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Influence of anionic stabilization of alumina particles in 2-propanol medium on the electrophoretic deposition and mechanical properties of deposits

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Abstract

The ceramic dispersions were prepared using 0.85, 1.70, 4.25, 12.75 or 21.25 wt.% of monochloroacetic, dichloroacetic or trichoroacetic acid, 15 wt.% alumina and 2-propanol. The mechanism of anionic stabilization in 2-propanolic media was described. Alumina green bodies were prepared from the stable dispersion via electrophoretic deposition (EPD). It was found that increasing dispersion conductivity significantly influenced the EPD yields. The most effective electrophoretic depositions were performed from dispersions with conductivity in range 4.0–5.3 × 10^{-4} S m^{-1}. Deposits with the highest green density were prepared from the dispersion stabilized by trichloroacetic acid. This behavior was explained by low voltage drop during deposition. The surface roughness was high at low dispersion conductivity and with increasing acid concentration in dispersion the surface of deposits was smoother. The mechanism of particle arrangement in deposit was discussed. Influence of stabilizer amount in the dispersion on the hardness and fracture toughness was described.

Keywords: Anionic stabilization; Electric conductivity; Alumina; Electrophoretic deposition

1. Introduction

Electrophoretic deposition (EPD) is an ordinarily used ceramics shaping method utilizing the deposition of ceramic particles from stable dispersions via electric current. This method enables fabrication of fiber composites, laminates, functionally graded materials, thin/thick films, etc., thanks to its simplicity, low cost and versatility.[1–6] EPD can be divided into two processes: electrophoresis and deposition.[7] The electrophoresis is a motion of charged particles through the dispersion and the deposition is an agglomeration of particles near the electrode surface. It is commonly accepted that composition of dispersion has a decisive effect on the physical properties of deposits prepared by electrophoretic deposition.[8]

The organic solvents are used more often than the aqueous solvents for preparation of stable dispersions, because of the electrolysis of water that negatively affects the EPD process.[9] In case of alcoholic solvents the main problem is the description of stabilizing mechanism. Cihlar et al.[10] showed that the control of charge on the surface of amphoteric oxides in 2-propanolic medium is based on addition of acidic or basic stabilizers and measurements of their electrophoretic mobility or ζ-potential, respectively. In this system the interaction of these oxides with acids produced a negative surface charge of oxides, while interactions of oxides with bases produced a positive charge and this phenomenon had a significant impact on the final properties of deposits.

The electric conductivity and its influence on the physical and mechanical properties of deposits is one of the key parameters of electrophoretic deposition, but it is still inadequately studied. Ferrari et al.[11] showed that with high electric conductivity of dispersion the particle motion was slow and the dispersion became unstable. Another result was the observation of electrophoretic deposition at different electric conductivity of dispersion. The obtained results indicated an optimal range of electric conductivity for successful deposition. Stappers et al.[12] studied the

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uniformity of alumina deposits prepared from ethanol dispersion stabilized by HNO_3 at different electric conductivities. It was found that high electric conductivity of dispersion provided uniform deposits while its low electric conductivity resulted in non-uniform ones. This behavior was explained by resistance over the deposit which was caused by the interaction of ions with the deposit and by the depletion of ions at the deposition electrode. Another approach may be the study of influence of pH on the particle agglomeration of yttria stabilized zirconia (YSZ) in acetyl acetone dispersions examined by Xu et al.[13] The low level of an agglomeration of particles was reached at low pH of dispersion, i.e. at high electric conductivity, and the deposit had a high green density. The optimal range of dispersion pH for preparation of deposits with high green density was observed too. In the work of Guo et al.[8], the electrophoretic deposition of YSZ from ethanol–acetyl acetone dispersion stabilized by HCl was made. In this work the mechanism of arrangement of ceramic particles due to pH and electric conductivity was studied. The dispersion composition and conditions of electrophoretic deposition for receiving highest green density were presented within this work.

In the present work, the influence of ceramic dispersion on physical and mechanical properties of deposits prepared by electrophoretic deposition was studied. 2-propanolic dispersion containing submicroscopic particles of alumina anionically stabilized by chloro derivatives of acetic acid were prepared. Addition of monochloroacetic acid, dichloroacetic acid or trichloroacetic acid ensured different electric conductivity in concentrated dispersions. From stable dispersion were prepared alumina deposits by EPD. The yields after EPD, green density and density of sintered bodies were evaluated. The influence of electric conductivity of dispersions on the surface roughness and mechanical properties of sintered deposits were investigated.

2. Experimental

2.1. Materials

Ceramic dispersions used in this paper were composed of alumina (Al_2O_3, Malakoff, Ind., USA), 2-propanol solvent (p.a., Lachner, Czech Republic) and acidic stabilizers: monochloroacetic acid (MCAA, p.a., Aldrich, Germany), dichloroacetic acid (DCAA, p.a., Merck, Germany), trichloroacetic acid (TCAA, p.a., Merck, Germany). The size distribution and surface area of alumina particles were measured by laser diffraction analysis (Horiba LA-500, Japan) and Chembet 3000 machine (Quantachrome, USA), respectively. Alumina particles had the average particle size of 500 nm and the surface area about 7 m^2/g. Ceramic powder was dried before using at 100 °C for at least 2 h in drying chamber. 2-propanol was dried with the calcium metal and re-distilled for keeping water content on the minimum level.

2.2. Preparation of dispersions

Dispersions used for electrophoretic deposition were composed of 15 wt.% of alumina, 0, 0.85, 1.70, 4.25, 12.75, and 21.25 wt.% of acidic stabilizer and 2-propanol. Prepared dispersions were placed into ultrasonic field and mechanically stirred for 30 min. The electric conductivity of dispersions was measured by conductivity probe (InLab 710, Mettler Toledo, Switzerland) and Seven Compact Conductivity machine (S230, Mettler Toledo, Switzerland). The measurement of electrokinetic behavior of alumina dispersions was performed at 25 °C by Laser Doppler Velocimetry (LDV) using a Zetasizer 3000 HS (Malvern Instruments, UK). The Henry equation was used to calculate the ζ-potential.[14]

2.3. Electrophoretic deposition

The 80 ml of dispersion was placed into a vertical electrophoretic cell between two stainless steel electrodes having effective surface area of $S = 18.7\ cm^2$. The distance between electrodes was set to $d = 26$ mm. The electrophoretic deposition was carried out in constant current regime at $I = 5$ mA. To prevent the dispersion from sedimentation of ceramic particles the deposition was interrupted every 5 min and dispersion was mechanically stirred. At the same time the deposit mass was measured in solution of solvent and stabilizer like as was described elsewhere.[15]

2.4. Thermal treatment and testing of mechanical properties

The deposits were then dried at room temperature at least 24 h in desiccator. After drying the deposits were annealed at 800 °C for 1 h and pressurelessly sintered at 1500 °C for 2 h in air.

The relative density of the annealed deposits was established from soaking capacity and the relative density of the sintered deposits was established by the Archimedes method (EN 623-2). Samples were grinded, polished and thermally etched. The Vickers hardness *HV* of the prepared deposits was measured by the instrumented hardness tester (Z2.5, Zwick/Roel, Germany) by using load F of 5 kg (49 N). Values of indentation fracture toughness were calculated from crack length after hardness indentation. For calculation the Anstis equation was used[16]:

$$K_{Ic} = 0.018 \cdot \sqrt{\frac{E}{HV}} \cdot \frac{F}{c^{3/2}}, \quad (1)$$

where F is the applied load, E is Young's modulus, *HV* is the Vickers hardness, and c is the length of the surface trace of the crack measured from the center of the indent.

The microstructure of the sintered deposits was observed by using the FEG/FIB scanning electron microscope (Lyra 3, Tescan, Czech Republic).

3. Results and discussion

3.1. Mechanism of stabilization

The 2-propanolic dispersion used in this work for electrophoretic deposition of alumina particles contained stabilizing