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Electrophoretic deposition for fabrication of ceramic microparts

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Abstract

Electrophoretic deposition (EPD) is mostly used for producing moulds and layers. The present work shows the fabrication of ceramic microparts by the use of structured electrodes. As electrode structures euro coins and spinning nozzles were used. Additionally a cost effective and simple method was developed, which allows preserving the original master mould by using microstructured silicone moulds as substrate. This was enabled by coating the silicone moulds with graphite to obtain an electrically conductive surface, required for electrophoretic deposition.

Keywords: Electrophoretic deposition; Microparts; Shaping; Suspensions; ZrO_2; Structural applications

1. Introduction

During the last years, the development of high-performance ceramics has increased in importance. This is due to their excellent chemical, mechanical and physical properties. The most common properties are abrasion resistance against corrosive media, high temperature strength and high hardness [1]. In microchemical engineering and microsystem technology, the application of submicron and nanosized ceramic particles is gaining importance because of the required smooth surfaces and dimensional accuracy. In conventional shaping techniques like slip casting, axial pressing or microinjection moulding nanosized powders are difficult to apply. But for handling and processing of nanopowders electrophoretic deposition (EPD) is a very well suitable colloidal processing technique [2,3], because the nanoparticles can easily be dispersed in a suspension, the solid content of which does not play a major role, and the deposition rate is independent of particle size as long as EPD is carried out perpendicular to sedimentation [4,5].

EPD was first observed in 1808 by the Russian scientist Reuss [6] and after many years, in 1940 the first description of the deposited yield was made by Hamaker [7] which can be written as follows:

$$\frac{dm}{dt} = ac\frac{\varepsilon_0\varepsilon_r\zeta f}{\eta}EA \quad (1)$$

In this equation a describes the quantity of particles reaching the electrode (in most cases a is assumed to be close to 1), c is the particle concentration, $\varepsilon_0 \cdot \varepsilon_r$ is the permittivity, ζ is the zeta-potential, f is the related correction factor, η is the viscosity of the suspension medium, E is the applied electric field strength, A is the surface area of the electrodes and t is the deposition time.

Electrophoretic deposition combines two processes: electrophoresis in a first step and deposition in a second step. In the first step particles suspended in a solvent move in presence of an electric field to an oppositely charged electrode. In a second step the particles deposit on the electrode [2,8–11] or on a thereto parallel arrangement of an ion-permeable membrane [9,12]. Homogeneous deposits with high mechanical strength and low surface roughness can only be obtained by using well-dispersed suspensions [13]. EPD is used for many applications, such as for the manufacturing of coatings, laminated or graded materials or for infiltration of porous materials [8–10,12,14]. A wide range of materials and combinations can be employed [2,13,15]. In addition to the fabrication of layers, EPD can also be used for producing moulds and microparts. Only few research groups are using EPD for fabrication of microparts [1,16]. Von Both et al. showed the fabrication of triple mirrors by the use of conductive paraffin electrodes. The master mould was produced by stereolithography and replicated into the electrically conductive paraffin. The so fabricated electrodes were thermally

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removed in a subsequent processing step after EPD [16]. Laubersheimer et al. used the same principle but with a microstructured PMMA form sputtered with gold [17]. Tabellion used porous PMMA moulds to produce near-net shape ceramics and glasses by membrane method. The moulds were mechanically peeled off. Demoulding was in a strong matter depending from the geometry, the form of the mould and the surface property of the green deposit [18].

2. Objectives

Both methods named above are using electrodes or membranes which can be employed once only. So the goal was to produce structured electrodes which can be used several times to fabricate ceramic microparts by EPD. Also the electrodes have to be fabricated in a simple and cost effective way.

The present work shows the fabrication of this structured electrodes and microparts.

3. Experimental

3.1. Materials and suspensions

For the fabrication of ceramic microparts zirconia was used because of its high strength. Also it is available as a fine scaled powder.

So the following powder was used: ZrO_2 Unitec −5 μm with 5 wt.% Y_2O_3 (Unitec Ceramics, UK), with a d_{50} of 0.95 μm. The non-aqueous slurry was made with ethyl alcohol (Carl Roth GmbH, Germany) as solvent; a trioxadecanoic acid (TODS, Clariant GmbH, Germany) was used as dispersant. The dispersant serves to the stabilisation of the suspension as well known among experts, so it will not be gone into any further detail in this publication.

The slurry was prepared using a magnetic stirrer to suspend the powder in the solvent containing the dispersant. Dispersion of the particles and homogenisation of the suspension was carried out for 5 min in an ultrasonic bath and for 1 h at 200 min^{-1} in a planetary ball mill using zirconia balls and a grinding beaker (PM 400/2, Retsch, Germany). The slurry was prepared with a powder concentration of 25 vol.% and a dispersant quantity of 2 wt.%. The conductivity of the slurry was 8 μS/cm at 23 °C.

3.2. Structured electrodes

Conventional Euro coins were used as structured electrodes as a simple alternative to micromilled metallic substrates. As a second possibility to use structured electrodes for EPD, a master structure—here also an Euro coin—was replicated into silicone rubber (Elastosil M 4370, Wacker, Germany). Both electrode types, coins and the structured silicone can be reused several times. After a couple of electrophoretic depositions, it became obvious that the details of the metallic coins showed degradation effects by grating due to the abrasive ceramic. This was not the case when silicone moulds were used. Also silicone has the great advantage to be very simply replicated from the master as often as needed.

The coins and the structured silicone were spray-coated with graphite (Graphit 33, CRC Industries Deutschland GmbH, Germany). In case of the silicone substrates, using graphite is necessary to obtain an electrically conductive electrode surface required for EPD. Also graphite has the advantage to adhere primarily onto the ceramic micropart and less onto the silicone or the coins. So graphite acts as a mould release agent, too. During the sintering step, it burns completely.

3.3. Electrophoretic deposition

For the electrophoretic deposition a glass beaker was used as EPD-cell. As negatively charged working electrodes graphite-coated silicone moulds as well as metallic electrodes (coins) were used. Generally stainless steel was used for the counter electrodes. The distance between the electrodes was 13 mm, the electrodes were positioned vertically.

Electrophoretic deposition was carried out at constant current; the current was set at 3 mA. Because the particles are positively charged, they move to the microstructured cathode where the deposition was carried out. Due to preliminary tests the deposition time was varied between 2 min for the first deposited microparts and 6 min for the last ones. This increase in deposition time is due to the depletion of powder in the suspension as a result of the deposited mass. So for the achievement of approximately the same layer thickness (made by optical comparison) the time has to be increased gradually with each subsequent deposition, dependent on the powder volume ratio in the suspension chamber compared to the deposited volume.

3.4. Demoulding and sintering of the microparts

The ceramic microparts were demoulded mechanically by peeling off the structured electrode. Due to the fact that graphite adheres primarily onto the ceramic, the microparts can be stripped off easily, in some cases they drop off on their own.

Drying of the ceramic microparts was carried out in a dryer (LHT 6/30, Carbolite, Germany) for 1 h at 100 °C under flowing air (5 l/min). Then the microparts were sintered in a chamber furnace (RHF 17/3E, Carbolite, Germany) also for 1 h at 1550 °C under flowing air (5 l/min).

4. Results

In the present work, two fabrication methods were employed: electrophoretic deposition on a conductive coin and deposition on the silicone microparts as described in Section 3.2.

The manufacturing of the structured microparts needs a master mould, e.g. a 10 Cent coin, shown in Fig. 1 on the left hand side. Inverting the master mould into silicone rubber produces the structured silicon electrode required for the electrophoretic deposition, also shown in Fig. 1 on the right hand side. Silicon has the great advantage to copy the original piece free from bubbles and with highest attention to detail. Also it can easily be copied in a second step to obtain a mould similar with the original master mould with the same attention to detail.

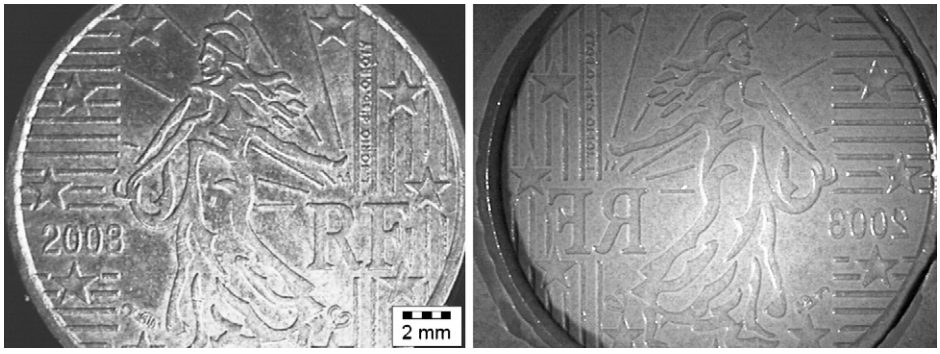

Fig. 1. Verso of an Euro coin (left hand side) and the inversed silicone substrate (right hand side).

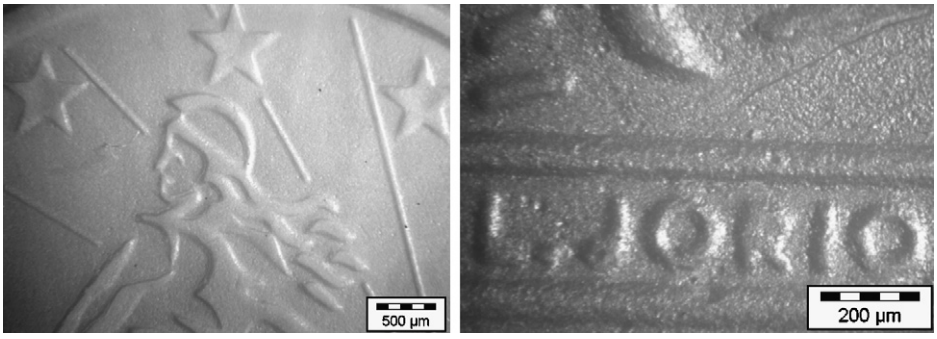

Fig. 2. Details of the sintered ceramic euro coin.

Onto this substrate the ceramic was deposited electrophoretically, the substrate was peeled off and the ceramic micropart was dried and sintered as described in Section 3.4. Since graphite adheres better on ceramic as on the mould, the green ceramic parts were black. During the sintering step the graphite burned out completely, so the ceramic has the same colour as usually. In Fig. 2 on the left picture a detail of the ceramic coin is shown. The lettering on the right of the coin is also shown in Fig. 2 on the right picture. The lettering shows a detailed reproduction of structures with dimensions smaller than 40 μm. Both figures show that sharp edges and round structures can be replicated precisely by EPD.

In Fig. 3 a replication by EPD of the observation of a 2 Cent coin is shown on the left picture and an EPD-replication of the verso of a 2 Euro coin on the right picture. The small-sized structures are reproduced accurately. Both ceramic microparts were deposited directly onto the coin as electrode. So it could be shown that despite the stiff substrate electrophoretic deposition directly on a structured rigid electrode and flawless peeling off of the ceramic is possible.

As structures with higher aspect ratios, spinning nozzles are deposited electrophoretically onto a structured silicone substrate. A problem still to solve is the filling of the structures without enclosing air bubbles, when the substrate is immersed into the suspension. Also peeling off the substrate is much more difficult due to the higher aspect ratios compared to the coins. Aspect ratios up to 2.5 have been successfully peeled off mechanically. Microparts with higher aspect ratios could not be peeled of entirely; often the fine structured broke off. Another method for filling and demoulding has to be developed; therefore further experiences have to be done. In Fig. 4 details of two different spinning nozzles are shown. At the bottom of the right hand side picture, absence of ceramic because of an enclosed air bubble during filling of the structure with slurry can be seen.

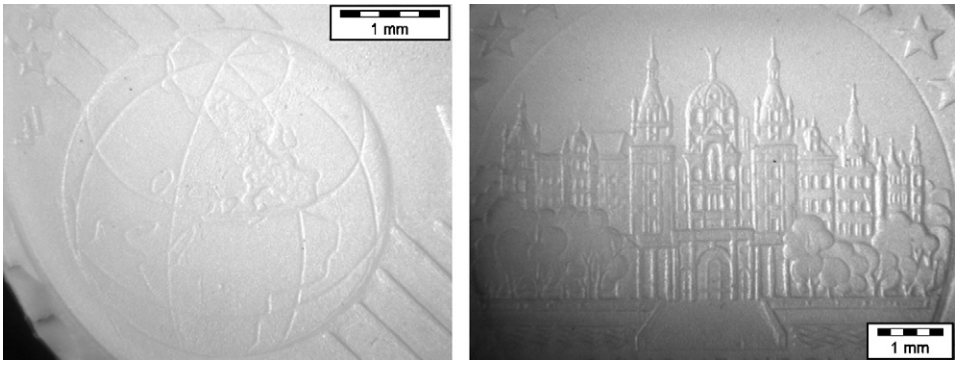

Fig. 3. Observation of a 2 Cent coin (left hand side) and verso of a 2 Euro coin (right hand side).

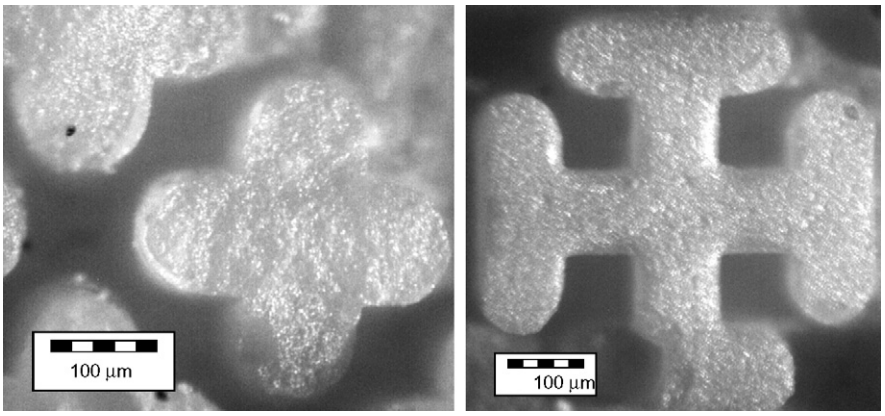

Fig. 4. Details of sintered ceramic spinning nozzles.

The electrophoretic deposition presents a method to produce ceramic microparts with a diversity of moulds of different aspect ratios unless undercuts are avoided. The absence of draft angles poses problems when the aspect ratio of the microstructures is larger than on coins.

Apart from these limitations a fast and shape conserving moulding of ceramic microparts is possible by EPD, especially due to the simple demoulding of the green deposits with aspect ratios up to 2.5. Besides the coins and spinning nozzles shown in this paper, also screw threads, dental crowns and a diversity of micro-pyramids could successfully be replicated by electrophoretic deposition.

5. Conclusions

It was shown that the fabrication of ceramic microparts by electrophoretic deposition of a fine powder was carried out successfully. Deposition was made directly onto microstructured electrodes, for demonstration EURO coins were used. Additionally a simple and cost effective method was developed, which allows preserving the original master mould, by using silicone as inexpensive substrate. The silicone was coated with graphite to make it electrically conductive. The graphite acts advantageously as a mould release agent, too. Various structured microparts were fabricated and aspect ratios up to 2.5 could be realised.

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