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Ceramic Coatings Obtained by Electrophoretic Deposition: Fundamentals, Models, Post-Deposition Processes and Applications

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1. Introduction

Electrophoretic Deposition (EPD) is one of the most outstanding coating techniques to be based on electrodeposition. Nowadays, increasing interest has been gained both from academic and industrial payers, due to its wide potential in ceramic coating processing technology.

The main advantages of this technique are:
its high versatility when used with different materials and their combinations;
its cost effectiveness, because it requires simple and cheap equipment.

Moreover, it can be used both on a large scale, also to coat objects with a complex shape, and on small scale, to fabricate composite micro- and nanostructures, as well as near net-shape objects having accurate dimensions (micro- and nano-manufacturing).

The basic phenomena involved in EPD are well-known and have been the subject of extensive theoretical and experimental research. Nevertheless, further efforts have to be devoted in order to understand the fundamental mechanisms of EPD and to optimise the working parameters, especially when multicomponent suspensions are used.

EPD is a two-step process. In the first step, charged particles suspended in a liquid medium move towards the oppositely charged electrode under the effect of an externally applied electric field (electrophoresis). In the second step, the particles deposit on the electrode forming a more or less thick film, depending on the process conditions (concentration of particles in solution, applied electric field, time). The substrate acts as an electrode and the deposit of particles is the coating.

The aim of this paper is to provide an updated review of the wide potential of EPD as a technique to produce ceramic coatings, without omitting possible problems and drawbacks.

Applications of EPD, especially on nanoparticles, are in continuous expansion both in industry and academia, stimulating a great interest in developing of predictive analytical and numeric modelling of the EPD process. The proposed mechanisms have explained
experimental results, but the current experts opinion is that a full understanding is still lacking, mainly due to the phenomena that are at the base of the interaction between the charged particles approaching both each other and to the electrode to form the solid deposit.

For some applications, a requirement is that the ceramic EPD deposit is dense, so a post-deposition treatment should be performed in order to densify it. Usually, this consists of a conventional heating treatment in a furnace, but some problems could occur such as delamination, cracks or residual stress due to the differential coefficient of thermal expansion. Moreover, the high densification temperature of ceramics can be detrimental for the substrate which could be damaged.

Sometimes, the sintering temperature can be decreased by adding some low melting additives. Alternative sintering methods could be considered, such as microwave, laser or electron beam.

Finally, the wide range of applications of EPD deposits will be mentioned. EPD process is very versatile, therefore porous, layered, and graded deposits can be obtained besides dense coatings. Recently, it has been clearly demonstrated the possibility of obtaining nanocomposite materials, especially those containing carbon nanotubes (CNTs), by using EPD. As a consequence, the applications are in a spread number of sectors: biomaterials, fuel cells, barrier coatings, electronics, catalysis, optical devices.

2. Fundamentals and models

Electrophoretic Deposition is a traditional processing method in the ceramic industry that is gaining increasing interest for production of new materials coatings.

EPD is achieved through the movement of charged particles dispersed in a suitable liquid towards an electrode under an applied electric field. This movement results in the accumulation of the particles and in the formation of a homogeneous deposit at the appropriate electrode (Figure 1).

The main requirement to obtain an efficient EPD process is to use suitable suspensions where ceramic particles are well suspended and dispersed. When a ceramic particle is in a liquid medium, it can be charged through four mechanisms (Van der Biest & Vandeperre, 1999):

a. selective adsorption of ions onto the solid particle from liquid,

b. dissociation of ions from solid phase into the liquid,

c. adsorption or orientation of dipolar molecules at the particle surface, and
d. electron transfer between the solid and the liquid phase due to the difference in work function.

For the analysis and discussion on charging mechanisms and particles interactions, that are at the base of this ceramics processing method, one can refer to the fundamentals of colloid science widely discussed in literature (Lewis, 2000).

Since EPD is assumed to be a two-step process, electrophoresis and deposition, each step require accurate attention. Firstly, the kinetics of the process will be described giving particular attention to the relation between process parameters and time evolution of the deposit yield. Then, the mechanisms of deposition proposed in literature will be discussed.
2.1 Kinetic models

The first model used to describe EPD process is attributed to Hamaker (Hamaker, 1940) who proposed a general expression for the deposited mass per area unit \( m \) (g cm\(^{-2}\)) in a cell with planar geometry:

\[
m = C_S \mu A E t
\]

where \( C_S \), solids concentration in the suspension (g cm\(^{-3}\)); \( t \), deposition time (s); \( \mu \), electrophoretic mobility (cm\(^2\) V\(^{-1}\) s\(^{-1}\)); \( E \), electric field strength (V cm\(^{-1}\)); \( A \), surface area of the electrode (cm\(^2\)).

Several years later, Sarkar and Nicholson (Sarkar & Nicholson, 1996) considered again the first model of Hamaker and analysed the dependence of kinetics on some experimental conditions.

In eq. (1), \( \mu \) and \( A \) can be evaluated numerically and one reasonably supposes that they are constant during the process. It is not so true for \( C_S \) and \( E \), that vary as the process while the process is going on.

Sarkar and Nicholson considered the variation of the particles concentration in the suspension for long deposition time, starting with the condition that the only change in the concentration is due to the mass of powder deposited by EPD. It is equal to zero when the process starts and varies with time according to the expression:

\[
m(t) = m_0 (1 - e^{-t/\tau})
\]

where \( m_0 \), initial mass of powder in suspension (g) and \( \tau = V/\mu AE \) defined as characteristic time (V is the volume of the suspension considered constant). Actually, \( \tau \) is the reciprocal of \( k \), the “kinetic parameter” that represents a key parameter in the modelling of EPD process.
In order to consider that some particles arriving to the electrode do not take part to the formation of the deposit, Sarkar and Nicholson introduced a “sticking factor”, \( f \leq 1 \), a multiplicative efficiency factor.

For short time, eq. (2) is reduced to the Hamaker model, since in the early stages of the process the variation of bulk concentration is negligible due to the small amount of powder deposited. When the process advances, the deposited mass is relevant and its effect on the evolution of the deposition process is not negligible. In this condition, under the hypothesis that the resistivity of deposited layer is higher than that of the suspension, the electric field suffers a drop, also if the process is conducted under the condition of constant applied voltage.

In eq. (1), the electric field strength is the effective strength that affects the particles in the suspension and so it is decreased by the potential drops due to the resistance of electrodes, suspension and deposited layer. With respect to the applied voltage externally, \( v \), the expression of the electric field experienced by the particles is:

\[
E(t) = \left( v - \left[ \Delta V_{e1} + i R_d s(t) + i R_s (d - s(t)) + \Delta V_{e2} \right] \right) / d
\]  

(3)

\( \Delta V_{e1} \) and \( \Delta V_{e2} \) are the potential drop (V) at the electrode 1 and 2, respectively; \( i \) is the current (A); \( d \) is the distance between the electrodes (m); \( s(t) \) is the thickness of the deposited layer (m); \( R_d \) and \( R_s \) are the resistivity (\( \Omega/m \)) of the deposit and the suspension (Fig. 2).

Fig. 2. Variation of the potential in an electrophoretic cell during the deposition
The hypotheses and the conditions that are at the basis of the eq. (3) were widely discussed by Van der Biest (Van der Biest & Vandeperre, 1999), who cited also much experimental evidence on the dependence of the electric field in the suspension from the parameters above mentioned.

In order to avoid the effect of deposit resistivity increasing, Sarkar and Nicholson proposed to work in galvanostatic condition rather than in potentiostatic condition. In such a way the number of particles arriving on the electrode is constant and not influenced by the electrical condition of the suspension-deposit system. Ma (Ma & Cheng, 2002) determined the relationship between the kinetic parameter of Sarkar and Nicholson and the applied current density, \( i \), making the predictions of the deposition yield easier, when the deposition is at constant current density:

\[
k = k_0(e^{i/i_0} - 1)
\]

where \( k_0 \) a reference kinetic constant, and \( i_0 \) a reference applied current density.

Other factors that influence the drop of the electric field are a change in the polarization of the electrode and a change in the conductivity of the suspension, occurring in the progress of EPD process.

Changes in the electrode polarization can be due to a change in the concentration of the reactants at the electrode-electrolyte interface. When the process starts and a current flows towards the electrode, the concentration of reacting species at the electrode drops off. They are replaced by the species of bulk suspension through diffusion, convection or migration, but the presence of deposit layer can retard the transport of reactants to the electrode. As a consequence, the polarization at the working electrode changes.

As regards the suspension conductivity, a model introduced by Vandeperre and Van der Biest (Vandeperre & Van der Biest, 1998) affirms that both the particles and the ions surrounding the particles contribute to the conductivity. During the EPD process, the electric conductivity decreases due to the effect of the depletion of particles in the suspension and for the reduced presence of ions moving together with powder particles. This effect is more evident if the amount of deposited powder is high with respect to the powder in suspension and if the suspension ionic conductivity is relatively small.

Several studies were devoted to the investigation of the effect of suspension conductivity on the EPD process, through the study of the influence of binders, salts, stabilizers, and a liquid medium (aqueous and non aqueous)(Ferrari & Moreno, 1996; Westby at al., 1999; Moreno & Ferrari, 2000; De Riccardis et al., 2007). As a common result, in order to have an effective deposition process the electrostatic or electrosteric stabilisation of the suspension has to be such that the ionic concentration in suspension is low and the suspended particles are the main current carriers.

In order to schematize the EPD yield and according to Sarkar and Nicholson, it is possible to recognize four different behaviours, depending on the process conditions: constant voltage, constant current, constant concentration, and variable concentration.

In Curve A of Fig. 3 (constant current and constant concentration) the deposition rate is linear with respect to time. In curves B, C and D, the deposition rate decreases
asymptotically with deposition time. Obviously, the decreasing concentration produces a reduction of the final yield and therefore of the rate deposition either at constant current (Curve B) or at constant voltage (Curve C and D).

Comparing curve A and C (both with constant concentration), the final yield is considerably higher in curve A than in curve C. This is due to the electric resistance of the deposit layer, considered higher than that of an equal thickness taken up by the suspension. Therefore, when the process goes on, the voltage per unit length (or electric field) decreases and consequently decreases the particle velocity as function of deposition time.

In curve D, the deposition rate is lower than other curves for both the contribution of the concentration decrease and of the resistance of deposit layer. As a deduction, the nature of the deposit layer plays an important role on deposition rate.

Fig. 3. Schematic representation of the kinetics of EPD process: curve A, constant current-constant concentration; curve B, constant current-variable concentration; curve C, constant voltage-constant concentration, curve D, constant voltage-variable concentration.

Adopting the standard scheme of an electrochemical cell, a combined resistive-capacitive model can be used to represent the electrical behaviour of the EPD process (Fig. 4).

In addition to the resistors, discussed above, some capacitors are added to represent the current transient that occurs when the voltage starts to be applied, generally interpreted as due to the establishment of a concentration profile under a diffusion limited regime (Van der Biest & Vandeperre, 1999).

Ferrari (Ferrari et al., 2006) proposed a resistive model for the deposition kinetics, considering a linear relationship between the suspension resistivity and the solid loading in the suspension. This model agrees with the experimental data referred to a long time deposition of yttria stabilized tetragonal zirconia polycrystalline (Y-TZP), that shows a S-shaped variation of the mass per area unit with time.

Recently Baldisserri (Baldisserri et al., 2010) proposed some assumptions to define the electrical behaviour of a potentiostatic EPD cell: a) the effect of capacitive transients on cell current is negligible, b) the faradic resistance of both the electrode/deposit interfaces is
constant, c) the electrical resistance of the EPD deposit is proportional to its thickness, d) the electrical resistance of the suspension is constant.

Fig. 4. Electric model of EPD process with plane electrode (we= working electrode, ce= counter electrode, DL= double layer)

The assumption a) is based on the estimate of time required for double-layer charging. The assumption b) is supported by the consideration that after the formation of the first monolayer, the interface at the working electrode/suspension should be stabilised as the charging of double-layer should be completed. Similarly at the interface between counter electrode/suspension, but it is less relevant as no deposition occurs at that electrode.

The assumption c) relies on the compliance of the physical properties of deposited layer comparable with a porous media, where the electrical resistance is proportional to its thickness. The assumption d) is based on the consideration that the deposited layer is less thick than the electrodes distance, therefore the decrease in the volume filled by the suspension is negligible.

Baldisserri applied this model to EPD of TiO$_2$ particles and verified experimentally that the previously mentioned assumptions were satisfied. As a result, they derived a linear correlation between deposited mass and passed charge and a non-linear kinetic equation:

$$m(t) = A \frac{V_{Dx}}{i_{0}p_{d}} \left( \frac{1 + \alpha t}{(1 + \alpha t)^{1/2} - 1} \right), \quad \alpha = \frac{2K_i}{V} \left( \frac{p_{d}}{D_{d}} \right)$$

(5)
where \( i_0 \), current density at time \( t=0 \), \( K \), the deposited mass-passed charge ratio, \( V \), the external applied voltage, \( \rho_d \) and \( D_d \) resistivity and density of the deposited layer, respectively. This equation at short deposition time is approximated by:

\[
m(t) = A i_0 K t
\]

(6)

Therefore, this resistive model is able to describe the EPD process both at regime and during the transient of the deposition current, provided that suspension contains such dispersant or binder as the electroactive chemical species are available for all the deposition time, making deposition a diffusive control process.

2.2 Deposition models

Unlike the kinetic models regarding electrophoresis, the second step of EPD, that is the deposition, is still matter of discussion, especially for the arrangement of particles on the electrode surface. After arriving at the working electrode, particles are packed onto its surface reproducing the electrode shape. The aggregation and the arrangement of the particles on the electrode surface depend on surface chemistry of particles and on interactions between particles in suspension and between particles and substrate.

The fundamental condition for a performing EPD process is to use a stable suspension where particles are keep well dispersed in the liquid medium and can move towards the electrode without influencing or being influenced by other particles. Here, particles can be rearranged on the electrode surface during packing under the action of electric field.

Of course, from the electrical point of view, the suspension composition is critical because the presence of deflocculants, binders or dispersants influences the surface charge of particles and their electrical response.

The interactions between particles inside a liquid medium is largely described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. When an external force exists, as the driving force of an electric field, the minimum of the energy curve is shifted towards an higher value (Fig. 5). If the applied field exerts a force so great as to overcome the mutual repulsion force, two particles coagulate. Similar phenomenon occurs when a particle moves toward an electrode in an EPD cell.

Some deposition mechanisms are proposed to explain the phenomenon of particles accumulation:

- flocculation by particles accumulation,
- particles charge neutralization at the electrode,
- electrochemical coagulation of particles, and
- distortion and thinning of electrical double layer (EDL).

The last, proposed by Sarkar and Nicholson (Sarkar & Nicholson, 1996), is the most diffused and accepted. This theory affirms that when a positive charge moves toward an electrode together oppositely charged ions, its shell is distorted, thinning ahead and thickening behind, due to fluid dynamics. As a consequence, the particle feels a weak attraction toward another positively charged particle, so together they can move under the electric field. The EDL of the two particles is less wide than that of a single particle, so when another particle
is approaching, it can be close enough to interact through van der Waals attractive forces and so coagulates. Similar mechanism occurs at the electrode surface where the high particles concentration allows the formation of a particles deposit.

Fig. 5. Potential energy vs. separation distance for particles in absence (-----) and in presence (- - -) of an electric field.

This model was integrated by Fukada (Fukada et al., 2004) with a further consideration based on the experimental observation of De (De & Nicholson, 1999). According to De, Fukada verified that $H^+$ are depleted at the cathode because of particle discharge, through the reaction:

$$H_{X=0}^{+} \xrightarrow{\text{transport process}} H_{X=0}^{+} + e^{-} \xrightarrow{\text{charge transfer}} \frac{1}{2}H_2$$  \hspace{1cm} (7)

This implies an increase of local pH toward the isoelectric point and then the coagulation is facilitated. Fukada found an analytical expression for the variation of the $H^+$ concentration with time, validated by experimental results for alumina suspension in ethanol. This expression, generally suitable for suspensions containing $H^+$ or $H_3O^+$, shows that the steady state with respect to diffusion and charge transfer of $H^+$ ions corresponds to a reduction of zeta-potential at the cathode and consequently to coagulation.

Other deposition mechanisms, mentioned above, although explain experimental results in some conditions, are not valid in general. In fact, flocculation by particles accumulation suggests a deposit formation by electrophoresis similar to gravitation, so that the pressure exerted by the arriving particles at the electrode makes the particles close to form a deposit, overcoming the repulsion forces between particles. This hypothesis does not explain why the deposition occurs on a membrane which does not act as an electrode.

Similarly, particles charge neutralization at the electrode suggests the charged particles are neutralized by the contact with the electrode surface, but it does not explain the deposition mechanism when the deposit is thicker than a monolayer.

With respect to electrochemical coagulation of particles, the hypothesis is that an increase of electrolyte concentration around particles produces a reduction of the repulsion between particles near the electrode, where particles can coagulate. However, time required to have an increased electrolyte concentration is not negligible, experimentally estimated as...
inversely proportional to the square of applied voltage. Moreover, this mechanism is invalid when there is no increase of electrolyte concentration near the electrode.

Recently, new models considering particles flow from an electro-dynamic point of view are developed (Guelcher et al., 2000; Ristenpart et al., 2007). Experimental results of Guelcher confirmed a numerical prediction of clustering of colloidal particles deposited in a DC electric field by considering an electro-osmotic particles flow. By analysing the long-range attraction force intra-particles, Ristenpart demonstrated the flow direction of a particle depends on the sign of its dipole coefficient. Under particular conditions, the electro-osmotic component and the electrohydrodynamic component of flow can have the same direction and so can produce aggregation.

This overview demonstrates that the discussion on models and mechanisms of electrophoresis and deposition of ceramic particles in presence of an electric field is still open, and that many efforts have been made for some decades, from Hamaker to today, to explain and understand the large amount of experimental results.

3. Post-deposition processes

Depending on coating functions, a post-EPD process may be required in order to densify the coating and to improve its mechanical properties and adhesion to substrate. Usually, this post-EPD process is a heat treatment devoted to cure or sinter the coating, but some precautions should be followed to avoid defects inside the coating or at interface with the substrate.

As mentioned before, EPD is especially regarded as a suitable method to obtain coatings on bodies of a complex shape. To respect this feature, one of the main requirements is to have a low concentration of powder agglomerates in the ceramic suspension. The size of these agglomerates define the order of magnitude of the size of stacking defects during consolidation. Therefore, all methods for quality assurance, such as control of powder dimension and phase, impurity content, process parameters, have to be pursued in order to minimize the defects in the final product and therefore improve its functional properties.

With respect to other colloidal consolidation processes, in EPD the deposition rate is almost unrelated to particle size and thickness of the deposited layer, so high deposition rates can be achieved. In order to avoid defects during deposit coagulation, especially at high deposition rates, very fine particles should be used. Moreover, the use of suspensions in an organic solvent could minimise the incorporation of gas bubbles in the deposit due to electrolysis. Zithomirsky (Zhitomirsky & Gal-Or, 1997) deposited hydroxyapatite (HA) coatings on Ti6Al4V. They found that suspension presedimentation had a significant effect on the deposit quality, because it allowed the removal of undesirable agglomerates from the suspension and, as a result, the deposit consisted of finer particles. This reduced the porosity in the deposited layer and a denser packing was obtained.

After deposition, the coating has to be dried. While the green deposit is still immersed in the suspension, it is saturated by liquid. After removing from the suspension and drying, the green density can reach 60%. Also during drying some shrinkage occurs so that cracks can appear due to stress induced by the flow and evaporation of the liquid through the pores (Scherer, 1990). Cracks occurring during drying may be reduced if the deposit
thickness is lower than a critical value which depends on the powders used for deposition. Van der Biest (Van der Biest et al., 2004) obtained coatings on stainless steel with WC-5Co, Al₂O₃, TiC, and TiB₂ powders, having an average particle size and a surface area equal to 1, 0.3, 2, and 1.5-2 µm, and 2.47, 10, 1-2 and 0.5-1.5 m²/g, respectively. The thickness below which no cracking was observed was 125, 316 and 56 µm, for the first three powders, whereas surprisingly a layer 5 mm thick was deposited without observing cracks in the case of TiB₂. This result supports the influence of the powder characteristics on the quality of the deposit.

Generally, an EPD coating is deposited on a metal substrate that can be non resistant to high temperature which is necessary to sinter ceramics. Two approaches exist to limit damages of substrate: to use some method to lower the sintering temperature, such as powders with a fine grain or a low melting additive, or to use a different sintering treatment, such as microwave or irradiation. In the following, some of the methods cited before are reported.

In order to lower the sintering temperature, a first stratagem that could be used is the choice of precursors suitable to form a ceramic material. Some examples were those of Boccaccini (Boccaccini et al., 1996, 1997) and Kooner (Kooner et al., 2000) who prepared EPD sols based on boehmite (γ-AlOOH), fumed amorphous silica, and fumed δ-alumina with appropriate concentrations, as precursors of mullite. Mullite has a number of attractive properties for high-temperature structural applications, but its sintering temperature is higher than 1600°C. The use of nano-particles and fine mullite seeds lowered the sintering temperature by up to 1300-1400°C, making possible the formation of mullite matrix by EPD in fabrics based on silicon carbide and Nextel 720 fibres.

Reaction bonding (RB) is a forming technique developed to produce near net-shape ceramics and to overcome problems caused by shrinkage during sintering. It consists of introducing some elements or compounds that, by reacting with an oxidant or reducing atmosphere at a temperature higher than room temperature, can produce a ceramic matrix.

Aluminium particles were added to PSZ suspensions by Wang (Wang et al., 2000b; Wang et al., 2002). During heat treatment in air at low temperature (600°C), metal powder was converted to nanometer sized oxide crystals, that subsequently were sintered and bonded to PSZ at 1200°C. The volume expansion associated with the Al→Al₂O₃ reaction partially compensated the sintering shrinkage. The combined use of EPD with the reaction bonding process allowed to fabricate crack-free and relatively dense ceramic coatings, maintaining the sintering temperature lower than that usual one (1350-1500°C). However, as the oxidation of the Al powder in the green form is affected by the thermal processing profile, the oxidation and sintering temperature has to be appropriately chosen to optimise the density and the quality of coatings.

Another candidate for reaction bonding is ZrN due to its low reaction temperature. Baufel (Baufel et al., 2008) utilised a suspension with zirconia and zirconium nitride to obtain an EPD coating on Ni alloys. Two different contents of ZrN were mixed together with YSZ in ethanol and milled in order to reduce the grain size of powders. After deposition and drying in ambient conditions, a heat treatment was performed in air at 1000 °C for 6 h. In XRD spectra, the treated samples showed only pronounced peaks of zirconia without evidence of ZrN peaks, so they concluded that all ZrN transformed into zirconia, within the detection limit of XRD. As a result, combining EPD and reaction bonding, Baufel obtained zirconia
coatings, about 100 µm thick, sintered at 1000°C, with a microstructure comparable with the one prepared without reaction bonding and sintered at 1200°C.

EPD was successfully applied by Lessing (Lessing et al., 2000) to obtain reaction bonded joints using several compositions of silicon carbide and silicon nitride mixed to graphite and carbon black particles. The use of EPD allowed to form joints filling a large gap and coatings rounded corners or undercut sections, with structures originated by molten silicon at 1450°C.

A very interesting application of reaction bonding process is that optimised by Hang (Hang et al., 2010) who combined EPD and RB to achieve a graded coating based on hydroxyapatite (HA). HA is a material extensively studied and used as a biomaterial, thanks to its biocompatibility and osteoconductivity. EPD is potentially an attractive method to obtain HA coatings on Ti substrate, but often the bonding strength between EPD coating and substrate was not high enough for the requirement of clinic application. Moreover, a great difficulty is represented by the sintering. In fact, as high temperature produces degradation of Ti substrate and thermal decomposition of HA, sintering temperature should be ideally below 1000 °C under which HA is difficult to be fully densified. On the other hand, the thermal expansion coefficient of Ti substrate is much lower than that of HA, so a large thermal contraction mismatch could arise and tend to induce the formation of cracks when cooled from an elevated temperature. Again, a significant firing shrinkage during sintering will lead to the formation of cracks also in coatings.

As a solution, HA/Al₂O₃ composite coatings were produced by a combination of EPD and reaction bonding process at a relatively low sintering temperature of 850 °C. Reaction bonded Al₂O₃ with relatively lower coefficient of thermal expansion (CTE) was introduced into HA coating to reduce the difference of CTE between Ti substrate and HA coating, and to overcome problems caused by the firing shrinkage during sintering. Both advantages were proven to be beneficial in avoiding the formation of cracks and improving the bonding strength of ceramic coatings. On the coating containing HA and reaction bonded Al₂O₃, a further coating with a gradient of composition was deposited, up to the top coating composed only by HA. The development of this functionally gradient coating (FGC) based on HA, contributed to reduce the discontinuity in thermal expansion coefficients and, as a result, minimised the residual stress in the coatings.

Therefore, electrophoretic deposition and reaction bonding process were successfully combined to produce HA functionally gradient coatings on Ti substrate at a relatively low sintering temperature of 850 °C. HA FGC was uniform and crack-free, having a chemical composition and microstructure with a gradient variation along its cross section. The content of HA increased gradually from the inner part of HA FGC (diffusion layer) to the outer part (top layer), and proportionally the density increased from the inner part to the outer part. The HA FGC took efficiently the advantages of both the mechanical properties of Ti and the biological performances of HA ceramic.

Microwave heating is a method fundamentally different from the conventional techniques used to densify materials. The direct coupling of energy to a material with dielectric loss results in extremely rapid heating. Typical heating and cooling rates are of the order of
hundreds of degrees Celsius per minute, much higher than those of conventional heating sintering. This can be very advantageous, especially when conventional temperature and time of sintering can result detrimental to the substrate material.

A combination of EPD process and microwave sintering was used by Streckert (Streckert et al., 1997) to prepare SiC composites formed by silicon carbide-based perform and SiC matrix. After achieving infiltration with SiC powder by EPD, microwave sintering at 2.45 GHz was performed under fluxing a mixture of nitrogen and hydrogen. A high density in composite was obtained by applying a load during microwave heating. Therefore, the combined use of EPD process and microwave sintering has the potential to produce good quality composite rapidly and economically, due to short process time and simple equipments required.

Dense, uniform and crack-free Al₂O₃/YSZ composite coatings on Ni based superalloy were prepared by a novel sol-gel process, optimised by Ren (Ren et al., 2010). The composite coatings were firstly prepared by the electrophoretic deposition of a suspension containing aluminium oxide sol, nano-Al₂O₃, and micro YSZ particles and then treated by Pressure Filtration Microwave Sintering (PFMS). Suspensions with several mass ratios of ceramic powders versus aluminium oxide sol were used to produce thick deposits by EPD. After drying at room temperature for 24 h, the green deposits were treated in a 2.45 GHz microwave oven for 10 minutes. Ren obtained coatings with micro-cracks, pores and a granular structure when the mass ratio of ceramic powders/aluminium oxide was the lowest. On the contrary, at maximum of the mass ratio, the coating was dense, without cracks and with a microstructure composed by YSZ particles embedded in nano-Al₂O₃ particles. Moreover, no defects and spallations were found across the interface, as an indication that the thermal match between coating and substrate was good. In the Ren’s opinion, the pressure and microwave heating were doubly beneficial for the sintering and densification of YSZ/Al₂O₃ coatings at a relatively lower temperature. In fact, the compound effect of pressure and filtration in PFMS process constrained the shrinkage of coating in three-dimensional directions and therefore micro-cracks were avoided and the adhesion to the substrate was improved. Furthermore, nano-sized α-Al₂O₃ decreased the phase transition and the crystallization temperature of aluminium oxide sol and at the same time the microwave energy lowered the phase transformation temperature of α-Al₂O₃.

In general, the use of sol-gel suspensions for the EPD process has two advantages: it allows to obtain thicker deposits than those prepared by a conventional sol-gel method, and the heating treatment is performed at a temperature typical of a sol-gel process, certainly lower than that used to sinter ceramics. The sol-gel method should be suitable to obtain protective coatings on metal against corrosion, due to the low temperature of densification which are not detrimental for the metal substrate, but the typical maximum thickness of sol-gel coating is approximately 2 µm. Moreover, the presence of pores and microcracks due to drying shrinkage, limits the applicability of sol-gel coating as protection. Castro (Castro et al. 2004) incorporated silica nano-particles to an acid-catalysed SiO₂ sol in order to increase the coating thickness without increasing the sintering temperature. Then this hybrid organic-inorganic suspension was used to produce EPD coatings 5 µm thick. After sintering at 500°C for 30 min, these coatings demonstrated to have a good corrosion resistance.
Laubershiemer (Laubershiemer et al., 1998) produced a deposit by EPD using a synthesised liquid precursor of lead-zirconate-titanate (PZT) according to a modified sol-gel route. Besides the advantage mentioned before, it is worthy to note that the sol-gel process has the advantages of the conventional mixed-oxide route, such as much greater purity and compositional control with liquid-mix homogeneity and a lower process temperature. In order to obtain a PZT micro-component, Laubershiemer used a polymeric gel by introducing polymerisable chelating agents in the synthesis of the precursors. After performing EPD into a microstructured mould simultaneously to the gelation of the sol, a gel-body was obtained, that then was hardened by polymerisation induced by UV-light. After drying and removing of the mould, a heating treatment was performed in a furnace at 550°C to obtain a ceramic component. The addition of polymerisable agents allowed the creation of an organic network which was interpenetrated into the inorganic chains. This reduced the risk of cracks formation and considerably increased the mechanical stability of the gel-body. It was demonstrated that this method is suitable for production of micro components based on ceramic materials.

Fig. 6. Scheme of the EB treatment on the surface of Alumina-Zirconia EPD coating and SEM images referred to the zones inside and outside the EB track. The EB track presents a different contrast with respect to the untreated coating. Inside the EB track, the grains are more compact than those ones outside the track.

An alternative method was successfully used to densify the electrophoretic deposit and to make it more adherent to substrate. It was based on the irradiation of the green ceramic coating surface by a high power density energy source, such as an electron beam (EB).
Compared to laser energy sources, in EB treatment the reflectivity by the irradiated material is lower and therefore the beam efficiency is higher. Moreover, the thickness of affected material can be varied by changing the beam power. So 10 kW power is usually employed to cut or weld materials, whereas a lower power allows to treat few micrometers of the material surface.

De Riccardis (De Riccardis et al., 2008) used EB treatment up to 13.75 J/mm² of fluence, to sinter the alumina-zirconia EPD coatings, by confining the high temperature to the ceramic material without affecting deeply the metallic substrate (Fig. 6). The EB irradiation on alumina–zirconia coatings produced a nanostructured ceramic composite material, formed by micro-particles of \( \alpha\)-Al\(_2\)O\(_3\) and tetragonal ZrO\(_2\), embedded in an amorphous matrix containing also nano-sized crystals. Nevertheless some residual porosity, the electron beam treatment had two positive effects: it increased the ceramic coating density and improved the adhesion between coating and substrate. In fact, the adhesion stress values evaluated for coatings applied on sandblasted substrates were comparable to those typical of plasma-sprayed coatings. It is worthy to note this method can be applied to sinter ceramic coating deposited on metallic support having low temperature resistance. Moreover, since EB irradiation did not damage the material outside the EB track, several adjacent tracks could be performed in order to obtain densified coating on a large area.

4. Applications: From traditional to advanced materials

After its first use in 1933 to deposit thoria particles on a platinum cathode for electron tube application, EPD was mainly utilized for traditional ceramic processing. Its industrial application was the deposition of clay or vitreous enamel coatings on metals, which after firing showed an evident improvement in the finishing properties of coatings with respect to conventional dipping or spraying processes.

In the last 20 years the interest shown by the academic and the industrial world regarding EPD has increased thanks to its wide range of applications, especially due to the insertion and diffusion of nanomaterials which allow to obtain structures with characteristics never conceived before.

A numbers of reviews reported extensively on the several applications of EPD as coatings and free standing objects, based on ceramics and metals (Sarkar & Nicholson, 1996; Van der Biest & Vandeperre, 1999; Boccaccini & Zhitomirsky, 2002; Boccaccini et al., 2003; Besra & Liu, 2007; Corni et al., 2008). Particularly successful is the use of EPD to produce porous, laminated and graded ceramic coatings (Hatton & Nicholson, 2001; Put et al, 2004; You et al, 2004) as well as fibres reinforced composites (Boccaccini et al., 1996, 1997; Wang et al., 2000a; Freidrich et al., 2002; Kaya et al., 1999, 2000, 2001). Moreover, EPD has proven to be an effective method to texture superconductors structures, such as BSCCO and YBCO (Hang et al., 1995; Yau & Sorrell 1997; Greci et al., 2006) and electrodes for solid oxide fuel cells (Zhitomirsky & Petric, 2000; Hosomi et al., 2007).

The aim of this review is to present more extensively those that are the current and most appealing applications for the most recent material science: biomaterials and nanomaterials.
4.1 Biomaterials

Numerous studies have been devoted to the development of coatings based on the conventional bioactive inorganic materials, such as hydroxyapatite and bioglass, in order to improve the adhesion of tissue to the implant surface and so increase the performance of metal implants.

As calcium phosphates are the mineral component of bone, dentine and dental enamel, hydroxyapatite \([\text{Ca}_5(\text{PO}_4)_3(\text{OH})]\) is the best candidate to form a chemical bonding with hard tissues. EPD is particularly advantageous in the deposition of HA coatings because this technique allows the control of coatings composition, thickness and microstructure, that are essential to obtain the maximum benefit. As mentioned before, the first requirement to obtain a densely packed HA layer is to use very fine particles and to prepare well stable suspensions. Xiao (Xiao & Liu, 2006) optimised a HA suspension using nano-HA particles prepared by hydrothermal method, in primary aliphatic alcohols (C1-C4) with triethanolamine as a dispersant. Maximum stability was achieved when n-butanol was used as liquid medium. EPD process (30 V for 1 min) produced a deposit with a high packing density, small drying shrinkage, and therefore optimal mechanical properties.

Meng (Meng et al., 2005) studied the effect of applied voltages on the microstructure of HA coatings, both with constant voltage, equal to 20 and 200 V, and with dynamic voltage, varying between 0 and 200 V. The dynamic voltage process consisted of three increments with three different rates, slowly in the first step and faster during the third. After sintering at 800°C for 2 h, the coating prepared at low constant voltage was dense and consisted of fine particle whereas the coating prepared at high constant voltage was porous and with large HA agglomerates. Differently, the coating prepared at dynamic voltage consisted of continuously gradient particles, with smaller particles building up in the inner layer and bigger particles forming the outer layer, both with a high packing of particles.

Bioactive glasses, such as Bioglass 45S5 which is composed by \(\text{SiO}_2\) (45 wt%), \(\text{NaO}_2\) (24.5 wt%), \(\text{CaO}\) (24.5 wt%) and \(\text{P}_2\text{O}_5\) (6wt%), readily react with physiological fluids forming a hydroxyapatite layer on their surface and creating tenacious bonds to hard and soft tissue. Coatings of Bioglass 45S5 were obtained on stainless steel and Nitinol (Ti 50wt% and Ni 50wt%) by EPD (Krause et al., 2006). The conditions of the coatings deposition and sintering were optimised for the two types of substrates. After sintering at 800°C, the Bioglass coating covered completely the stainless steel substrate surface even if not uniformly. When the substrate was Nitinol, a diffusion of nickel and titanium was observed in the Bioglass coating, as a consequence of sintering process performed at 950°C.

Recently, the advantages of polymers composites containing HA or bioactive glass have been highlighted. In fact, the combination of polymeric and inorganic bioactive phases is common to several natural materials, like bone which is a composite containing collagen and HA crystals. Moreover, the interfacial bonding strength of HA or Bioglass coatings on metal substrate can be improved by their combination with polymers.

For these reasons, different types of composite coatings, based on HA or Bioglass or both, were deposited, where the organic component was chitosan or alginate (Zhitomirsky et al., 2009). Both the organic component enabled the electrosteric stabilisation of HA and Bioglass particles in suspension and promoted a co-deposition of the organic and inorganic
components in EPD process. The presence of chitosan and alginate allowed to obtain coatings with improved strength with respect to the pure HA or Bioglass coatings. Moreover they did not obstruct the bioactive function of HA and Bioglass.

Bioglass was successfully co-deposited with polyetheretherketone (PEEK) by EPD (Boccaccini et al., 2006a) on Nitinol wires. PEEK is a semicrystalline thermoplastic polymer (\(T_m=340^\circ C\)) with excellent performance also for biomedical applications. A suspension containing PEEK and Bioglass in ethanol was used for EPD co-deposition. Sintering was performed at 340°C for 20 min, just to melt the polymer and therefore to embed the ceramic particles. After sintering, the surface of coatings became smooth due to viscous flow of melted polymer. The PEEK/Bioglass coating deposited on Nitinol showed to be adherent to substrate also when it was bent. Moreover, the composite coating demonstrated to have two functions: to protect the NiTi substrate from corrosion when it was in contact with body fluids, and to improve the bonding of bone or soft tissue to an implant, being Bioglass a bioactive material.

Another example of application of composite coatings based on Bioglass concerns composites containing carbon nanotubes (Charlotte Schausten et al., 2010). The EPD parameters were optimised in order to obtain both co-deposition and sequential deposition of Bioglass particles and multi-walled CNTs on stainless steel substrates. Co-deposition produced homogenous and dense coatings with well-dispersed CNTs placed between the Bioglass particles. So, the network of CNTs acted as a reinforcement and contributed to the improvement of the mechanical stability of the coatings. The coatings obtained by sequential deposition formed a two-dimensional nanostructured mesh of CNTs on the Bioglass layer and produced a surface nanotopography, with a great potential in the formation of bone-like nanosized HA crystal with the presence of body fluids.

The combined use of Bioglass and CNTs is motivated also by recent results on differentiation of osteoblast cells during their growth based on the substrate nanostructure. Moreover, as CNTs have a similar dimension to proteins, they demonstrated a high reactivity for interactions involved in the cell attachment mechanism. An interesting formation of CNTs/Bioglass composites by EPD was described by Boccaccini (Boccaccini et al., 2007) who referred to CNTs deposited on porous Bioglass-based scaffolds for bone tissue engineering. Concentrated CNTs suspensions (0.5-5 g/l) were used to create a deposit on interconnected and macroporous structure of Bioglass, placed between two stainless steel electrodes. The final structure showed a scaffold with substantially unchanged porosity, with nanostructured pore walls. Moreover, the presence of CNTs conferred biosensing properties to the scaffold by adding an electrical conduction function, potentially useful for stimulation of cell growth and tissue regeneration by a physioelectrical signal transfer.

Alumina and ultrahigh molecular weight polyethylene (UHMWPE) are used as biomaterials for prostheses and joint replacement, but they do not bond with live bone. Coatings of bioactive ceramics can improve the osteoconductivity of these materials. Wollastonite (Yamaguchi et al., 2009) was used to form a composite bioactive material based on Alumina and UHMWPE. Wollastonite powder was prepared by calcination of silicon dioxide and calcium carbonate in an equimolar ratio. Substrates of porous alumina (10 µm average pore size) and porous UHMWPE (30 µm average pore size) were placed between two gold plates, acting as electrodes. After EPD, the substrates were placed in simulated body fluid (SBF),...
then after 14 days an apatite layer was observed on the cathode-side of the porous substrates, induced by deposited wollastonite. The adhesive strength of the apatite layer to the porous substrates was higher than commercially available coated alumina and UHMWPE.

As a biomaterial, titania is normally applied as a coating on metallic substrates in order to improve the integration of orthopaedic implants. Bacterial colonisation of implanted materials occurring on the coating surface represents major complications in orthopaedic surgery. Therefore, in order to reduce the risks of bacterial infection after implantation, inorganic antibacterial materials were used with better results than those organic in terms of durability, toxicity and selectivity. Silver is one of the preferred elements as antibacterial agent, so Ag-TiO$_2$ coatings were developed with both bioactive and antibacterial properties (Santillán et al., 2010). Ag nano-particles (4 nm) were grown directly on the surface of commercial TiO$_2$ nano-particles (23 nm) from nucleophilic reaction. In such a way, the Ag nano-particles were uniformly distributed on TiO$_2$ nano-particles, contributing to control the release of Ag, in the presence of bacterial colonies. An aqueous stable suspension containing Ag-TiO$_2$ particles was used to deposit a composite coating on Ti sheets. EPD parameters (3V for 90 s) were optimised referring to macroscopic homogeneity of coatings and to absence of cracks. In vitro bioactivity tests in SBF showed an increasing formation of HA at increasing time and decreasing silver content in the coatings.

4.2 Nanomaterials

Among nanomaterials, enormous attention is devoted to CNTs for their extraordinary properties due to structure, aspect ratio and size. Their applications range from microelectronics to structural composites and to biomedical materials, but particular arrangements of CNTs need to enhance their positive contribution in specific applications. If CNTs are used in combination with other materials to form a composite, appropriate processing methods have to be adopted in order to obtain homogeneous distribution of CNTs in a matrix. EPD is a very convenient technique for manipulating CNTs and producing ordered CNTs arrays (Boccaccini et al., 2006b). As for all EPD experiments, the composition of suspensions and EPD parameters (electric field, deposition time and electrode material) are critical for the performance of CNTs based coatings. The functionalisation of CNTs is also very important, which obviously influences the interaction between CNTs and other components both in EPD suspension and in a formed deposit. Boccaccini (Boccaccini et al., 2010) reported on two alternative methods to produce CNTs based composite coatings by EPD. In the first method, a CNTs layer was deposited with a more or less isotropic planar distribution of CNTs on a substrate. Then the CNTs coating was employed as an electrode to deposit ceramic or metallic nanoparticles, again by EPD, with the aim of infiltrating the porous CNTs structure. The second method consisted of a co-deposition of ceramic particles with CNTs. Three are the alternative cases of the components arrangement in the suspension: i) self-assembly of nano-particles coating individual CNT, ii) heterocoagulation of CNTs on individual larger particles, and iii) simultaneous deposition of CNTs and particles (ceramic or metallic) with the same charge polarity in suspension. As an example, the first approach was used to obtain a CNT-TiO$_2$ coating. The presence of CNTs together with titania enhanced the photocatalytic effectiveness of titania and improved the mechanical properties of titania coatings.
CNTs have been also used to make more effective the interface between fibres and matrix in SiC/SiC composites for fusion reactor applications (König et al., 2010). EPD was used to deposit multi-walled CNTs onto SiC fibres and to infiltrate the CNTs coated fibres mats with SiC powder. The CNTs coating obtained on fibres was firm and homogeneous, with uniformly distributed nanotubes on the surface of the fibres. The fibre mats were then placed in contact with an electrode of the EPD cell and the migration of SiC particles under the electric field allowed to gradually fill the spaces between the fibres with a high grade of infiltration. After sintering at 1300°C in air, a denser composite than the one without CNTs on the surface of the fibres was obtained.

An improved planar-gate triode with CNTs field emitters was successfully realised by combining photolithography, screen printing, and EPD (Zhang et al., 2011). In order to deposit selectively CNTs acting as field emitters onto cathode electrodes, an EPD suspension containing CNTs was used. Previously, an acid activating treatment was performed in order to functionalise the CNTs’ surface. During the EPD process, gate electrodes of a planar-gate triode were used as an anode electrode of the EPD cell and cathode electrodes of the triode were used as a cathode electrode of the EPD cell. In such a way, positively charged CNTs were selectively deposited onto the cathode of the triode. The field emission performance of the realised devise was so good that practical applications of dynamic back light units and field emission displays could be implemented.

To improve further the field emission performance of CNTs, they should be vertically aligned so as to obtain a well-defined structural anisotropy and a maximal packing density with the characteristics of a 1D nanomaterial. CNTs forests could be grown in situ by vapour, liquid or solid mechanisms, or could be aligned by a post-growth method. EPD was the method utilised successfully by Santhanagopalan (Santhanagopalan et al., 2010) to control CNTs’ orientation and to obtain an alignment in direction of the applied electric field. A high-voltage electrophoretic deposition (HVEPD) process was optimised through three key elements: i) high deposition voltage, to align of nanomaterial with electric field, ii) low concentration of nanomaterial in a suspension to prevent aggregation before deposition and to avoid bundle formation, and iii) simultaneous formation of an holding layer to keep the nanomaterial deposit resistant to manipulating.

This method was also successfully used to deposit aligned manganese oxide nanorods on stainless steel plates, demonstrating the versatility of HVEPD that potentially can be utilised to obtain forests from any nanomaterial that can be charged suitably in a solvent.

Porous template were often used to obtain aligned nanomaterials, which were then removed after the growth of aligned nanostructures. Also in this subject, EPD demonstrated its effectiveness. Deposition of diamond nanoparticles (4-12 nm) was performed (Tsai et al., 2011) on a surface of porous anodic alumina (PAA) with pore size of 20 nm. These diamond nanoparticles acted as nucleation sites for the following growth of diamond nano-tips by HFCVD process. EPD allowed to obtain a continuous diamond HFCVD film with a very fine microstructure. On the contrary, when no EPD of nucleating diamond nanoparticles was performed, diamond film grown up by HFCVD showed a fragmentary distribution of large diamond particles (200 nm).
In order to control the structure of an EPD coatings, other stratagems can be used. Uchikoshi (Uchikoshi et al., 2004, 2010) and Kawakita (Kawakita et al., 2009) demonstrated diffusely that the use of a magnetic field during an electrophoretic deposition induced a preferential orientation of particles with an anisotropic magnetic susceptivity. For example, titania particles in the form of anatase were deposited with c-axis aligned with a strong external magnetic field. The deposit was dense, uniform and crack-free, and therefore suitable for energy conversion applications, where the efficiency depends strongly on the crystals orientation.

An AC or a pulsed DC electric field can modify the structure of the EPD deposit. Riahifar (Riahifar et al., 2011) varied time, frequency, voltage, and particles concentration in suspension and obtained titania nanoparticles coatings with different deposition patterns. They used two gold planar electrodes, with a spacing of 150 µm, realised by scratching a continuous gold film on glass substrate. The AC field applied between the two electrodes produced a deposit on the electrodes edge at a low voltage, in a short time, with low particle concentration and high frequencies. On the other hand, at high voltages, a longer time, a higher particle concentration, and lower frequencies, the deposited particles filled the gap between the electrode, demonstrating how it was possible to control the deposition pattern by changing appropriately the process parameters.

The use of EPD is a relatively new technique in the field of polymer electronics. One of the most useful features is the use of dilute solutions, not suitable for other conventional casting techniques, such as spin coating. Particularly interesting results were obtained by Tada (Tada & Onoda, 2011) who prepared composite films of conjugated polymers and fullerene by EPD, starting with the optimisation of the suspension composition. Therefore dense composite coatings, suitable for heterojunction systems, were deposited. Moreover, they found different distributions of fullerene crystals depending on conjugated polymer, with spontaneous stratification in presence of an inhomogeneous suspension. This result confirmed the possibility to control the deposit morphology by EPD.

Other examples of the use of EPD in the energy conversion field are represented by the deposition of nanomaterials such as supercapacitors, photofuntional compounds, or photo anodes in dye-sensitised solar cell (DSSC). As a supercapacitor, manganese oxide is a low cost raw material and therefore it is an alternative material to the conventional oxides, that are RuO$_2$ and IrO$_2$. Coatings of needle-like MgO powders with a diameter of 10 nm and a length ranging from 50 to 400 nm, were deposited by EPD by Chen (Chen et al., 2009). The deposited coating showed a porous microstructure and a slight decrease of specific capacitance, from 200 to 190 F/g after 300 cycles, attributed to reduction reaction from Mn$^{4+}$ to Mn$^{3+}$ during EPD process and recovered during the cyclic voltammetry tests.

Titania nanosheets (TN) are promising nanomaterials for the design of UV-visible light sensitive energy conversion systems. EPD was used to deposit TN from an aqueous suspension on ITO substrates (Yui et al., 2005). The addition of poly (vinyl alcohol) (PVA) made the TN coating more adherent to substrates. Then intercalation of methyl viologen (MV$^{2+}$) was achieved by soaking the EPD TN deposit in an aqueous MV$^{2+}$ solution. The photocatalytic activity was demonstrated under irradiation at the absorption band of TN for the TN/MV$^{2+}$ thin films, that maintained stable for a longer time than those in absence of TN.
Electrodes for flexible DSSCs were prepared by EPD depositing commercial zinc oxide powders on a conducting plastic substrate (Chen et al., 2011). After deposition under an electric field of 200 V/cm for 1 min, ZnO coatings showed some cracks and porosity. Then, in order to improve the films quality, a mechanical compression was applied at different pressures (25-100 MPa). The adhesion of ZnO coatings to the plastic substrates was clearly improved, so that they could not be peeled off even after bending the substrate. Experimental tests on DSSC prepared with this ZnO electrode demonstrated that the photocurrent density and the light-to-electricity conversion energy correlated with the applied pressure during the compression. EPD confirmed again to be a versatile and efficient coating technique.

5. Conclusions

By using EPD it is possible to obtain coatings with an excellent performance in a very large range of applications. However, it needs to control process parameters and to design suitable suspensions in order to obtain outstanding results. Moreover, the properties of the coatings can be tailored through the tuning the applied electric field and the choice of appropriate starting materials, which also influence the eventual densifying post-deposition treatment.

In spite of its numerous advantages and the wide range of applications, efforts have to be devoted to develop theories and models valid for the electrophoretic deposition of nanoscaled materials. In fact, it is expected that the field in which EPD will expand its applications will be those related to nanotechnology, especially for fabrication of nanostructured and hybrid composite materials, both in the form of dense and porous materials.

6. References

Baldisserri, C.; Gardini, D. & Galassi, C. (2010). An Analysis Of Current Transients During Electrophoretic Deposition (EPD) From Colloidal TiO$_2$ Suspensions, Journal of Colloid and Interface Science, Vol. 347, No. 1 (2010), pp. 102–111, ISSN 0021-9797

Baufeld, B., Van der Biest, O. & Rätzer-Scheibe, H.-J. (2008). Lowering The Sintering Temperature For EPD Coatings By Applying Reaction Bonding, Journal Of The European Ceramic Society, Vol. 28, No. 9 (2008), pp. 1793–1799, ISSN 0955-2219

Besra, L. & Liu, M. (2007). A Review On Fundamental And Application Of Electrophoretic Deposition (EPD), Progress In Materials Science, Vol. 52, No. 1 (2007), pp. 1-61, ISSN 0079-6425

Boccaccini, A.R.; Trusty, P.A. & Telle, R. (1996). Mullite Fabrication From Fumed Silica And Bohemite Sol Precursors, Materials Letters, Vol. 29, No. 1-3 (1996), pp. 171-176, ISSN 0167-577X

Boccaccini, A.R.; MacLauren, I.; Lewis, M.H. & Ponton, C.B. (1997). Electrophoretic Deposition Infiltration Of 2-D Woven SiC Fibre Mats With Mixed Sols Of Mullite Composition, Journal of The European Ceramic Society, Vol. 17, No.13 (1997), pp. 1545-1550, ISSN 0955-2219

www.intechopen.com
Boccaccini, A.R. & Zhitomirsky, I. (2002). Applications of Electrophoretic Deposition Techniques in Ceramic Processing, *Current Opinion in Solid State & Materials Science*, Vol. 6, No. 3 (2002), pp. 251-260, ISSN 1359-0286

Boccaccini, A.R.; Roether, J. A.; Thomas, B.J.C., Shaffer, M.S.P.; Chavez, E.; Stoll, E. & Minay, E.J. (2003). The Electrophoretic Deposition of Inorganic Nanoscaled Materials, *Journal of The Ceramic Society of Japan*, Vol. 114, No. 1 (2003), pp. 1-14

Boccaccini, A. R.; Peters, C., Roether, J. A.; Eifler, D.; Misra, S. K. & Minay, E. J. (2006a). Electrophoretic Deposition Of Polyetheretherketone (PEEK) And PEEK/Bioglass Coatings On NiTi Shape Memory Alloy Wires, *Journal of Materials Science*, Vol. 41, No. 24 (2006), pp. 8152-8159, ISSN 0022-2461

Boccaccini, A.R.; Cho, J.; Roether, J. A.; Thomas, B.J.C.; Minay, E.J. & Shaffer, M.S.P. (2006b). Electrophoretic Deposition Of Carbon Nanotubes, *Carbon*, Vol. 44, No. 15 (2006), pp. 3149-3160, ISSN 0008-6223

Boccaccini, A.R.; Chicatun, F., Cho, J.; Brencanu, O., Roether, J.A.; Novak, S. & Chen Q. (2007). Carbon Nanotubes Coatings On Bioglass-Based Tissue Engineering Scaffolds, *Advanced Functional Materials*, Vol. 17, No. 15 (2007), pp. 2815-2822, ISSN 1616-301X

Boccaccini, A.R.; Cho, J.; Subhani, T.; Kaya, C. & Kaya, F. (2010). Electrophoretic Deposition Of Carbon NanoTube-Ceramic Nanocomposites, *Journal of The European Ceramic Society*, Vol. 30, No. 5 (2010), p. 1115-1129, ISSN 0955-2219

Castro, Y.; Ferrari, B.; Durán, A. & Moreno, R. (2004) Effect Of Rheology And Processing Parameters On The EPD Coatings Of Basic Sol-Gel Particulate Sol, *Journal of Materials Science*, Vol. 39, No. 3 (2004), pp. 845-849, ISSN 0022-2461

Charlotte Schausten M.; Meng, D.; Telle, R. & Boccaccini, A.R. (2010). Electrophoretic Deposition Of Carbon nanotubes And Bioactive Glass particles For Bioactive Composite Coatings, *Ceramics International*, Vol. 36, No. 1 (2010), p. 307-312, ISSN 0272-8842

Chen, C.-Y.; Wang, S. C.; Lin C.-Y.; Chen, F.-S. & Lin C.-K. (2009). Electrophoretically Deposited Manganese Oxide Coatings For Supercapacitor Application, *Ceramics International*, Vol. 35, No. 8 (2009), pp. 3469-3474, ISSN 0272-8842

Chen, H.-W., Lin, C.-Y., Lai, Y.-H., Chen, J.-G., Wang, C.-C., Hub, C.-W., Hsu, C.-Y., Vittal, R. & Ho, K.-C. (2011). Electrophoretic Deposition Of ZnO Film And Its Compression For A Plastic Based Flexible Dye-Sensitized Solar Cell, *Journal of Power Sources*, Vol. 196, No. 10 (2011), pp. 4859-4864

Corni, I.; Ryan, M.P. & Boccaccini, A.R. (2008). Electrophoretic deposition: From traditional ceramics to nanotechnology, *Journal of The American Ceramic Society*, Vol. 28, No. 7 (2008), pp. 1353-1367, ISSN 0002-7820

De, D. & Nicholson P. S. (1999). Role Of Ionic Depletion In Deposition During Electrophoretic Deposition, *Journal of The American Ceramic Society*, Vol. 82, No. 11, (1999), pp. 3031-3036, ISSN 0002-7820

De Riccardis, M.F.; Carbone, D. & Rizzo, A. (2007). A Novel Method For Preparing And Characterizing Alcoholic EPD Suspensions, *Journal of Colloid and Interface Science*, Vol. 307, No. 1 (2007), pp. 109-115, ISSN 0021-9797

De Riccardis, M.F.; Carbone, D.; Piscopio, E. & Vittori Antisari, M. (2008). Electron Beam Treatments Of Electrophoretic Ceramic Coatings, *Applied Surface Science*, Vol. 254, No. 6 (2008), pp. 1830-1836, ISSN 0169-4332
Ferrari, B. & Moreno, R. (1996). The Conductivity Of Aqueous Al₂O₃ Slips For Electrophoretic Deposition, *Materials Letters*, Vol. 28, No. 4-6 (1996), pp. 353-355, ISSN 0167-577X

Ferrari, B.; Moreno, R. & Cuesta, J.A. (2006). A Resistivity Model For Electrophoretic Deposition, *Key Engineering Materials*, Vol. 314 (2006), pp. 175-180, ISSN 1013-9826

Friedrich, C.; Gadow, R. & Speicher, M. (2002). Protective Multilayer Coatings For Carbon Carbon Composites, *Surface & Coatings Technology*, Vol. 151-152 (2002), pp. 405-411, ISSN 0257-8972

Fukada, Y.; Nagarajan, N.; Mekky, W.; Bao, Y.; Kim, H.-S. & Nicholson, P.S. (2004). Electrophoretic Deposition - Mechanisms, Myths, And Materials, *Journal of Materials Science*, Vol. 39, No. 3 (2004), pp. 787-801, ISSN 0022-2461

Grenci, G.; Denis, S.; Dusoulier, L.; Pavese, F. & Penazzi, N. (2006). Preparation And Characterization Of YBa₂Cu₃O₇-x Thick Films Deposited On Silver Substrates By The Electrophoretic Deposition Technique For Magnetic Screening Applications, *Superconductor Science and Technology*, Vol. 19, No. 4 (2006), pp. 249-255, ISSN 0953-2048

Guelcher, S.A., Solomentsev, Y. & Anderson, J.L. (2000). Aggregation Of Pairs Of Particles On Electrodes During Electrophoretic Deposition, *Powder Technology*, Vol. 110, No. 1-2 (2000), pp. 90-97, ISSN 0032-5910

Hamaker, H.C. (1940). Formation Of A Deposit By Electrophoresis, *Transactions of The Faraday Society*, Vol. 35 (1940), pp. 279-287

Hatton, B. & Nicholson, P.S. (2001). Design and Fracture of Layered Al₂O₃/TZ3Y Composites Produced By Electrophoretic Deposition, *Journal of The American Ceramic Society*, Vol. 84, No. 3, (2001), pp. 571-576, ISSN 0002-7820

Hosomi, T.; Matsuda, M. & Miyake, M. (2007). Electrophoretic Deposition For Fabrication Of YSZ Electrolyte Film On Non-Conducting Porous NiO-YSZ Composite Substrate For Intermediate Temperature SOFC, *Journal of The European Ceramic Society*, Vol. 27, No. 1 (2007), pp. 173-178, ISSN 0002-7820

Huang, S.-L.; Schoenwaelder, B.; Dew-Hughes, D. & Grovenor, C.R.M. (1995). Thermal Shock Resistance And Bending Strain Tolerance Of Electrophoretically Deposited Bi₂Sr₂CaCu₂O₇/Ag Tapes, *Materials Letters*, Vol. 24 (August 1995), pp. 271-274, ISSN 0167-577X

Huang, J.-C.; Ni, Y.-J. & Wang, Z.-C. (2010). Preparation Of Hydroxyapatite Functionally Gradient Coating On Titanium Substrate Using A Combination Of Electrophoretic Deposition And Reaction Bonding Process, *Surface & Coatings Technology*, Vol. 204, No. 21-22, (2010), pp. 3387-3392, ISSN 0257-8972

Kawakita, M.; Uchikoshi, T.; Kawakita, J. & Sakka, Y. (2009) Preparation of Crystalline-Oriented Titania Photoelectrodes on ITO Glasses from a 2-Propanol-2,4-Pentanediol Solvent by Electrophoretic Deposition in a Strong Magnetic Field, *Journal of The American Ceramic Society*, Vol. 92, No. 5 (2009), pp. 984-989, ISSN 0002-7820

Kaya, C.; Boccaccini, A. R. & Trusty, P.A. (1999). Processing And Characterization Of 2-D Woven Metal Fibre-Reinforced Multiplayer Silica Matrix Composites Using Electrophoretic Deposition And Pressure Filtration, *Journal of The European Ceramic Society*, Vol. 19, No. 16 (1999), pp. 2859-2866, ISSN 0955-2219
Kaya, C.; Boccaccini, A. R. & Chawla, K.K. (2000). Electrophoretic Deposition Forming of Nickel – Coated – Carbon – Fiber - Reinforced Borosilicate – Glass - Matrix Composites, *Journal of The American Ceramic Society*, Vol. 83, No. 8 (2000), pp. 1885-1888, ISSN 0002-7820

Kaya, C.; Kaya, F.; Boccaccini, A. R. & Chawla, K.K. (2001). Fabrication And Characterisation Of Ni-Coated Carbon Fibre-Reinforced Alumina Ceramic Matrix Composites Using Electrophoretic Deposition, *Acta Materialia*, Vol. 49, No. 7 (2001), pp. 1189-1197, ISSN 1359-6454

König, K.; Novak, S.; Iverkovic, A.; Rade, K.; Mang, D.; Boccaccini A.R. & Kobe, S. (2010). Fabrication of CNT/SiC/SiC Composites By Electrophoretic Deposition, *Journal of The European Ceramic Society*, Vol. 30 (2010), pp. 1131-1137, ISSN 0955-2219

Kooner, S.; Westby, W.S.; Watson, C.M.A. & Farries, P.M. (2000). Processing of Nextel™ 720/Mullite Composite Using Electrophoretic Deposition, *Journal of The European Ceramic Society*, Vol. 20, No. 5 (2000), pp. 631-638, ISSN 0955-2219

Krause, D., Thomas, B.; Lienenbach, C.; Eifler, D.; Minay, E J. & Boccaccini, A.R. (2006) The Electrophoretic Deposition Of Bioglass Particles On Stainless Steel And Nitinol Substrates, *Surface & Coatings Technology*, Vol. 200, No. 16-17 (2006), p. 4835-4845, ISSN 0257-8972

Laubersheimer, J.; Ritzhaupt-Kleissl, H.-J.; Haußelt, J. & Emig, G. (1998). Electrophoretic Deposition of Sol-Gel Ceramic Microcomponents Using UV-curable Alkoxide precursors, *Journal of The European Ceramic Society*, Vol. 18, No. 3 (1998), pp. 255-260, ISSN 0955-2219

Lessing, P.A., Erickson, A.W. & Kunerth, D.C. (2000). Electrophoretic Deposition [EPD] Applied To Reaction Joining Of Silicon Carbide And Silicon Nitride Ceramics, *Journal of Materials Science*, Vol. 35, No. 35 (2000), pp. 2913-2925, ISSN0022-2461

Lewis, J.A. (2000). Colloidal Processing Of Ceramics, *Journal of The American Ceramic Society*, Vol. 83, No. 10 (2000), pp. 2341-2359, ISSN 0002-7820

Ma, J. & Cheng, W. (2002). Electrophoretic Deposition Of Lead Zirconate Titanate Ceramics, *Journal Of The American Ceramic Society*, Vol. 85, No. 7 (2002), pp. 1735-1737, ISSN 0002-7820

Meng, X.; Kwon, T.-Y.; Yang, Y.; Ong, J.L. & Kim, K.-H. (2005). Effects Of Applied Voltages On Hydroxyapatite Coating Of Titanium By Electrophoretic Deposition, *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, Published online 16 December 2005 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/jbm.b.30497

Moreno, R. & Ferrari, B. (2000). Effect Of The Slurry Properties On The Homogeneity Of Alumina Deposits Obtained By Aqueous Electrophoretic Deposition, *Materials Research Bulletin*, Vol. 35, No. 6 (2000), pp. 887-897

Put, S.; Anné, G.; Vleugels, J. & Van der Biest, O. (2004), Advanced symmetrically graded ceramic and ceramic-metal composites, *Journal of Materials Science*, Vol. 39, No. 3 (2004), pp. 881-888, ISSN 0022-2461

Ren, C.; He, Y.D. & Wang, D.R. (2010). Al2O3/YSZ Composite Coatings Prepared By A Novel Sol-Gel Process And Their High-Temperature Oxidation Resistance, *Oxidation of Metals*, Vol. 74, No. 5-6 (2010), p. 275-285, ISSN 0030-770X

Riahiifar, R.; Raissi, B.; Marzbanrad, E. & Zamani C. (2011) Effect Of Parameters On Deposition Pattern Of Ceramic Nanoparticles In Non-Uniform AC Electric Field.
Ceramic Coatings Obtained by Electrophoretic Deposition: Fundamentals, Models, Post-Deposition Processes and Applications

Journal of Materials Science: Materials in Electronics, Vol. 22, No. 1 (2011), pp. 40–46, ISSN 0957-4522

Ristenpart, W.D.; Aksay, I.A. & Saville, D.A. (2007). Electrically Driven Flow Near A Colloidal Particles Close To An Electrode With A Faradaic Current, Langmuir, Vol. 23, No. 7 (2007), pp. 4071-4080, ISSN 0743-7463

Santhanagopalan, S.; Teng, F. & Meng, D.D. (2010). High Voltage Electrophoretic Deposition For Vertically Aligned Forests Of One-Dimensional Nanoparticles, Langmuir, Vol. 27, No. 2, (2010), p. 561-569, ISSN 0743-7463

Santhanagopalan, S.; Teng, F. & Meng, D.D. (2010). High Voltage Electrophoretic Deposition For Vertically Aligned Forests Of One-Dimensional Nanoparticles, Langmuir, Vol. 27, No. 2, (2010), p. 561-569, ISSN 0743-7463

Santillán, M.J.; Quaranta, N.E. & Boccaccini, A.R. (2010). Titania And Titania-Silver Nanocomposite Coatings Grown By Electrophoretic Deposition From Aqueous Suspensions, Surface & Coatings Technology, Vol. 205, No. 7 (2010), p. 2562-2571, ISSN 0257-8972

Sarkar, P. & Nicholson, P. S. (1996). Electrophoretic Deposition (EPD): Mechanisms, Kinetics, and Application to Ceramics, Journal of The American Ceramic Society, Vol. 79, No. 8,(1996), pp. 1987-2002, ISSN 0002-7820

Shacham, R.; Mandler, D. & Avnir, D. (2004). Electrochemically Induced Sol-Gel Deposition Of Zirconia Thin Films, Chemistry - A European Journal, Vol. 10, No. 8 (2004), pp. 1936-1943, ISSN 0947-6539

Scherer, G.W. (1990). Theory of Drying, Journal of The American Ceramic Society, Vol. 73, No. 1 (1990), pp. 3-14, ISSN 0002-7820

Streckert, H.H.; Norton, K.P.; Katz, J.D. & Freim, J.O. (1997). Microwave Densification Of Electrophoretically Infiltrated Silicon Carbide Composite, Journal of Materials Science, Vol. 32, No. 24 (1997), pp. 6429-6433, ISSN 0022-2461

Tada, K. & Onoda M. (2011). Spontaneous Stratification In Composite Films Consisting Of Conjugated Polymers And Neat C_60 Prepared By Electrophoretic Deposition, Materials Letters, Vol. 65, No. 9 (2011), pp. 1367–1370, ISSN0167-577X

Tsai, H.-Y; Liu, H.-C.; Chen, J.-H. & Yeh, C.-C. (2011) Low Cost Fabrication Of Diamond Nano-Tips On Porous Anodic Alumina By Hot Filament Chemical Vapour Deposition And The Field Emission Effects, Nanotechnology, Vol. 22, No. 23 (2011), art. no. 235301 (5p), ISSN 0957-4484

Uchikoshi, T.; Suzuki, T.S.; Okuyama, H. & Sakka, Y. (2004). Fabrication Of Textured Alumina By Electrophoretic Deposition In A Strong Magnetic Field, Journal of Materials Science, Vol. 39, No. 3 (2004), pp. 861-865, ISSN 0022-2461

Uchikoshi, T.; Suzuki, T. S. & Sakka, Y. (2010) Fabrication Of C-Axis Oriented Zine Oxide By Electrophoretic Deposition In A Rotating Magnetic Field, Journal of the European Ceramic Society, Vol. 30, No. 5 (2010), pp. 1171–1175

Van der Biest, O. & Vandeperre, L.J. (1999). Electrophoretic Deposition of Materials, Annual Review Material Science, Vol. 29, (1999), pp.327-352, ISSN 0084-6600

Van der Biest, O.; Put, S.; Anné G. & Vleugels, J. (2004). Electrophoretic Deposition For Coatings and Free Standing Objects, Journal of Materials Science, Vol. 39, No. 3 (2004), pp. 779-785, ISSN 0022-2461

Vandeperre L.J. & Van der Biest, O. (1998). Electric Current And Electric Field for electrophoretic deposition from non-aqueous suspensions, In: Innovative Processing and synthesis of ceramics, glasses, and composites, Ed. Bansal N.P., Logan, K.V., Singh J.P., Ceramic Transaction, Vol 85 (1998), Westerville, OH, ISSN: 1042-1122
Wang, Z.; Shemilt J. & Xiao P. (2000a). Novel Fabrication Technique For The Production Of Ceramic/Ceramic And Metal/Ceramic Composite Coatings, *Scripta Materialia*, vol. 42, No. 7 (2000), pp. 653-659, ISSN 1359-6462

Wang, Z.; Xiao, P. & Shemilt J. (2000b). Fabrication Of Composite Coatings Using A Combination Of Electrochemical Methods And Reaction Bonding Process, *Journal of the European Ceramic Society*, Vol. 20, No. 10 (2000), pp. 1469-1473, ISSN 0955-2219

Wang, Z.; Shemilt J. & Xiao P. (2002). Fabrication of Ceramic Composite Coatings Using Electrophoretic Deposition, Reaction Bonding And Low Temperature Sintering, *Journal of The European Ceramic Society*, Vol. 22, No. 2 (2002), pp. 183-189, ISSN 0955-2219

Westby, W.A; Kooner, S.; Farries, P. M.; Boother, P. & Shatwell, R. A. (1999). Processing Of Nextel 720/Mullite Composition Composite Using Electrophoretic Deposition, *Journal of Materials Science*, Vol. 34, No. 20 (1999), pp. 5021-5031, ISSN 0022-2461

Xiao, X. F. & Liu, R.F. (2006). Effect Of Suspension Stability On Electrophoretic Deposition Of Hydroxyapatite Coatings, *Materials Letters*, Vol. 60, No. 21-22 (2006), pp. 2627-2632, ISSN 0167-577X

Yamaguchi, S.; Yabutsuka, T.; Hibino, M. & Yao, T. (2009). Development Of Novel Bioactive Composites By Electrophoretic Deposition, *Materials Science and Engineering C*, Vol. 29, No. 5 (2009), p. 1584-1588, ISSN 0928-4931

Yau, J.K.F. & Sorrell, C.C. (1997). High-$J_c$ (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$ Tapes Fabricates By Electrophoretic Deposition, *Physica C*, Vol. 282-287, Part 4 (1997), pp. 2563-2564, ISSN 0921-4534

You, C.; Jiang, D.; Tan, S. (2004) Deposition of Silicon Carbide/Titanium Carbide Laminar Ceramics by Electrophoresis and Densification by Spark Plasma Sintering, *Journal of The American Ceramic Society*, Vol. 87, No. 4,(2004), pp. 759-761, ISSN 0002-7820

Yui, T.; Mori,T.; Tsuchino,T.; Itoh,T.; Hattori, T.; Fukushima, Y. & Takagi, K. (2005) Synthesis of Photofunctional Titania Nanosheets by Electrophoretic Deposition, *Chemistry of Materials*, Vol. 17, No. 1 (2005), pp. 206-211, ISSN 0897-4756

Zhang, Y.A; Wu, C.X.; Lin, J.Y.; Lin, Z.X. & Guo, T.L. (2011). An Improved Planar-Gate Triode With CNTs Field Emitters By Electrophoretic Deposition, Applied Surface Science, Vol. 257 (2011), pp. 3259-3264, ISSN 0169-4332

Zhitomirsky, I. & Gal-Or, L. (1997). Electrophoretic Deposition Of Hydroxyapatite, *Journal of Materials Science: Materials in Medicine*, Vol. 8, No. 4 (1997), pp. 213-219, ISSN 0957-4530

Zhitomirsky, I. & Petric, A. (2000). Electrophoretic Deposition Of Ceramic Materials For Fuel Cell Applications, *Journal of the European Ceramic Society*, Vol. 20, No. 12 (2000), pp. 2055-2061, ISSN 0955-2219

Zhitomirsky, D.; Roether, J.A.; Boccaccini, A.R. & Zhitomirsky, I. (2009). Electrophoretic Deposition Of Bioactive Glass/Polymer Composite Coatings With And Without HA Nanoparticles Inclusions For Biomedical Applications, *Journal of Materials Processing Technology*, Vol. 209, No. 4 (2009), p. 1853-1860, ISSN 0924-0136
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