

Electrophoretic Deposition of Sol–Gel Ceramic Microcomponents using UV-curable Alkoxide Precursors

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Abstract

A process was developed, by which piezoceramic microparts can be produced directly using liquid metal–organic lead–zirconate–titanate (PZT) precursors. Electrophoretic deposition (EPD) was used as the shaping method; the precursors were PZT-sols synthesized by a modified sol–gel technique. After EPD into a microstructured mould, simultaneous to the gelation of the sol, the deposited gel-body was then dried and the mould was removed, followed by pyrolysis of the organics and final sintering. Special emphasis was placed on the development of the precursor. By introducing polymerisable chelating agents into the synthesis, the gel can additionally be hardened by radical polymerisation. By using UV-sensitive initiators, the gel-hardening can be performed by photo-induced polymerisation. The resulting solid gel shows considerably better mechanical strength than comparable inorganic gels due to mutually interpenetrating inorganic and organic networks in the gel instead of just an inorganic network built up by gelation. © 1997 Elsevier Science Limited.

Introduction

Based on the processing experiences in microelectronics, primarily metallic and polymer materials have been used up to now in microsystem technology.

Due to the specific properties of ceramic materials like outstanding hardness, resistance against corrosive media, high temperature resistance and special, e.g. piezoelectric properties, ceramic materials have become interesting for applications in

microsystem technology. Thus, the development of high-performance ceramics has increased in importance in recent years. Development efforts have started in various areas, especially in the field of ceramic powder synthesis as well as in ceramic shaping. Considering ceramic microparts with overall dimensions of a few millimeters and internal dimensions in the range of micrometers, it becomes obvious that the requirements on both the starting material and the production route are much more stringent than with larger parts. This means that a maximum of material homogeneity even at the molecular level must be achieved and the grain size in the sintered ceramic should be at least one order of magnitude smaller than the minimum internal dimensions of the microparts.¹

In this work a powderless process was developed, in which a liquid precursor of lead-zirconate-titanate (PZT) was synthesized according to a modified sol–gel route and then directly shaped by electrophoretic deposition into a microstructured mould. The shaped gel-body can then be hardened by polymerisation induced by UV-light, dried and heated in a furnace to obtain the ceramic component² (see Fig. 1).

The sol–gel process offers advantages over the conventional mixed-oxide route, such as much greater purity and compositional control with liquid-mix homogeneity and lower process temperatures. Additionally, by direct shaping of the precursor, the process saves a number of process steps compared to the ‘classical’ route by avoiding the production and conditioning of a ceramic powder.

Basics

The sol–gel process is a modern synthesis technique for special ceramics, in which a molecular solution is converted by chemical reaction to a sol which reacts further to a gel, which by firing gives an

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Direct Electrophoretic Moulding of PZT-Microstructures from a Sol

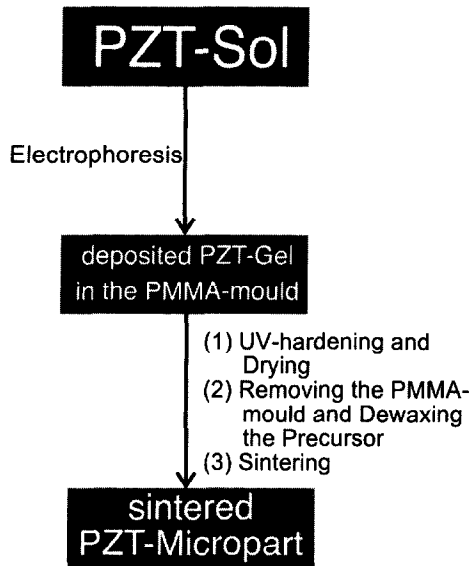
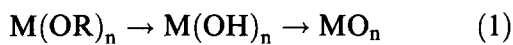


Fig. 1. Schematic representation of the direct electrophoretic shaping process of PZT-microcomponents from the sol.

inorganic solid [eqn (1)]. There are two fundamentally different types of gels to be synthesized from which ceramics can be formed, namely, colloid or polymeric gels.^{3,4} In this work, polymeric gels were synthesized.



Mostly, metal alkoxides $M(OR)_n$ are used as educts (M = metal, OR = alkoxide group, n = metal valency), in which case the conversion of the molecular solution into a gel is achieved through the reaction with water. Hereby, the alkoxide molecules are hydrolyzed and then undergo condensation reactions to form a macromolecular network of metal–oxygen units. During the last step, the transformation of the gel to the ceramic by annealing, the amorphous network of the wet gel is first dried and then slowly solidified while the

remaining water and traces of organic material coming from the alcohol inside the pores of the dried gel are removed by pyrolysis.⁵

When applied to a multinary system like lead–zirconate–titanate, this principal synthesis technique has to be extended and modified. The choice of starting materials is dictated by a number of factors including reactivity, solubility, viscosity, organic content, decomposition temperature, by-products, costs and availability.³ Initial efforts focused on an liquid alkoxide system with low carbon alkyl groups. As alkoxides of Zr and Ti are easily hydrolyzed by alcohols, they have to be complexed by chelating agents to prevent premature hydrolysis before adding the lead compound. As such chelating agents, substances like acetylacetonone (acac) can be used. In this work, preferably molecules were used that are both able to form stable chelate complexes with Zr and Ti and can be radically polymerised due to one or more $C=C$ -double bonds, e.g. methacrylic anhydride (Fig. 2). By polymerisation, these molecules form organic polymer-chains within the gel and thus the gel itself is stabilized by interpenetrating polycondensated inorganic and organic polymeric chain molecules.⁶ The complete polymerisation can be proved in IR-spectra of the solid gel, in which the bands of the $C=C$ -double bonds (marked X) have disappeared compared to the spectra of the respective liquid sols (Fig. 3).⁷

Lead alkoxides tend to be insoluble and unstable, thus solid lead compounds, mostly salts of organic acids like lead-hydroxyacetate, are used in the synthesis of the PZT-precursor.

Direct Electrophoretic Shaping

The process of direct electrophoretic shaping of ceramic microstructures from a liquid sol–gel derived precursor is based on the fundamental principle of electrophoresis. Solid particles, dispersed in

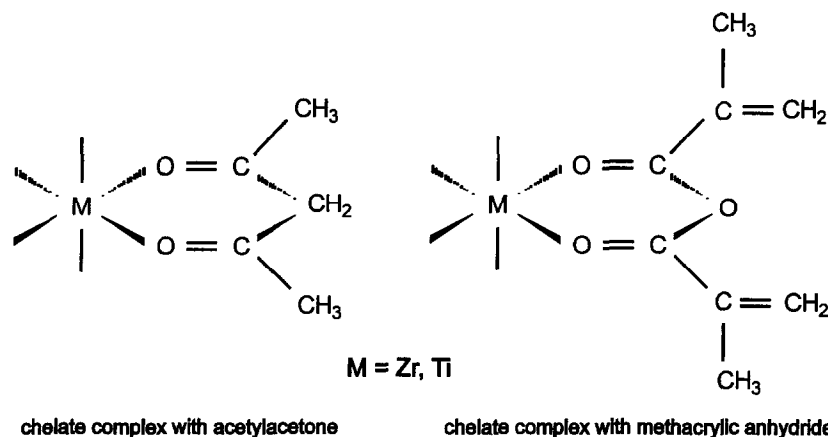


Fig. 2. Chelate complexes of Zr and Ti with acetylacetonone and methacrylic anhydride.

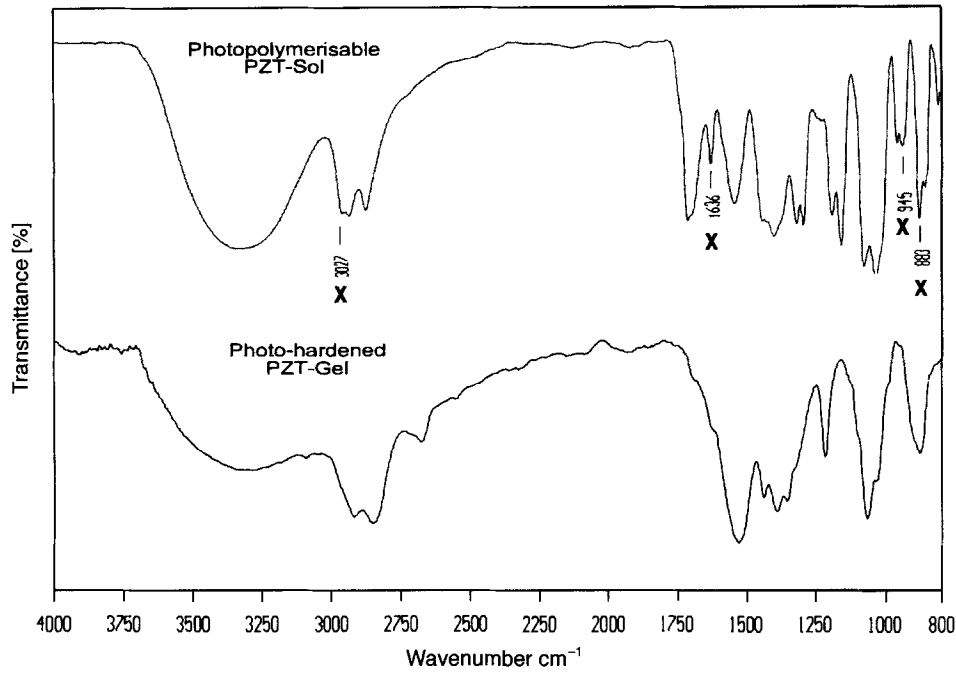


Fig. 3. Infrared spectra of a photopolymerisable PZT-sol and the hardened gel.

liquid medium, migrate to the corresponding electrode in the electric field due to their surface charge, which results from the different dielectric constants of the particles and the dispersion medium.⁸ Deposited on a microstructured electrode, the particles create a replica of this structure.

To characterize the electrophoretic behaviour, the particle migration velocity ν [m/s] or the electrophoretic mobility μ [m²/V.s] can be used respectively, which can be expressed by the Smoluchowsky equation:⁹

$$\mu = \varepsilon\nu/E = \varepsilon\zeta/4\pi\eta \quad (2)$$

(ε = dielectric constant of the liquid medium, η = dynamic viscosity, ζ = zeta-potential).

The zeta-potential ζ describes the stability of a suspension and the particle orientation in an applied electric field and depends on shape, surface properties and conductivity of the particles:

$$\zeta = 4\pi\nu\eta/\varepsilon E \quad (3)$$

Thus, the zeta potential is a suitable parameter to describe the electrophoretic deposition of ceramic suspensions and sols. The mass of electrophoretically deposited material is given by the Hamaker-equation⁹ with C = particle concentration and A = electrode surface:

$$M = \int AC\mu Edt \quad (4)$$

If developing a kinetic model for the EPD, it must be based on:¹⁰

$$dM/dt = A \cdot C \quad (5)$$

and

$$M = M_0 - V \cdot C \quad (6)$$

M_0 being the starting weight of the particles in the sol, V being the sol volume. Thus, for the deposition rate follows:

$$M = M_0(1 - e^{-kt}) \quad (7)$$

respectively:

$$dM/dt = M_0 \cdot k \cdot e^{-kt} \quad (8)$$

The rate constant k of the electrophoretic deposition (EPD) is, considering the above mentioned Smoluchowsky equation:¹⁰

$$k = F/V \cdot \varepsilon\zeta/4\pi\eta \cdot E = F/V \cdot \mu \quad (9)$$

It becomes obvious that the EPD is an interesting method especially when short deposition times are required due the exponential decrease of the deposition rate. By applying longer process times, no considerable increase of deposited material can be expected.

Experimental

Stoichiometric amounts of Zirconium-n-propoxide (70% in n-propanole, Johnson-Matthey, D-76185 Karlsruhe) and Titanium-ethoxide (Aldrich, D-89555 Steinheim) were mixed at 90–95°C under nitrogen-atmosphere and stirred. The complexing

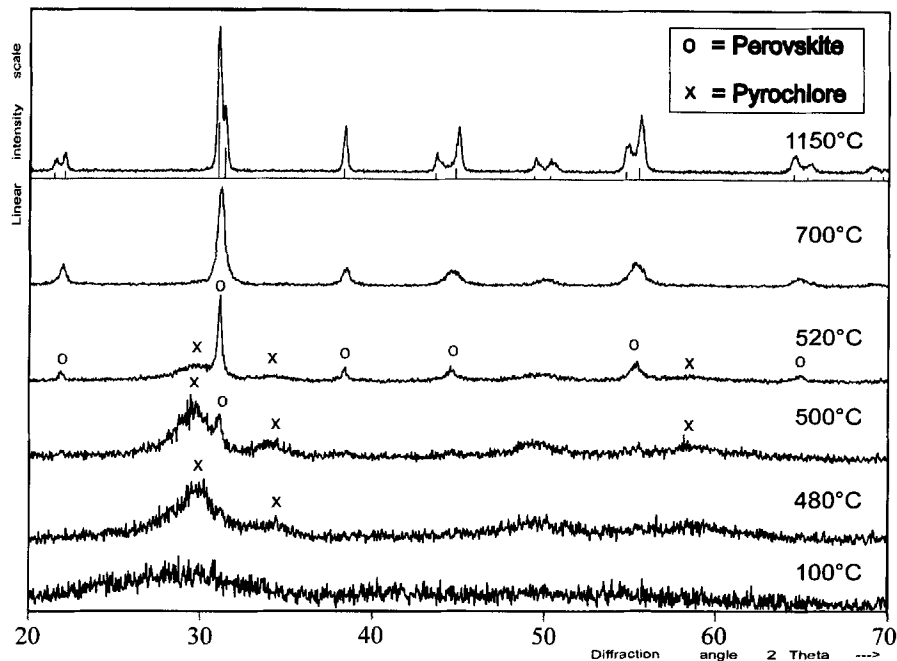


Fig. 4. X-ray diffraction patterns showing the development of crystal structures in the PZT-gel at various temperatures.

agent was then added to complex Zr and Ti as protection against hydrolysis. Lead-hydroxyacetate (Aldrich) was then slowly added to the mixture until it was completely dissolved. Partial gelation was performed by adding less than the stoichiometric amount of water to avoid a complete transformation into a solid gel. Then, formamide (99%, Aldrich) as DCCA (drying control chemical additive) and polyethylene glycol (M.W. 10-000, Sigma) as organic binder were added. The resulting PZT-precursor was a brown, viscous liquid, partially gelled sol with a typical density of 1.5 g cm^{-3} .

The electrophoretic deposition of the PZT-sol was performed in an electrophoresis cell, in which the electrodes were fixed in a defined distance of 2–5 cm, the cathode being a platinum sheet and the anode being a microstructured PMMA-form sputtered with gold. The temperature of the sol was kept constant at 25°C . The EPD was performed under constant current strength with typical applied current densities of 2 mA cm^{-2} and field strengths of $10\text{--}40 \text{ V cm}^{-1}$. The sol particles are deposited on the gold layer while gelation occurs simultaneously. With ongoing process time, a layer of PZT-gel grows on the PMMA form. The usual process time was 20 to 25 min, after which the PMMA-moulds were covered with a layer of solid PZT-gel of an average thickness of about 3 mm.

After the successful deposition the PMMA-form with the adherent layer of wet PZT-gel is removed from the sol. The gel is hardened by UV-induced radical polymerisation and then slowly dried.

The next processing steps are the thermal decomposition of the PMMA mould and the simultaneous burnout of the organic gel ingredients.

Therefore, the PMMA with the adherent gel is slowly ($0.1^\circ\text{C min}^{-1}$) heated in a furnace to $500\text{--}550^\circ\text{C}$. At this temperature, the PMMA and all the organics in the gel have been pyrolysed and the amorphous gel is beginning to crystallize. The first crystalline phase to be formed is the intermediate pyrochlore phase, which at 500°C undergoes a phase transition into the piezoelectric Perovskite phase. At 700°C , the PZT is present in the pure Perovskite phase (Fig. 4). The temperature is raised to the actual sintering temperature of 1150°C . After sintering, densities of $\sim 6.4 \text{ g cm}^{-3}$ were reached ($\approx 80\%$ of the theoretical density of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$), coming from green densities of $2.3\text{--}2.4 \text{ g cm}^{-3}$ ($\approx 30\%$ TD) of the dried gel bodies. Thus, the sintering process leaves a porosity of about 20% in the ceramic microstructure.

Due to the great amount of organics in the basic PZT-sols used for EPD, the shaped micro-structured gel bodies lose 35–40% of their mass and shrink to about 30% of their volume from drying to sintering. Figure 5 shows the change of mass

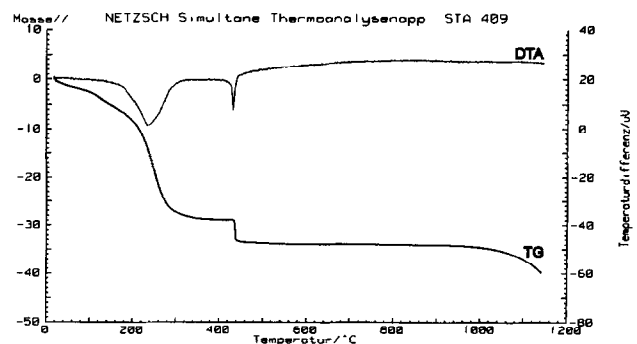


Fig. 5. Thermo-gravimetric analysis (TGA)- and differential thermo analysis (DTA)-signals of photo-hardened PZT-gel.

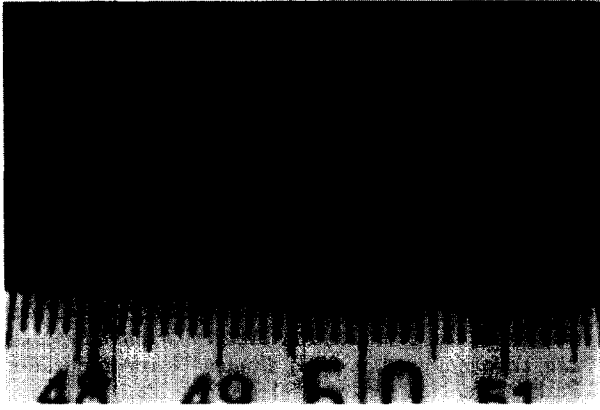


Fig. 6. Sintered PZT-micropart produced by direct electrophoretic deposition from the sol.

(TG-signal) and the DTA-signal of a PZT-gel as a function of temperature.

In Fig. 6 an example of a sintered PZT-microcomponent is shown. The macroscopic dimensions of this part are 1.6×1.6 cm. The microstructured surface, a honeycomb structure with hexagonal holes of about 25 μm edge length can be seen in the SEM-micrograph in Fig. 7 (right). The structured surface is a reproduction of the moulding tool (Fig. 7, left) with smaller inner dimensions due to the shrinkage during pyrolysis and the sintering process. The porosity of the microstructure, and some micro-cracks can be seen on the surface. The hexagonal columns of the PMMA-tool, the negative of the ceramic structure, were of 250 μm in height and 50 μm in diameter.

Piezoelectric properties are dependant on the density of the material, so the dielectric constants, coupling factors and piezoelectric moduli of the sintered PZT- microparts do not reach the values of fully densified PZT due to their density of 80% TD. Table 1 shows the measured values for bulk specimen, produced from a non-polymerisable PZT-sol (PZT-np) and from a photopolymerisable sol (PZT-pp) compared to a composite for hydrophone applications made of porous PZT¹¹ and to a fully dense PZT.¹²

Summary and Outlook

In this work a process was developed on a laboratory scale, in which precursor sols of lead zirconate titanate can be electrophoretically deposited on a microstructured mould to form microstructured gel-bodies, which can be transferred into piezoceramic microcomponents by pyrolysis of the inherent organics and sintering. To optimize the basic precursors for this process, a special sol-gel synthesis had to be developed. By incorporating polymerisable complexing agents in the synthesis, novel liquid PZT-precursors were produced that can be radically polymerized additionally to the inorganic network built up by polycondensation reactions during gelation. Interpenetrating organic and inorganic chains in the gel reduce the risk of crack formation and considerably increase the mechanical stability of the gel-body and thus

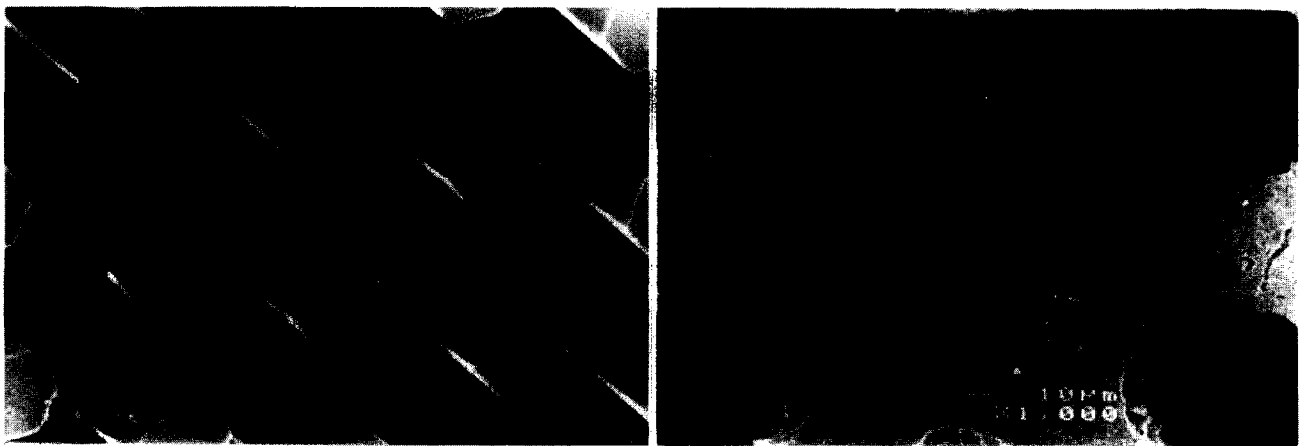


Fig. 7. SEM-micrograph of a electrophoretically deposited PZT-honeycomb structure after sintering (right) and the microstructured PMMA-tool used for shaping process (left).

Table 1. Typical electromechanical data of electrophoretically deposited PZT compared with reference values

| | Density ρ (g cm ⁻³) | Dielectric constant $\epsilon(-)$ | Coupling factor $k_t(-)$ | Piezo modulus d_{33} (10^{-12} C/N) |
|--------------------------|--------------------------------------|-----------------------------------|--------------------------|--|
| PZT-np | 5.89 | 283 | 0.49 | 34 |
| PZT-pp | 6.45 | 351 | 0.45 | 106 |
| Porous PZT ¹⁰ | — | 201 | — | 82 |
| Dense PZT ¹¹ | 8.01 | 1180 | 0.67 | 223 |

improve the further processing. The replication exactness of the moulds' microstructure in the ceramic is good, the density and electromechanical properties of the microparts qualify them for sensor applications as ceramic-polymer composites.

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