mixture milled in absolute ethanol increased to 4.7 %. Mechanical properties such as bending strength and toughness of the sintered ceramics depend on the water content of the powder precursors. Higher bending strength, 350 MPa and toughness, 3.7 MPa $m^{1/2}$ were observed in the sample milled in absolute ethanol. Higher water content of the mixture milled in absolute ethanol is the main reason of the high mechanical properties.

INTRODUCTION

Since 1990, reaction bonded aluminium oxide (RBAO) ceramics has been studied extensively because of its superior mechanical properties, easy preparation method and near-net-shape forming capability [1]. This method utilizes a 28 % volume expansion associated with the reaction $Al \rightarrow \alpha\text{-}Al_2O_3$ to neutralize the sintering shrinkage. A composition with Al 45 vol. %, Al_2O_3 35 vol. % and ZrO_2 20 vol. % was established to give superior properties of sintered ceramics.

RBAO powder precursors are usually prepared by milling in an organic medium to achieve desired particle size without hydrolysis and serious oxidation of raw materials (Al and oxides) in order to keep advantages of low-shrinkage capability. As milling media, ethanol, aceton, cyxclohexane or mineral spirit can be used [2]. Ethanol is used most extensively due to its capability of surface passivation of finely milled aluminium particles. In some cases water is added by ≈5 vol. % or more to the ethanol for faster passivation of the surface [3]. Our previous research indicates that the water content of ethanol influences the stability of suspension and milling efficiency [4]. It is therefore important to establish optimal water content of milling medium in order to tailor the properties of RBAO precursors. There are no reports on the relation of mechanical properties of RBAO ceramics with respect to water content of milling medium during powder preparation. The present report describes the effect of water content of ethanol on the microstructures and mechanical properties of RBAO ceramics.

EXPERIMENTAL

50 g RBAO precursor mixtures with a composition Al 45 vol. % (Al from Eckart AS081, $d_{50} \approx 20$ μm), Al_2O_3 35 vol. % (Al_2O_3 from Condea HPA 0.5, $d_{50} \approx 0.5$ mm), and ZrO_2 20 vol. % were milled in ethanol containing 0, 2, 4, 6, 8 and 10 vol. % water with an attrition mill (Netzsch PE075, Netzsch Feinmahltechnic, Germany) by 1700 g of 3 mm zirconia grinding balls (3Y-TZP, Tosoh, Japan), for 7 h. Stirring arm was kept at 700 rpm and the amount of the milling liquid was 220 ml. After milling, the samples were dried at room temperature for 24 h and sieved through 200 μm sieve. Water content of the powder precursors were determined by a Carl-Fischer titration instrument (Aqua 40.00, Electrochemie GmbH, Halle, Germany) with a static mode at 250 °C for 30 min. The specific surface area was calculated by single point BET method using a Quantasorb Jr. (Quantachrome, US) instrument. Green samples were prepared by uniaxial pressing at 100 MPa using a steel die with 4.5 × 40 mm. The green specimens were obtained by cold isostatic press at 300 MPa for 2 min. Samples were oxidized at 900 °C with the heating and cooling rates at 0.38 °C/min. After oxidation, the specimens were sintered at 1450 °C for 2 h with the heating and cooling rates at 10 °C/min.

Samples were ground and polished with 1mm finish on the tensile surface. The 4-point bending (fracture) strength was measured with a universal testing machine. Fracture toughness was determined by indentation method. Green densities were estimated from the mass and dimensions, using the theoretical densities of the individual components. Bulk densities of the specimens were determined by the water-based Archimedes method. Samples were denoted as R-0, R-2, R-4, R-6, R-8 and R-10, where the suffix means the volume percent of water present in the milling medium.

RESULTS AND DISCUSSION

Figure 1 shows the water content of the milled mixtures determined at 250 °C with a static mode by a Carl–Fischer titration method.

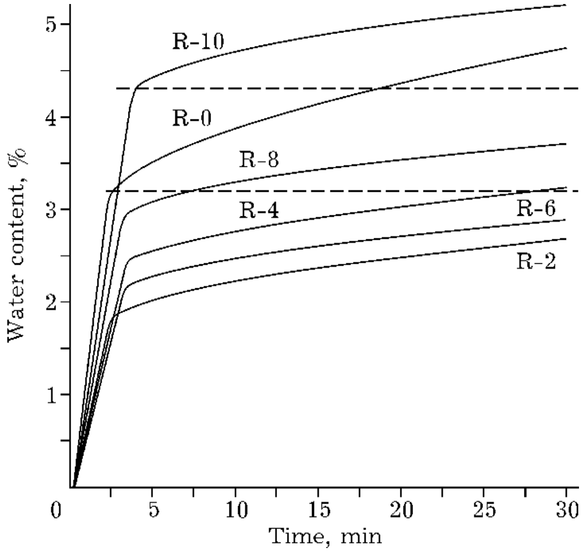

Fig. 1. Water releasing curves of the mixtures.

Higher water content was observed in samples milled in ethanol containing 10 % of water. In spite of milling in absolute ethanol, the water content of the R-0 mixture is higher than that in R-2, R-4, R-6 and R-8 mixtures. After 5 min of heating at 250 °C, most of physically adsorbed water is removed, so that the remaining water released after a longer period of time can be assigned as hydroxides rather than physically adsorbed water. Therefore, the initial linear increase of the water release from all the samples should be associated with physically adsorbed water. The slope of water release of R-0 is higher after 5 min of heating than that of other samples milled in water-containing ethanol. This indicates that samples milled in absolute ethanol contain more chemically bound water, although we did not observe any crystalline aluminium hydroxides in the milled mixtures. However, one cannot exclude that the aluminium hydroxides might exist in fine-grained nanocrystalline form. Among the water containing ethanol-milled samples, the slope of water release of R-10 sample is the highest. It indicates that R-10 contains more chemically bound water than other water-containing ethanol-milled samples. Appearance of the physically and chemically bound water agrees well with the findings of Holz *et al.* [5]. Moreover, R-0 mixture contains larger amount of physically adsorbed water than R-2, R-4, R-6 and R-8 mixtures. We have

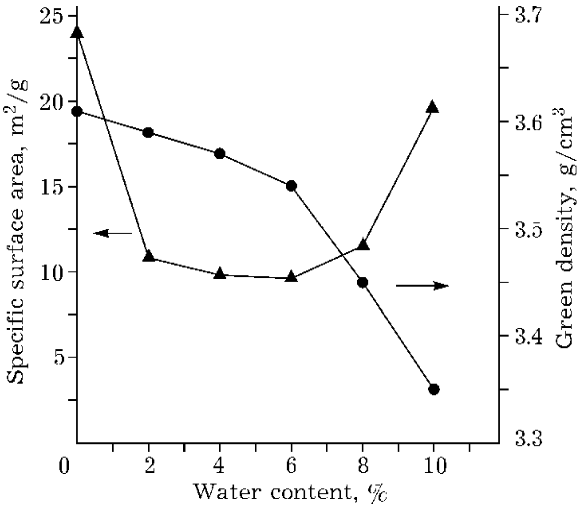

Fig. 2. Changes in the specific surface area and green density against water content of the milling medium.

suggested that the increase in the water content may be related with the dehydration and dehydrogenation of ethanol on the surface of oxide or coordination of ethanol to the unsaturated metal centres [4].

Figure 2 shows the changes in the green density and the specific surface area of the samples with water content of the milling medium. Specific surface area of R-0 was highest of all the mixtures, followed by R-10. It reaches to 23.91 m^2/g in absolute ethanol with a decrease to 10.8, 9.8, 9.6, 11.5 and 19.6 m^2/g for 2, 4, 6, 8, 10 % water-containing ethanol, respectively. This indicates the appearance of more porous fine structure in R-0 mixtures. Hence, the specific surface area depends on the water content of the mixtures. The green density of the pressed sample decreased from 3.61 in absolute ethanol to 3.59, 3.57, 3.54, 3.45 and 3.35 g/cm^3 in 2, 4, 6, 8 10 % of water-containing ethanol, respectively. Higher green densities of RBAO ceramics are usually attributed to the strong Al/Al contact bridging among the ceramic particles as a consequence of plastic deformation of Al. The latter is caused by the compaction force during pressing. It is obvious that sample milled in the absolute ethanol contains high percentage of Al and is in agreement with the less oxidized state of the mixtures milled in ethanol without or with small amount of water [4].

Figure 3 shows change in the bending strength of the sintered RBAO ceramics against water content of the starting milling medium. The experimental results clearly indicate the effects of water content in the milling medium on the mechanical properties of the RBAO ceramics. The highest mechanical properties were observed in the samples milled in absolute ethanol. The difference in the bending strength with water content of the milling medium is very significant, *i. e.* more than 2-fold between samples milled in absolute and 2 or 4 % water-containing ethanol. However, the sintered density exhibits little difference. Final sintered densities were 99.66, 97.80, 98.60, 99.16, 98.29 and 99.87 % of theoretical density for the R-0, R-2, R-4, R-6, R-8 and R-10 samples, respectively. Thus, the influence of the sintered density on the bending strength is rather strong. Low bending strength of the R-2 sample is possibly related with higher residual porosity of this sample since it shows the lowest sintered density. The change in the specific surface areas of the milled mixtures suggests that the contact area between A_2O_3 grains in the R-0 and R-10 samples is larger than that in R-2, R-4, R-6 and R-8 samples. In other words, R-0 and R-10 samples contain smaller grains than those of other mixtures, although we do not have direct evidence on this matter. This is in good agreement with the water content of the samples, where R-0 and R-10 samples showed higher content of both physically and chemically bound water. Deng *et al.* suggested that the fracture strength of Al_2O_3 ceramics is substantially increased with addition of $Al(OH)_3$, due to strong grain bonding by fine Al_2O_3 grains produced by the decomposition of $Al(OH)_3$ [6]. Samples R-0 and R-10 contain

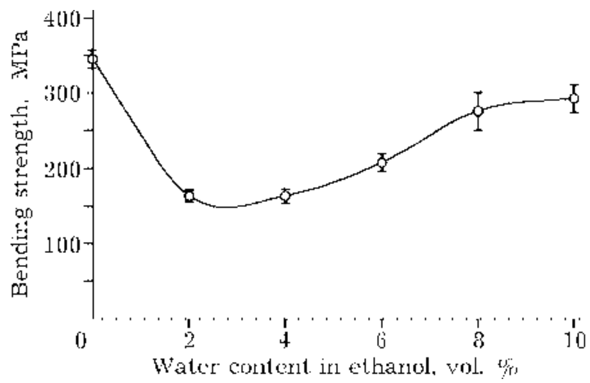

Fig. 3. Plots of the bending strength of the sintered RBAO against starting water content in the milling medium.

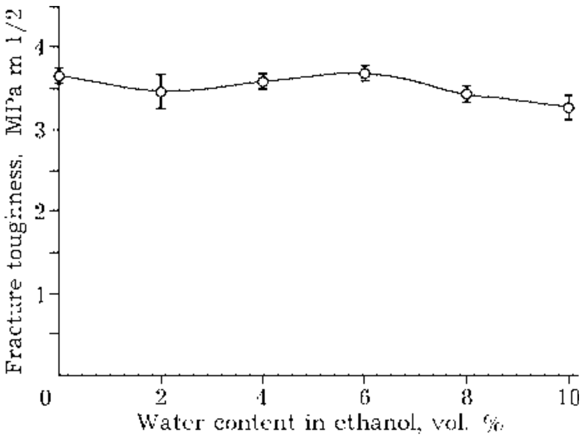

Fig. 4. Plots of the fracture toughness of the sintered RBAO against water content in the milling medium.

higher amount of chemically bound water, as it can be seen from water releasing slope of the samples (see Fig. 1). Therefore, lower bending strength of the R-2, R-4 and R-6 samples should be assigned to the lower content of the chemically bound water in these samples.

Figure 4 exhibits a change in the fracture toughness against water content of the milling medium. It lies around 3.5–3.7 MPa $m^{1/2}$ with its change smaller than that of the bending strength. It was reported that the fracture toughness does not increase with increasing amount of the $Al(OH)_3$ at higher density [6]. Since, all the samples show almost similar high theoretical density with low porosity, so that they possess a common fracture-mode, regardless of the water content of the mixtures.

Although milling in absolute ethanol brings higher mechanical properties and better near-net-shape forming capability, drying process should be carried out carefully to avoid self-ignition of fine-grained aluminium. On the other hand, an increase in the bending strength of the RBAO ceramics with further increasing of water content of the ethanol after the minimal value between 2–4 vol. % indicates that tailoring of the mechanical properties is possible by changing the water content of ethanol. Increased water content of ethanol gives not only improved mechanical properties but also economical benefits by reducing the ethanol amount. Care should be taken, however, since the higher water content in the milling medium causes more oxidation of aluminium particles, which might reduce the near-net shaping ability of the RBAO ceramics.

CONCLUSIONS

Mechanical properties of the RBAO ceramics depend on the water content of the starting mixtures. RBAO mixtures milled in absolute ethanol contain higher amount of water both physically and chemically bound, up to 4.7 %. The bending strength of this sample was the highest of all, to be 350 MPa. The mixtures milled in water-containing ethanol show less water content at the end of milling and result in the poorer mechanical properties. The samples with fine microstructure were obtained with decomposition of aluminium hydroxide in the sample that was milled in absolute ethanol. This is the main reason of the improved mechanical properties.

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