Ceramics International 30 (2004) 853–863

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Electrophoretic deposition of alumina and zirconia
II. Two-component systems

Hynek Hadraba*, Karel Maca, Jaroslav Cihlar

Department of Ceramics, Brno University of Technology, Brno 616 69, Czech Republic

Received 30 May 2003; received in revised form 17 August 2003; accepted 25 September 2003

Abstract

The similar electrophoretic mobility of Al_2O_3 and ZrO_2 in the isopropanol suspensions containing monochloroacetic acid enabled a controlled preparation of layered and particle composites Al_2O_3/ZrO_2 as well as functionally gradient materials with gradual composition transition from Al_2O_3 to ZrO_2. In view of the negative charge of Al_2O_3 and ZrO_2 particles in the isopropanol suspensions used, all the prepared types of composite were deposited on the anode and thus they were not affected by possible solvent electrolysis, which contributed to their defect-free and low-porosity structure. Phenomena related to the deposition kinetics of these composites as well as some properties of as-sintered composites are described in the paper.

Keywords: B. Composites; D. Al_2O_3; D. ZrO_2; Electrophoretic deposition

1. Introduction

Depending on the geometry of the reinforcement phase, composite materials can be subdivided into particle, fiber and layered composites [1]. The technique of electrophoretic deposition appears to be of much promise in the preparation of particle and layered composites.

In electrophoretic deposition of particle composites it is necessary that all the simultaneously deposited phases should have identical charge polarity and electrophoretic mobility in order to obtain a homogeneous deposit [2]. To obtain maximum density and homogeneity of the chemical composition of deposit it is also important that the deposited phases be thoroughly dispersed in the suspension and not coagulated. Deliso et al. [2] predicted the theoretical possibility of electrophoretic deposition of particle composite based on Al_2O_3 and ZrO_2 as early as 1988, when they found that Al_2O_3 and ZrO_2 particles in aqueous medium had the same electrophoretic mobility if stabilized by ammonium polyacrylate. Although in the literature much data is given on electrophoretic preparation of layered Al_2O_3/ZrO_2 composites and also on particle composites of other than Al_2O_3/ZrO_2 composition, the present authors could not find in the available literature any experimental work on electrophoretic deposition of Al_2O_3/ZrO_2 particle composites. Only Wang et al. [3] described the preparation of a particle composite based on Al_2O_3/ZrO_2, which was formed when a deposit of Al/ZrO_2 particles was sintered in oxygen atmosphere.

Layered composite materials are produced by alternating electrophoretic depositions of suspensions of different composition. The preparation of Al_2O_3/ZrO_2 layered composite via alternating electrophoretic deposition from aqueous [4,5] but more often from ethanol [6–8] suspension of Al_2O_3 and ZrO_2 particles was reported in the literature. The preparation of ceramic layered composites made up of thin layers poses problems from the viewpoint of the appearance of stresses on the interface of two different materials. These stresses appear in the process of deposit drying and sintering due to different deposit green densities, and also due to different thermal expansion of materials while the sintered composite is cooling [9]. These stresses may lead to the deformation of the deposit [5] or even to the appearance of cracks [9].

One of the ways of avoiding the problems related to the sharp transition between two layers is to introduce weak interfaces between them, another way is to prepare functionally gradient materials (FGM in the following), which are in this paper understood as heterogeneous multi-component materials with composition gradient. The consequence of a

---

* Corresponding author. Fax: +420-541143202.
E-mail address: hadraba@umi.fme.vutbr.cz (H. Hadraba).

0272-8842/$30.00 © 2003 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.09.020

change in the composition of the material is a change in the physical or chemical properties of the material in a certain direction.

In electrophoretic deposition of FGM composite materials it is important that all the simultaneously deposited components be of the same charge polarity and the same electrophoretic mobility because in that case the deposit composition corresponds to the suspension composition [2].

In the works of Cihlar et al. [10] and Maca et al. [11], the electrokinetic behavior of Al_2O_3 and ZrO_2 particles in isopropanol suspensions and the deposition of single-component deposits were studied. This experience was applied in the present work to the preparation of two-component composite ceramic materials with a low content of defects. The aim of the experiments was to describe the application of this suspension in the preparation of layered, particle and functionally gradient composite materials.

2. Experimental

2.1. Materials

The same ceramic powder materials were used as in the preceding work [11]: Al_2O_3 of the RC HP DBM type (HP in the following, manufacturer Malakoff Ind., USA) and ZrO_2 of theTZ-3Y type (3Y in the following, manufacturer Tosoh, Japan). A more detailed description of these powders is given in previous work [11].

Isopropanol (p.a., Onex, Czech Republic) was used as the dispersion medium for the preparation of suspensions of Al_2O_3 and ZrO_2 powders while monochloroacetic acid (MCAA) (p.a., Lachema, Czech Republic) was used as the stabilizing and dispersing agent. The content of water in the suspensions was reduced to a minimum (0.01%) using the same procedure as in previous work [11].

2.2. Suspension composition

One-component suspensions (employed for electrophoretic deposition of layered and functionally gradient materials) were prepared by mixing 15 wt.% of powder (either Al_2O_3 or ZrO_2) and 12.75 wt.% of MCAA in 72.25 wt.% of isopropanol. This composition was established as optimal for the deposition of one-component Al_2O_3 and ZrO_2 systems [11]. Two-component suspensions employed in electrophoretic deposition of particle composite materials contained 15 wt.% of powder mixture (made up of Al_2O_3 and ZrO_2 in volume ratios of 75:25, 50:50 and 25:75), 12.75 wt.% of MCAA and 72.25 wt.% of isopropanol.

2.3. Electrophoretic deposition

A detailed description of the horizontal electrophoretic cell is given in previous work [11]. All electrophoretic depositions were conducted under constant current (5 mA) conditions.

The layered alumina/zirconia composite material (LC HP/3Y in the following) consisted of 30 layers of Al_2O_3 and 29 layers of ZrO_2, which alternated regularly in the composite and were prepared by interrupted electrophoretic deposition, i.e. several consecutive depositions, alternately with the Al_2O_3 and the ZrO_2 suspension. The total deposition time of layered composite materials was 130 min. Since the particle concentration in the suspension decreased with time, it was necessary to increase continually the deposition time of individual layers so that they were of constant thickness. To do this, the relations derived in a previous work [11] were employed.

Particle composite materials with a constant ratio of type HP Al_2O_3 and type 3Y ZrO_2 (depending on the level of volume concentrations of individual components these composites were denoted PC 75/25, PC 50/50 and PC 25/75) were prepared by interrupted deposition, i.e. several consecutive depositions with one suspension, between which the suspension was stirred. Each partial deposition consumed 5 min and the total deposition time was 140 min.

The two types of FGM composite were prepared by interrupted electrophoretic deposition, i.e. a sequence of depositions from suspensions of slightly changed composition. Electrophoretic deposition started with pure Al_2O_3 suspension (of type HP). Every 5 min the deposition was interrupted and 2 ml (FGM HP/3Y-2 deposit) or 5 ml (FGM HP/3Y-5 deposit) suspension in the cell were replaced with ZrO_2 suspension (of type 3Y). With every interruption, the electrodes were taken out and the suspension was stirred manually, both before and after changing the suspension composition. The total deposition time was again 140 min.

2.4. Evaluation of deposit properties

When the deposition was finished, all the deposits with the electrode were first dried for 24 h at room temperature and for 1 h at a temperature of 70 °C and then taken down from the electrode, annealed (800 °C/1 h) and sintered (1500 °C/2 h) in air atmosphere. The course of sintering process was monitored using a high-temperature dilatometer (L75/50, Linseis, Germany). Coefficient of thermal expansion (CTE) was calculated from the cooling curves of sintered materials. The relative density of annealed deposit ($\rho_{\text{rel-800}}$) was established from soaking capacity and the relative density of sintered deposit ($\rho_{\text{rel-1500}}$) was found by the Archimedes method (EN 623-2).

Polished specimens of sintered deposits were thermally etched. The size of sintered ceramic grains was established by computer image analysis (Atlas Software, Tescan, Czech Republic) from microphotographs prepared by scanning electron microscopy (Philips XL30, The Netherlands).

The chemical composition of functionally gradient materials was determined by electron microprobe analysis (Philips, The Netherlands).

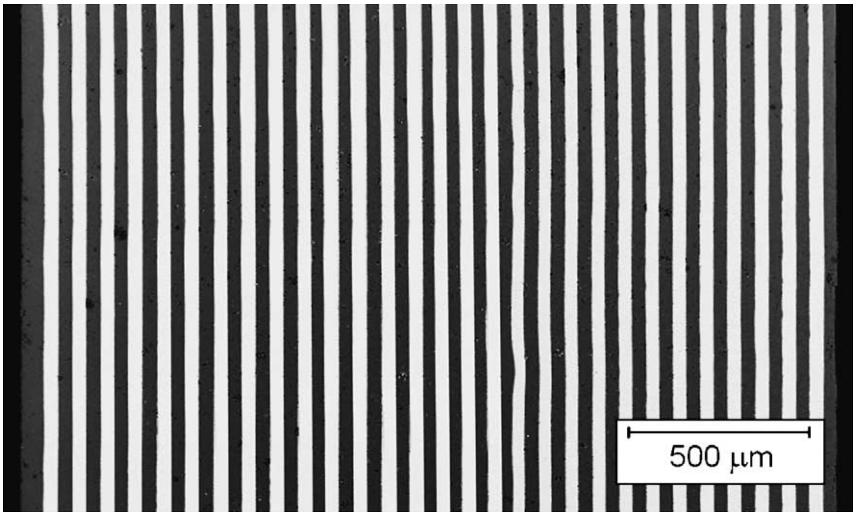

Fig. 1. Microphotographs of alumina/zirconia layered composite LC HP/3Y.

The fracture toughness of sintered deposits was measured by the indentation method (according to Japanese Industrial Standard JIS R 1607) on a Vickers indentor at a loading force of 98 N.

3. Results and discussion

3.1. Electrophoretic deposition of layered composite materials

All depositions were conducted at a constant current of 5 mA, with the particles depositing on the anode as in the preceding works [10,11].

First, a layered deposit with varied ZrO_2 layer thickness and constant Al_2O_3 layer thickness (70 μm) was prepared. ZrO_2 layers of more than 60 μm in thickness exhibited cracks. These cracks were of large opening displacement. Similar cracks were reported by Hillman et al. [9], who showed that such cracks had developed already in the stage of drying and sintering due to the different green densities of individual layers. The following depositions were therefore performed such that the thickness of Al_2O_3 and ZrO_2 layers in the produced layered composites were less than 50 μm, which was the thickness of the layers in which the cracks did not appear. Layered composite prepared in this way was really free from these defects (Fig. 1).

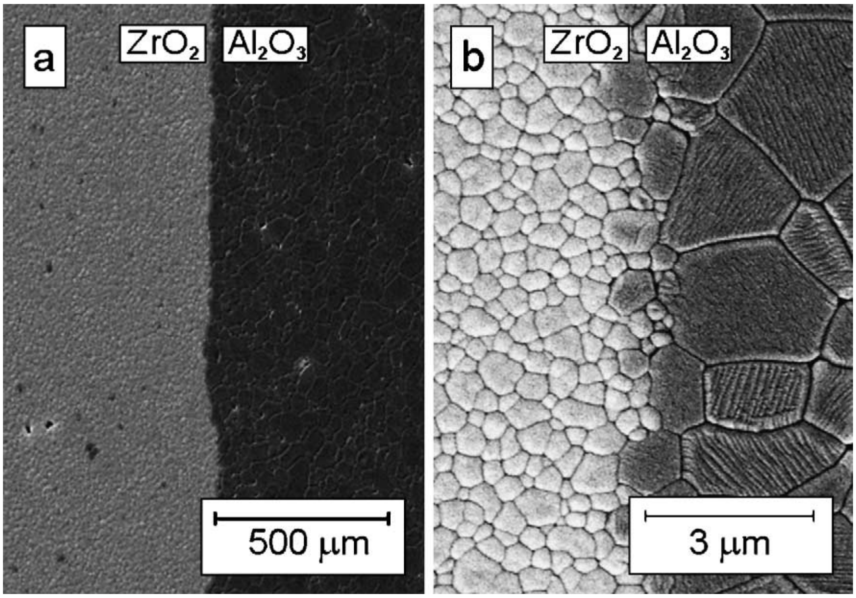

Fig. 2. Microstructure of alumina/zirconia interface in layered composite LC HP/3Y at (a) low and (b) high magnification.

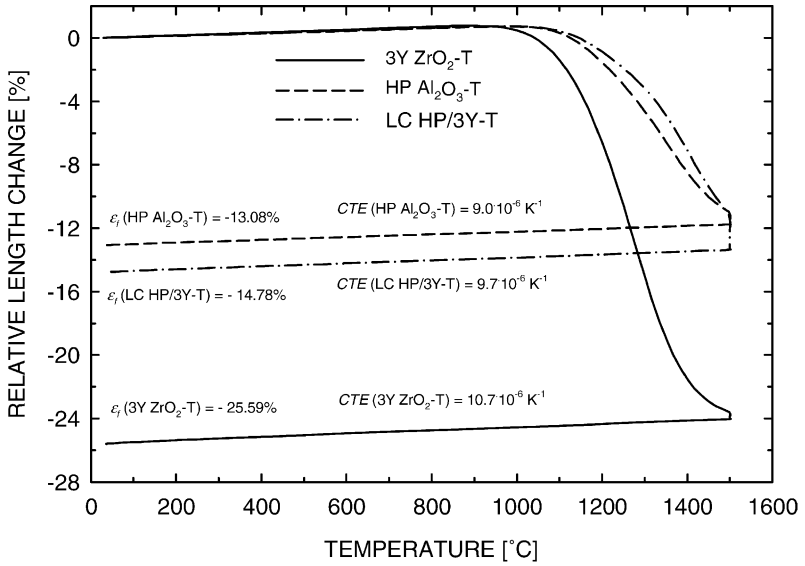

Fig. 3. Dependence of relative length change of alumina/zirconia layered composite LC HP/3Y and single-component alumina and zirconia deposits on sintering temperature.

The relative density of layered composite LC HP/3Y was 97%TD. Single-component deposits had a relative density of 99.2% (type HP Al_2O_3) or 99.9%TD (type 3Y ZrO_2) [11]. The higher porosity of the laminated composite was probably due to the inhomogeneities at the interface of individual phases. However, these inhomogeneities were responsible for about 2% of the porosity, the bond of layers in the composite was thus of good quality, as shown in Fig. 2.

Fig. 3 gives for the layered alumina/zirconia composite the dependence of shrinkage in parallel direction to the layers (transversal direction—T) on the temperature in the course of sintering and cooling. In this work the abbreviations T (transversal direction) and L (longitudinal direction) will have the same meaning as in the previous paper [11]. The shrinkage of the alumina/zirconia layered composite in this direction was given by the shrinkage of Al_2O_3, which shrinks less than ZrO_2 (for comparison, the sintering curves for one-component deposits in transversal direction are also given in Fig. 3). This result lends support to the considerations in the introduction to this chapter, namely that the appearance of cracks in ZrO_2 layers more than 50 μm thick was due to different green densities of individual layers. As can be seen from Fig. 3, in the course of sintering the ZrO_2 layer should shrink more than the surrounding Al_2O_3 layers in the composite permitted, which led to tensile stress in the layer. In the case of thicker layers this tension led in turn to the appearance of cracks. Whether in thinner layers this stress remained or relaxed at the sintering temperature (for example, via diffusion processes on grain boundaries) remains unanswered in this paper.

The slope of the cooling curve was used to calculate the CTE. As is obvious from Fig. 3, the CTE of the LC HP/3Y composite was roughly an average of $\mathrm{CTE}_{Al_2O_3}$ and CTE_{ZrO_2}, which differed by about 13%. This fact was the cause of residual thermal stresses (σ_r) in the layers. The magnitude of such stress in ZrO_2 can be calculated from the relation [9]:

$$\sigma_{\mathrm{rZrO_2}} = \frac{(\mathrm{CTE}_{\mathrm{ZrO_2}} - \mathrm{CTE}_{\mathrm{Al_2O_3}})\,\Delta TE_{\mathrm{ZrO_2}}}{1-\nu_{\mathrm{ZrO_2}}} \times \left(1 + \frac{t_{\mathrm{ZrO_2}}}{t_{\mathrm{Al_2O_3}}}\,\frac{E_{\mathrm{ZrO_2}}/(1-\nu_{\mathrm{ZrO_2}})}{E_{\mathrm{Al_2O_3}}/(1-\nu_{\mathrm{Al_2O_3}})}\right)^{-1} \qquad (1)$$

where $t_{\mathrm{ZrO_2}}$ and $t_{\mathrm{Al_2O_3}}$ are the average layer thickness values, $\nu_{\mathrm{ZrO_2}}$ and $\nu_{\mathrm{Al_2O_3}}$ are the Poisson ratios and $E_{\mathrm{ZrO_2}}$ and $E_{\mathrm{Al_2O_3}}$ are the elasticity moduli of ZrO_2 and Al_2O_3 of the composite (the stress in the Al_2O_3 phase, $\sigma_{\mathrm{rAl_2O_3}}$ is obtained by interchanging the subscripts of the quantities).

Employing the values given in Table 1, we obtain for the Al_2O_3 layer compression stress $\sigma_{\mathrm{rAl_2O_3}} = -362\,\mathrm{MPa}$ and for ZrO_2 tensile stress $\sigma_{\mathrm{rZrO_2}} = +373\,\mathrm{MPa}$. These stresses are parallel to the interface of Al_2O_3 and ZrO_2 layers; the tensile stresses (which originated in ZrO_2) are more dangerous. By analysing Eq. (1) it can be shown that in ZrO_2 residual stress increases with decreasing thickness of the ZrO_2 layer. By contrast, in the case of stresses appearing in the course of sintering it was shown that with increasing thickness of the ZrO_2 layer the danger of cracks appearing in this layer increased. From the viewpoint of defect-free layer a layered composite must thus have a certain optimum

Table 1
Properties of the ceramic materials being deposited

	Al_2O_3	ZrO_2
Elasticity module, E (GPa) [8]	380.0	210.0
Poisson ratio, ν [8]	0.26	0.31
CTE ($\times 10^{-6}\,\mathrm{K}^{-1}$) [11]	9.0	10.3
Average layer thickness, t (μm)	41.5	42.8

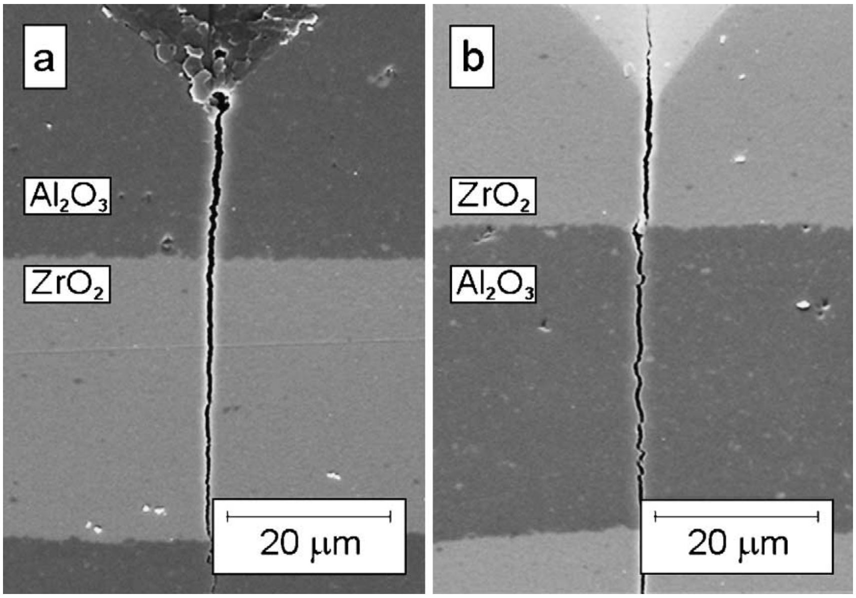

Fig. 4. Microphotographs of indentation cracks in alumina/zirconia layered composite LC HP/3Y propagated perpendicular to the interface of alumina and zirconia (crack initiated in (a) alumina and in (b) zirconia).

thickness range. The composites prepared as part of the present work satisfied this requirement.

From a comparison of dilatometric curves of the Al_2O_3 and ZrO_2 layered composite with the curves of the individual pure components it could be seen that there were at least two sources of the stress introduced into the composite during the sintering process: the different sintering kinetics of individual components resulting from their different green densities, and their different thermal expansion. Both these phenomena introduce tensile stresses into ZrO_2 layers and compression stresses into Al_2O_3 layers. What effect these stresses have on the mechanical properties of the composite is shown in the following paragraph.

Figs. 4–6 are microphotographs of indentation cracks in layered composite materials. The effect of layer interface on indentation crack propagation was studied. The indentation

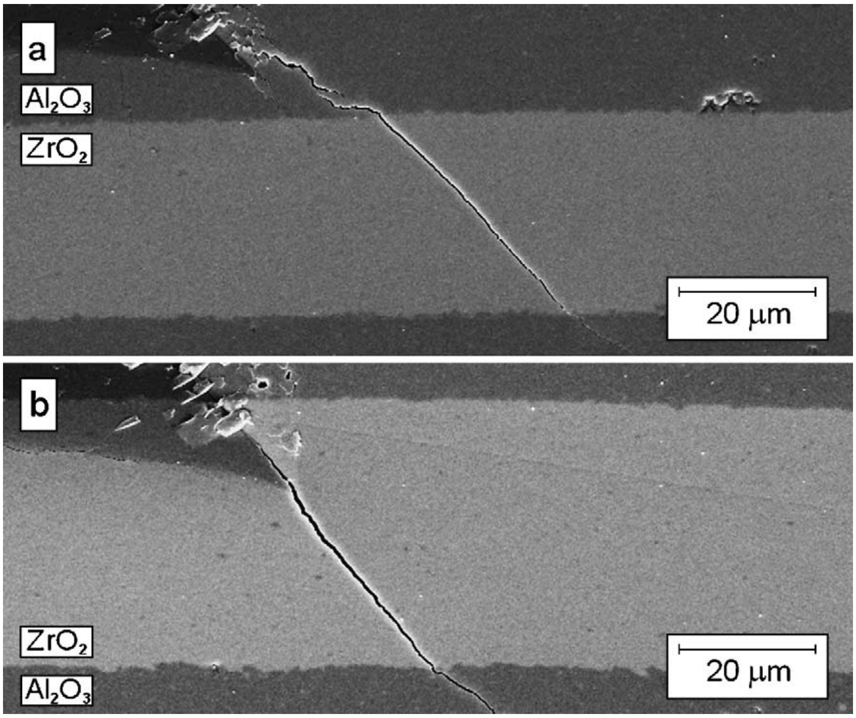

Fig. 5. Microphotographs of indentation cracks in alumina/zirconia layered composite LC HP/3Y propagated askew to the interface of alumina and zirconia (crack initiated in (a) alumina and in (b) zirconia).

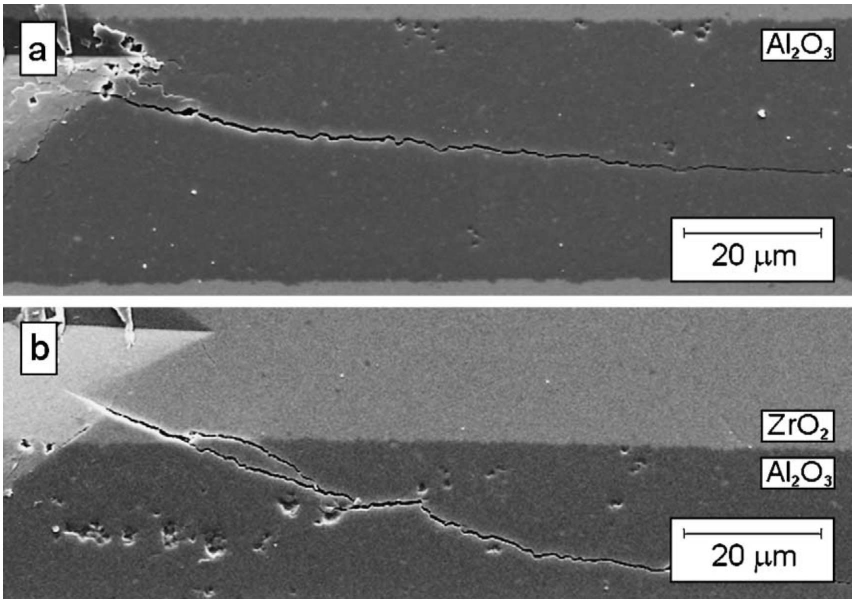

Fig. 6. Microphotographs of indentation cracks in alumina/zirconia layered composite LC HP/3Y propagated parallel with the interface of alumina and zirconia (crack initiated in (a) alumina and (b) zirconia).

was conducted such that the appearing crack propagated from the Al_2O_3 or ZrO_2 material in three different directions: perpendicular, askew and parallel to the interface.

If the crack propagated perpendicular to the interface and was initiated in Al_2O_3 or ZrO_2 (see Fig. 4), it propagated through the Al_2O_3/ZrO_2 interface without changing the direction of propagation.

When the indentation crack propagated askew to the Al_2O_3/ZrO_2 interface (see Fig. 5) the direction of crack propagation got deflected. When passing through the interface, a crack that was initiated in Al_2O_3 was deflected in the ZrO_2 layer from the layer interface (towards the normal to the interface area) and thus its path in the ZrO_2 layer was shortened. A crack that was initiated in ZrO_2 and was propagating askew to the ZrO_2/Al_2O_3 interface deflected towards the layer interface when passing through the interface.

The authors of recent papers [6,7] also described a similar indentation crack propagation askew to the interface of Al_2O_3 and ZrO_2 layers. Hatton and Nicholson [8] explained this behavior of Al_2O_3/ZrO_2-based layered composites by the presence of residual thermal stresses in composite layers. In the compression field, the crack propagated parallel to the direction of compression while in the tensile field it propagated perpendicular to the direction of tension [8]. This also shows in the behavior of indentation cracks passing through the Al_2O_3/ZrO_2 interface described above: in the ZrO_2 layer the crack was deflected from the layer interface and propagated perpendicular to the tensile tension in the layer while in the Al_2O_3 layer it was deflected towards the layer interface, i.e. parallel with the compression tension in the layer.

A crack initiated parallel with the Al_2O_3/ZrO_2 interface (see Fig. 6) always propagated preferably in the Al_2O_3 material, again parallel with the interface (even a crack initiated in the ZrO_2 layer got deflected into the Al_2O_3 layer). As mentioned above, the direction of compression (in Al_2O_3) and tensile (in ZrO_2) residual thermal stresses in the layers is parallel with the layer interface. In the tensile stress field, a crack initiated in ZrO_2 parallel with the layer interface got in the ZrO_2 layer deflected perpendicular to the layer interface, where its propagation was made easier due to the crack opening out in the tensile field. After crossing the interface it propagated in the Al_2O_3 layer parallel with the tensile stresses in this layer. Another possible explanation for the crack deflection from ZrO_2 into Al_2O_3 is the deformation of the stress field close to the Al_2O_3/ZrO_2 interface. As can be seen from Figs. 5 and 6, near the interface the crack is not initiated from the indentation corner, it is shifted towards the Al_2O_3 layer (in the case of symmetrical indentations with respect to interface position (Fig. 4) it is initiated from the indentation corner). As Young's modulus of Al_2O_3 is almost twice that of ZrO_2 (see Table 1), the stress induced by the indentation tool was in Al_2O_3 almost twice that in ZrO_2. It is thus possible that maximum stress (and, consequently, the point of crack initiation) was not in the indentation corner. In the case of indentation in ZrO_2, the crack could have initiated even in the Al_2O_3 layer at a point close to the indentation corner. The crack then propagated on the one hand towards the indentation (in ZrO_2) and, on the other hand, parallel with the interface (in Al_2O_3) in order not to be closed by the acting compressive stress. It is not the aim of the present work to give a detailed description of mechanical properties of layered composites but important knowledge has been obtained through the changes in the trajectory of a crack propagating at the layer interface. It is a proof of the strength of the bond of

Table 2
Densities, hardness, fracture toughness and grain sizes of particle composite materials prepared by electrophoretic deposition

Composite designation	Relative density		Hardness, HV (GPa)	Fracture toughness, K_{IC} (MPa m$^{1/2}$)	Mean grain size (μm)	
	$\rho_{rel-800}$ (%)	$\rho_{rel-1500}$ (%)			$d_{g-Al_2O_3}$	d_{g-ZrO_2}
HP Al_2O_3 [11]	62.2	99.2	17.8	5.2	1.93	–
PC HP75/3Y-25	57.2	97.3	16.1	8.0	1.14	0.42
PC HP50/3Y-50	53.8	97.5	15.4	9.8	1.08	0.61
PC HP25/3Y-75	46.8	99.3	14.4	8.1	0.87	0.77
3Y ZrO_2 [11]	41.6	99.9	12.9	9.6	–	0.55

electrophoretically deposited layers. The possibility of making use of this behavior to improve the mechanical properties of ceramic materials is quite promising [9,12]. A positive result of the present work can be seen in the defectless structure of composites with low porosity (compared, for example, with some deposits prepared from aqueous [4,5] or ethanol [6,7] suspensions). This is probably due to the fact that in the isopropanol suspensions used both Al_2O_3 and ZrO_2 particles were charged negatively and thus deposited on the anode, which eliminated some negative phenomena (e.g. electrolysis of the solvent) during deposition on the cathode.

3.2. Electrophoretic deposition of particle composite materials

Particle composites were prepared from suspensions containing 15 wt.% of a mixture of alumina and zirconia. The composites were prepared with 75 vol.% Al_2O_3 (PC 75/25), 50 vol.% Al_2O_3 (PC 50/50) and 25 vol.% Al_2O_3 (PC 25/75). Electrophoretic deposition was performed at a constant electric current of 5 mA, with the suspension regularly stirred in 5 min intervals to prevent the suspension from sedimenting [11].

While the relative density of as-annealed deposit decreased almost linearly with increasing ZrO_2 content in the deposit, the final density had a minimum for composites with 75 and 50 vol.% concentrations of Al_2O_3, whose densities were only 97.3 and 97.5%TD, respectively (Table 2).

The hardness values established for particle composites are given in Table 2. With increasing ZrO_2 content in the composite the deposit hardness decreased. Table 2 also gives the fracture toughness values of particle composite materials. It can be seen from the table that even 25 vol.% ZrO_2 (PC 75/25) had a positive effect on the fracture toughness of Al_2O_3.

It can be seen from the mean sizes of Al_2O_3 and ZrO_2 grains in the composites (Table 2) that the particles of minority component in the particle composite practically did not increase in size in the course of sintering. The growth of the majority component grain was, of course, also hindered by the surrounding minority phase.

Limiting the growth kinetics of matrix grains (be it Al_2O_3 or ZrO_2) in Al_2O_3/ZrO_2 particle composite is no new knowledge, it was described as early as the 1980s [13,14]. What is new is the possibility of preparing the Al_2O_3/ZrO_2 particle composite of controlled composition by the method of electrophoretic deposition. A necessary condition of controlling the deposition process is the same electrophoretic mobility of the two components in the suspension. Identical electrophoretic mobility of Al_2O_3 and ZrO_2 in isopropanol suspensions stabilized by monochloroacetic acid was established in work of Cihlar et al. [10] and the homogeneous distribution of individual components over the whole deposit cross-section has confirmed it (see Fig. 7).

3.3. Electrophoretic deposition of functionally gradient materials

Also electrophoretic deposition of functionally gradient materials was conducted at a constant current of 5 mA and the deposit was formed on the anode.

A microphotograph of sections through deposits is shown in Fig. 8. Although the structure of the specimens prepared was layered, it featured the smooth concentration transition from Al_2O_3 to ZrO_2, as can be seen from Fig. 9. The reason probably lay in the thorough mixing of suspension, where the electrodes were removed during mixing.

It is obvious from Fig. 8 that the deposit FGM HP/3Y-2 developed crack. The crack ran parallel with the electrode plane. Deposit cracking was probably due to the differential shrinkage of individual parts of the composite. At the beginning of deposition pure Al_2O_3 was deposited (see Fig. 9), whose green density exceeded 60%TD [11] while at the opposite end of deposit the majority phase was ZrO_2, whose green density was less than 50%TD [11]. Thus in the course of sintering, individual parts of the deposit attained differential shrinkage, which generally leads to dimensional deformations [15]. In the present case they resulted in cracked deposit. To prevent cracking, it would thus be necessary to find such combinations of powder materials and deposition conditions that would lead to green bodies of comparable green density but also of similar CTE [16].

Fig. 10 gives a comparison of the composition of deposit with the composition of suspension. The composition of the composite FGM HP/3Y-5 was measured over the whole cross-section by linear (point-by-point) X-ray microanalysis in equidistant steps of 0.1 mm. The time t (min) in which the layer in the distance h (mm) from the electrode was

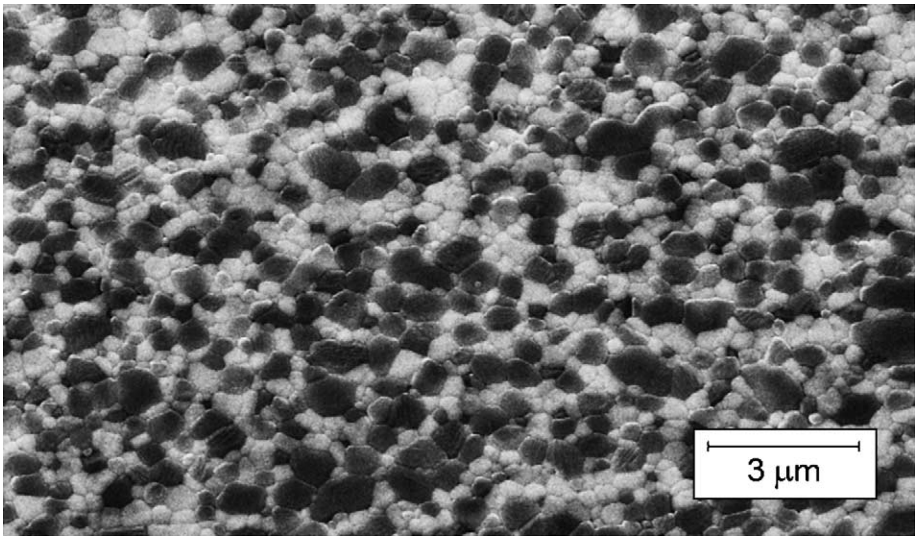

Fig. 7. Microstructure of alumina/zirconia particle composite of type PC 50/50.

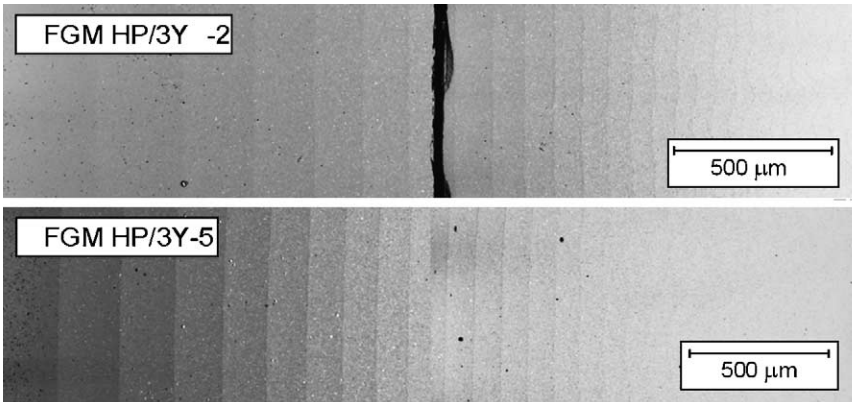

Fig. 8. Microphotographs of alumina/zirconia functionally gradient materials of type FGM HP/3Y-2 and FGM HP/3Y-5.

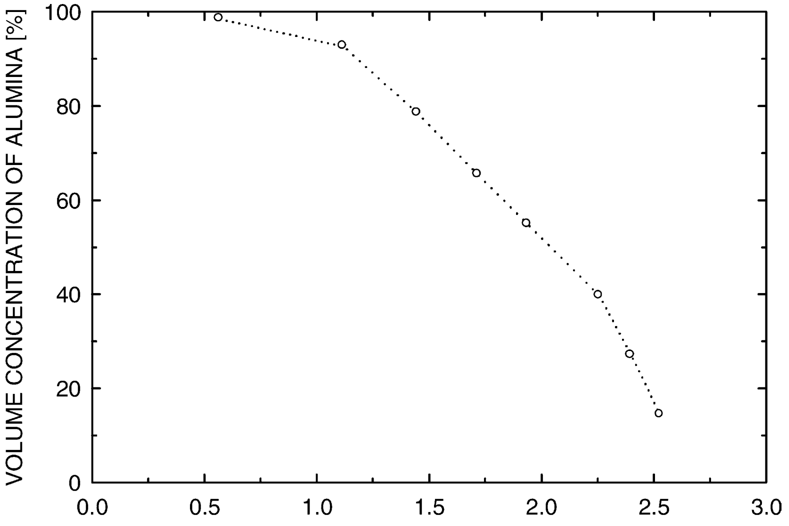

Fig. 9. Dependence of alumina volume concentration in alumina/zirconia fuctionally gradient material FGM HP/3Y-5 on distance from anode.

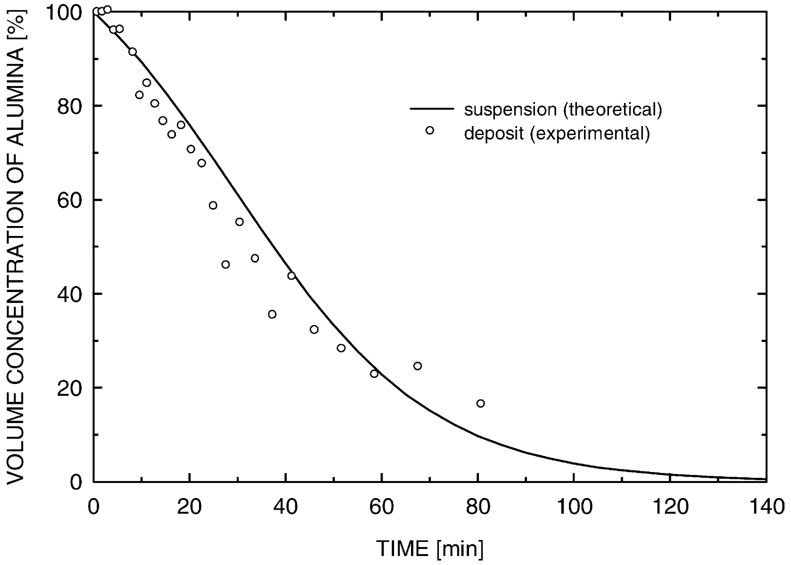

Fig. 10. Dependence of alumina volume concentration in alumina/zirconia suspension in alumina/zirconia functinally gradient material FGM HP/3Y-5 on deposition time.

deposited was calculated using the relation:

$$t = \ln \frac{(h/2.78) - 1}{0.0338} \quad (2)$$

which is inverse to the relation for one-component deposit Al_2O_3 [11]. Applying this relation also in the case of the functionally gradient composite Al_2O_3/ZrO_2 is justified in view of the fact that identical electrophoretic mobility of Al_2O_3 and ZrO_2 particles in isopropanol suspensions stabilized with MCAA was established [10] and the validity of this equality has also been confirmed in the case of a mixture of Al_2O_3 and ZrO_2 particles (Section 3.2).

The theoretical time dependence of the suspension composition was calculated on the basis of an iterative procedure, when for every interruption of deposition the new volume concentrations $Al_2O_3(c_{i+1}^{A})$ and $ZrO_2(c_{i+1}^{Z})$ in the solution were calculated from the initial volume concentrations $Al_2O_3(c_i^{A})$ and $ZrO_2(c_i^{Z})$ according to the relations:

$$c_{i+1}^{A} = \frac{c_i^{A} V_0 - c_i^{A} V_1 - c_i^{A} V_0 (1 - e^{-0.0338\,\Delta t})}{V_0} \quad (3)$$

$$c_{i+1}^{Z} = \frac{c_i^{Z} V_0 - c_i^{Z} V_1 - c_i^{Z} V_0 (1 - e^{-0.0338\,\Delta t}) + c_s^{Z} V_1}{V_0} \quad (4)$$

where V_0 is the total suspension volume, V_1 is the volume of removed and added ZrO_2 suspension when the deposition is interrupted (5 ml) and Δt is the time between individual deposition interruptions (5 min). The initial Al_2O_3 suspension concentration was $c_0^{A} = 3.61$ vol.%, $c_0^{Z} = 0$ and the concentration of added ZrO_2 suspension was $c_s^{Z} = 2.40$ vol.%. Relations (3) and (4) express both the change in suspension composition, which is given by the removal and addition of a small amount of suspension, and the change in this composition, which is given by the deposition of particles on the electrode. To express the change in suspension composition caused by particle deposition the relations and values were used that had been found for the deposition of one-component deposits [11]. The good agreement between the theoretical suspension composition and the deposit composition established (see Fig. 10) implies the validity of all the assumptions made: electrophoretic mobility of both components in the suspension was identical [10], the relations derived in the preceding work [11] for deposition kinetics are valid and they also hold for the two-component system.

As reported in the preceding work [11] the length of indentation cracks propagating from the corners of indentation by Vickers indentor to the material surface provides for conclusions as to the size of fracture toughness of the material. Using this method, Nicholson [17] demonstrated that the fracture toughness of functionally gradient material is directly proportional to its composition. Fig. 11 gives the fracture toughness of functionally gradient material FGM HP/3Y-5 as a function of its composition. As can be seen from Fig. 11, the fracture toughness in transversal direction is proportional to the composition of functionally gradient composite and it is higher than the fracture toughness of pure phases. The fracture toughness in longitudinal direction deflects from the linear dependence. As stated above, due to the different green densities throughout the deposit, the deposit was deformed during drying and sintering. This deformation was caused by internal stresses acting in parallel to the electrode, i.e. in the transversal direction. The part of deposit containing predominantly ZrO_2 was exposed to tensile stresses in transversal direction. These stresses opened up the crack in longitudinal direction and the fracture toughness established was in this direction lower than in transversal direction. Conversely, in

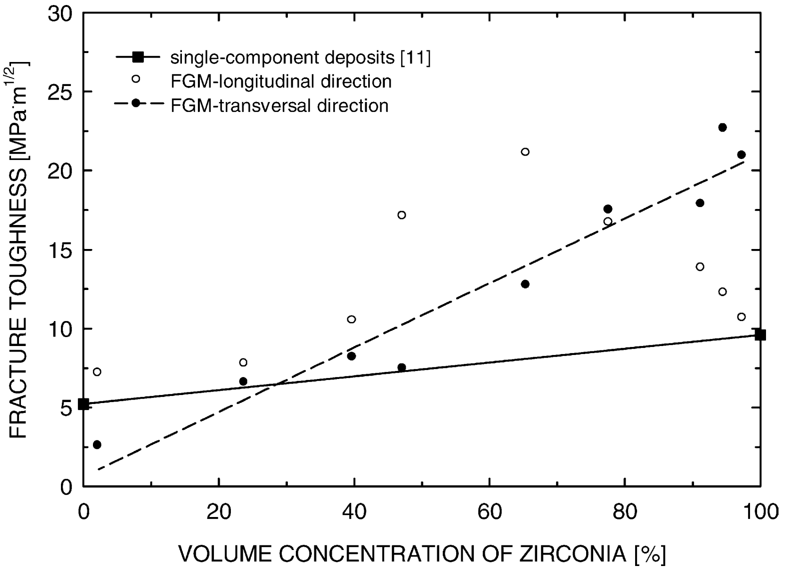

Fig. 11. Dependence of fracture toughness of functionally gradient material FGM HP/3Y-5 on zirconia volume concentration in deposit.

the layers with predominant Al_2O_3 of higher green density there appeared compression stresses that were closing the crack and this was reflected in the higher value of fracture toughness.

4. Conclusion

Layered composite materials were prepared by alternating deposition from isopropanol suspensions of Al_2O_3 and ZrO_2 and subsequent sintering. The particles at the layer interface were properly sintered and the layer interface did not contain an increased amount of pores. Thanks to this strong bond between layers and thanks to residual stresses introduced into the material in the course of drying, sintering and cooling from the sintering temperature, there occurred changes in the propagation of cracks in the composite, which makes the material interesting from the viewpoint of possible increase in fracture toughness and strength.

Using electrophoretic deposition of a mixture of Al_2O_3 and ZrO_2 from isopropanol suspensions stabilized with monochloroacetic acid it was possible to prepare particle composite materials with a constant controlled Al_2O_3/ZrO_2 ratio. Thanks to the similar electrophoretic mobility of Al_2O_3 and ZrO_2 particles in the suspension the composite composition was constant throughout the whole deposit volume.

Functionally gradient materials with a smooth concentration transition from Al_2O_3 to ZrO_2 were prepared by electrophoretic deposition of suspensions whose composition was changed in the course of deposition. The deposit composition copied the suspension composition and the deposition kinetics corresponded to the theoretical models derived for one-component deposits.

Acknowledgements

This work was supported by the Czech Ministry of Education by the grant no. VZ CEZ: J22/98.

References

[1] M.P. Harmer, H.M. Chan, G.A. Miller, Unique opportunities for microstructural engineering with duplex and laminar ceramic composites, J. Am. Ceram. Soc. 75 (1992) 1715–1728.

[2] E.M. Deliso, J. Kowalski, J.W.R. Cannon, Application of electrokinetic properties to the fabrication of an alumina–zirconia composite, Adv. Ceram. Mater. 3 (1988) 407–410.

[3] Z. Wang, P. Xiao, J. Shemilt, Fabrication of composite coatings using a combination of electrochemical methods and reaction bonding process, J. Eur. Ceram. Soc. 20 (2000) 1469–1473.

[4] T. Uchikoshi, K. Ozawa, B.D. Hatton, Y. Sakka, Dense, bubble-free ceramic deposits from aqueous suspensions by electrophoretic deposition, J. Mater. Res. 16 (2001) 321–324.

[5] B. Ferrari, A.J. Sánchez-Herencia, R. Moreno, Aqueous electrophoretic deposition of Al_2O_3/ZrO_2 layered ceramics, Mater. Lett. 35 (1998) 370–374.

[6] P. Sarkar, X. Haung, P.S. Nicholson, Structural ceramic microlaminates by electrophoretic deposition, J. Am. Ceram. Soc. 75 (1999) 2907–2909.

[7] O. Prakash, P. Sarkar, P.S. Nicholson, Crack deflection in ceramic/ceramic laminates with strong interfaces, J. Am. Ceram. Soc. 78 (1995) 1125–1127.

[8] B. Hatton, P.S. Nicholson, Design and fracture of layered Al_2O_3/TZ3Y composites produced by electrophoretic deposition, J. Am. Ceram. Soc. 84 (2001) 571–576.

[9] C. Hillman, Z. Suo, F.F. Lange, Cracking of laminates subjected to biaxial tensile stresses, J. Am. Ceram. Soc. 79 (1996) 2127–2133.

[10] J. Cihlar, Z. Cihlarova, H. Hadraba, Influence of weak acids on electrophoretic behavior of alcoholic suspensions of alumina and zirconia, submitted for publication.

[11] K. Maca, H. Hadraba, J. Cihlar, Electrophoretic deposition of alumina and zirconia—I. Single-component systems, Ceram. Int. 30 (2004) 843–851.

[12] D.B. Marshall, J.J. Ratto, F.F. Lange, Enhanced fracture toughness in layered microcomposites of Ce-ZrO_2 and Al_2O_3, J. Am. Ceram. Soc. 74 (1991) 2979–2987.

[13] F.F. Lange, M.M. Hirlinger, Hindrance of grain growth in Al_2O_3 by ZrO_2 inclusions, J. Am. Ceram. Soc. 67 (1984) 164–168.

[14] F.F. Lange, T. Yamaguchi, B.I. Davis, P.E.D. Morgan, Effect of ZrO_2 inclusions on the sinterability of Al_2O_3, J. Am. Ceram. Soc. 71 (1988) 446–448.

[15] P.K. Lu, J.J. Lanuti, Density gradients and sintered dimensional tolerance in compacts formed from spray-dried alumina, J. Am. Ceram. Soc. 83 (2000) 1393–1398.

[16] R. Torrecillas, A.M. Espino, J.F. Bartolome, J.S. Moya, Functionally graded zircon–molybdenum materials without residual stresses, J. Am. Ceram. Soc. 83 (2000) 454–456.

[17] P. Sarkar, X. Haung, P.S. Nicholson, Zirconia/alumina functionally gradiented composites by electrophoretic deposition techniques, J. Am. Ceram. Soc. 76 (1999) 1055–1056.