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Electrophoretic deposition of alumina on stainless steel from non-aqueous suspension

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Abstract Electrophoretic deposition of alumina on stainless steel has been investigated. The influence of different organic media and deposition parameters such as solid concentration, applied voltage and time of deposition on deposit yield has been evaluated. Maximum deposit yield was obtained for solvent media that imparts highest magnitude of surface charge on alumina in suspension. The deposit yield increased linearly with concentration of alumina powder in suspension, and applied voltage following Hamakers law. A similar linearity in yield was observed at short deposition times, but a deviation in linearity was observed at higher time of deposition, which is attributed to the shielding effect of the deposited layers and accumulation of ions at the electrode, and depletion of powder in the suspension with progress in deposition.

Introduction

Electrophoretic deposition (EPD) has been known since the beginning of the 19th century. But the first practical use of the techniques occurred in 1933 when the deposition of thoria particles on a platinum cathode as an emitter for electron tube application was patented in USA [1]. Although the basic phenomena involved in EPD are well known and have been the subject of extensive theoretical and experimental research, the EPD of ceramics was first studied by Hamaker [2] in 1940. In the beginning, the technique was adopted mainly in traditional ceramic technology [3] and only in the 80s did the process receive attention in the field of advanced ceramics not only because of the high versatility of its use with different materials and their combinations but also because of its cost-effectiveness requiring simple apparatus [4, 5]. There is general agreement in the scientific community that further R&D work needs to be done to develop a full, quantitative understanding of the fundamental mechanisms of EPD to optimise the working parameters for a broader use of EPD in materials processing. Some of the applications, in which EPD is being increasingly considered, include the fabrication of cathode and anode supported Solid Oxide Fuel Cells (SOFC), fiber-reinforced and graded ceramic composites, nano-structured materials as well as a variety of advanced film & coatings for electronics, biomedical, optical, catalytic and electrochemical application, fabrication of high quality fiber reinforced ceramic matrix composites, superconductors and micro laminated compositions [6–9].

Electrophoretic deposition is one of the colloidal processes in ceramic production and has the advantages of short formation time, little restriction of the shape of substrate, suitability for mass production and no requirement for binder burnout as the green coating contains few or no organics. In particular, despite being a wet process, EPD offers easy control of the thickness and morphology of a deposited film through simple adjustment of the deposition time and applied potential. In EPD, charged powder particles, dispersed or suspended in a liquid medium gets attracted and migrates towards an electrode of opposite charge and consequently gets deposited there under the influence of a DC electric field (electrophoresis), forming a relatively dense and homogeneously compact film.

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Since the mobility of the particles in an electric field is dependent on the surface charge, for electrophoretic deposition of larger particles, either a very strong surface charge must be obtained, or the electrical double layer region must increase in size. The charging mechanisms of particles in aqueous suspension are well understood and documented. Obviously, the use of water implies advantages such as higher temperature-control during the process or a faster kinetics, in addition to important health, environmental, and cost benefits. The water-based suspensions however, cause a number of problems in electrophoretic forming [10]. The main problems are related to electrochemical reaction in the electrodes when current is passed through, which seriously affects the efficiency of the process and the uniformity of the deposit. Secondly, the rate of deposition diminishes with time as the deposited layer increases [11]. Electrolysis of water occurs at low voltages, and gas evolution at the electrodes is inevitable at field strengths high enough to give reasonably good deposits. This causes bubbles to be trapped within the deposit unless special procedures are adopted, such as the use of absorbing or porous electrode materials, or high-speed chamber flows. Current densities are high, leading to Joule heating of the suspension, and electrochemical attack of the deposit. Secondly, when metallic electrodes are used, the normal potential of the electrode is largely over passed. This facilitates oxidation of the electrodes and migration of metallic impurities towards the slurry in the opposite direction to that of the migrating particles. In most cases, these impurities are retained in the deposit as heterogeneities and/or residual porosity, thus degrading its expected properties.

Therefore, in general, organic liquids are more popular and superior to water as a suspension medium for electrophoretic forming, because it eliminates the electrode reactions and gas evolution commonly encountered in aqueous suspension due to electrolysis of water on application of electric field [5, 12]. While the generally lower dielectric constant in organic liquids limits the charge on the particles as a result of the lower dissociating power, much higher field strengths can be used since the problems of electrolytic gas evolution, joule heating and electrochemical attack of the electrodes are greatly reduced or non-existent. Moreover, the organic liquids are preferred due to their higher density, good chemical stability and low conductivity. In EPD, the ionic concentration in the liquid must remain low; a condition favoured for low dielectric constant liquids, and is satisfied by organic liquids. Several other criteria are to be satisfied while selecting solvents for EPD suspension. Powder should be stable in the solvent (no reaction with the solvent, no agglomeration). Solvent should be able to generate charge on the surface of the powder (a high zeta-potential). There should be minimum charge carrier (ionic species) in the solvent. Current should be carried mostly by the suspended particles. The solvent should have low surface tension and evaporation rate to prevent cracking during drying.

So a proper selection of suitable solvent and optimisation of the operating parameters is necessary for obtaining deposition of desired thickness by EPD. Several authors have conducted electrophoretic deposition in a variety of different organic solvents. KrishnaRao and Subbarao [13] evaluated several organic solvents such as benzyl alcohol, amyl alcohol and dichloromethane on the basis of electrophoretic yield rate and uniformity of deposit of Magnesia (MgO) as a function of grinding time of suspension, voltage and time of deposition and electrode separation. They attributed the deposit yield to be dependent on dielectric constant of the solvent. No deposition occurred from suspension in low dielectric solvent like Dichloromethane. Powers [14] has shown that satisfactory deposit of β-alumina can be obtained only in solvents with dielectric constant in a limited range of 15–25. But, the principal driving force for electrophoretic mobility of particles is the surface charge/zeta potential in the suspension. Krishna Rao and Subbarao [13] did not evaluate the deposit yield with respect to surface charge of the particle. In the present investigation, we investigate and compare the deposit yield obtained by electrophoretic deposition in terms of direct measure of particle surface charge in each solvent with the objective of optimizing different operating parameters for obtaining desired deposit yield.

Experimentals

Materials

Alumina powder

The powder used for Electrophoretic deposition (EPD) was calcined alumina (Grade CT 1200SG) of particle size of 0.8–1.0 μm having surface area of 3.5–5.0 m^2/g and sintered density of 3.9 g/cm^3 supplied by Alcoa, India. The point of zero charge of the alumina in aqueous suspension was at a pH value of 9.1.

Solvent

Initially, three organic solvents and their mixtures were used for suspension preparation and deposition. The characteristic properties of the solvents are given in Table 1. After a preliminary screening based on deposition yield and quality in different solvents, we have selected butane-1-ol as our working solvent for detail optimisation studies.

Substrate

The deposition substrate for Electrophoretic deposition (EPD) is necessary to be electrically conductive. The substrate used as deposition electrode was a stainless steel strip of dimension 72 mm × 27 mm × 3 mm. A stainless steel strip of same dimension was used as the counter electrode. They were first ground with a coarse SiC paper and finally with fine SiC paper to remove any dirt and grease particles followed by washing with the respective EPD solvent prior to deposition.

Design and fabrication of electrophoretic deposition (EPD) set up

Although the equipment for electrophoretic deposition is simple, a number of features are needed to be taken into consideration during its design. The materials used in construction of the chamber must be selected carefully to avoid neutralisation of the charge on the suspended particles. It also must be stable in the solvent or its vapour during the deposition process. If the size of the particles is large and deposition times longer, then continuous agitation may be necessary to avoid gravitational settling. Agitation can be achieved by magnetic stirring or by continuous peristaltic pumping. The chamber geometry needs careful design to ensure a uniform electric field between the electrodes. The thickness profile of deposit can be influenced not only by the field distribution but also by the flow pattern of the suspension in the chamber. Figure 1 shows the schematic of a simple EPD set up designed and fabricated in our laboratory. It consists of two electrode holders made of Teflon & a supporting horizontal bar. The electrode holders are clamped on the lower side of the horizontal bar such that they are parallel and face each other. The chamber containing the suspension was made of silica glass.

Preparation of suspension

The first step in electrophoretic deposition is to prepare a stable, agglomerate-free colloidal suspension containing the ceramic particles. The ceramic particles are needed to be dispersed in a suitable solvent which can produce stable suspension as well as enhance deposition rate and produce homogeneous and crack free deposit. The suspension was prepared by adding the alumina powder into the solvent media and stirred by magnetic stirrer (REMI EQUIPMENTS) for 5 min followed by ultrasonication for 20 min by Vibronic Ultrasonic Processor (Model P2) at 200 V.

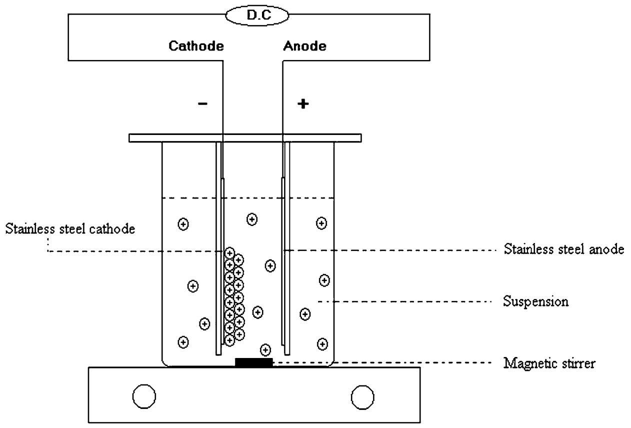

Fig. 1 A schematic diagram of the electrophoretic deposition setup

Measurement of surface charge

Measurements of surface charge on alumina suspended in different media were carried out using a particle charge detector (PCD-03-pH) of Muetek, Germany, as shown schematically in Fig. 2. It is based on the principle that colloidally soluble molecules or particle suspensions can carry electric charges when dissociable functional groups are found on their surface. As the diffuse cloud of counter-ions is sheared off the particles by the flow of liquid in the test cell, the so-called streaming potential is induced. By measuring the streaming potential, the PCD provides for quantitative estimation of the charge on the particles. When the measured streaming potential is exactly at 0 mV, the particle suspension is in a neutral state better known as isoelectric point (iep) or the point of zero charge (pzc). The existence of a measurable streaming potential denotes that the particle is either negatively or positively charged depending on the sign of the potential displayed.

The oscillating piston (4 Hz) forces the liquid to flow along the wall of the test cell so that a streaming potential is generated. Unless and otherwise mentioned, a suspension volume of 10 mL was taken in the test cell for each

Table 1 Physical properties of solvents at 25 °C

Solvents	Molecular weight	Molecular formula	Viscosity (cP) = 10^{-3} N s m^{-2}	Relative dielectric constant
Butan-1-ol	74.12	$CH_3(CH_2)_3OH$	2.5875	17.51
Isobutyl methyl ketone	100.16	$(CH_3)_2CHCH_2COCH_3$	0.58	13.11
Acetone	58.08	CH_3COCH_3	0.3087	20.7

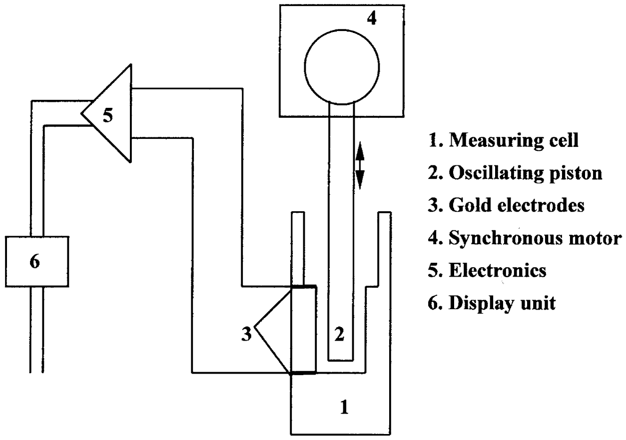

Fig. 2 Schematic diagram illustrating the assembly of PCD apparatus

measurement. The streaming potential as detected with the help of the two noble electrodes provided in the test cell is immediately shown on the LCD display. The magnitude of surface charge on alumina was determined by polyelectrolyte titration. In this method, a titrant of opposite charge is added in incremental concentration to the sample until the later reaches the point of zero charge (pzc) at which the streaming potential also becomes zero. The charge quantity was then calculated from the volume of titrant consumed. Sodium polyethylene sulphonate (PES-Na) and Poly-Diallyl-dimethyl-ammonium-chloride (Poly-DADMAC) of 0.001 N solutions were used as the standard anionic and cationic titrants, respectively, for the polyelectrolyte titration. The unknown specific charge quantity, q (in μ eq/g) on the alumina surface was calculated using the following equation [15]:

$$q = \frac{V \cdot c \cdot 1,000}{w}$$

where, V is the volume of titrant required in ml, c is the normality of the titrant (=0.001 N), 1,000 is a calculation factor for the unit of charge density and w is the amount of solid present in the suspension in gm. The total quantity of charge (in Coulomb/g) was then obtained by multiplying the specific charge (in eq/g) with the Faraday constant (=96,485 Coulomb/eq). The surface charge measured using the PCD was within an error of ±2.0%.

Deposition procedure

The electrodes were mounted on the electrode holders such that they face each other and were connected to DC terminal of desired polarity. Unless otherwise mentioned, the electrode spacing was maintained constant at 1.5 cm. The holder along with the electrodes was dipped into the reservoir (glass beaker) containing the suspension. Sedimentation of the particles was prevented by slow stirring by a magnetic bead stirrer as shown in the Fig. 1. EPD experiments were carried out at constant voltage varying in the range from 150 V to 300 V using a DC power supply unit (TARSON Model) with a deposition time from 2 min to 20 min. The positively charged particles get deposited on the cathode. After deposition the electrodes were carefully taken out and the deposits were allowed to dry at room temperature for 24 h. The deposits along with the substrate were then weighed to determine the yield. The influence of different processing parameters was studied to maximise deposition yield.

Results and discussion

Charge characteristics of alumina in suspension

For aqueous suspensions of ceramic powders, especially oxides, the role of protons as charge determining ions has been clearly established in literature. Yates et al. [16] proposed the following description of the interaction of surfaces of oxides with the liquid through simple ionisation reactions of surface groups:

$$\mathrm{S-OH \rightarrow S-O^{-} + H^{+}}$$

$$\mathrm{S-OH_2^{+} \rightarrow S-OH + H^{+}}$$

Later, the description was improved to account for the reaction of major electrolyte ions with ionisable surface sites. The net charge as evident by the above reactions, is controlled by pH and reaction constant for the respective dissociation reaction. The point of zero charge (pzc) is the pH value where the surface concentration of ($\mathrm{S-O^{-}}$) and ($\mathrm{S-OH_2^{+}}$) are equal. The surface charge is negative at $\mathrm{pH > pH_{pzc}}$ and positive at $\mathrm{pH < pH_{pzc}}$.

But the hydrogen ion concentration (pH) looses its validity as a general measure for the acidity or alkalinity in non-aqueous media. Therefore, we have first measured the surface charge in aqueous suspension in order to have a general idea about the point of zero charge (pzc) of alumina. Figure 3 presents the surface charge of alumina in aqueous suspension as a function of pH. Alumina suspension for surface charge measurement was prepared by suspending alumina powder in Millipore milli-Q deionised water with a conductivity of about 0.05 µS/cm, followed by magnetic stirring and equilibration at room temperature for 12 h. Figure 3 clearly show that alumina exhibits pzc at a pH value of 9.1. At lower pH, below the pzc, the alumina surface is positively charged and vice versa. From the sign of surface charge, it can be deduced that deposition on application of an electric field in the pH range below pzc will happen on cathode whereas anodic deposition will occur in the higher pH ranges above pzc.

However, in non-aqueous media, representation of surface charge is not so straightforward. It has been shown by Labib and Williams [17] that in the absence of water, the sign of the charge on the surface of ceramic powders depend on the donor number of the solvent (the tendency of the solvent to donate electrons) strongly suggesting that charging is possible through electron exchange with the solvent. The magnitude of specific surface charge of alumina measured in different organic solvents is presented in Table 2. In each of the solvent used, the surface of alumina has been found to be positively charged. Hence, a cathodic electrophoretic deposition is expected.

Deposition characteristics

Effect of solvent

To determine the influence of solvent, deposition experiments were carried out from 20 wt% alumina suspension in several organic solvents at 250 V and deposition time of 5 min. The solvents used were isobutyl methyl ketone, acetone, butan-1-ol, mixture of acetone and butan-1-ol (1:1 ratio). Since the alumina is positively charged in each solvent, deposition occurred on cathode. A typical photograph of alumina deposit obtained on stainless steel substrate by EPD from butan-1-ol at 250 V for 5 min is shown in Fig. 4. The results on deposit yield from each suspension are presented in Table 3.

The deposition behaviour differed greatly from suspension in different solvents. It was very difficult to obtain any deposit from suspension iso-butyl methyl ketone because the suspension became unstable within 30 s. To keep the alumina particles in suspension, a mild magnetic stirring was done, but no deposit could be formed. In case of acetone we obtained a thin deposition of 0.2951 mg/cm^2 from 20 wt% suspension by applying voltage of 250 V for 5 min. The suspension in acetone also became unstable after few minutes but it was comparatively more stable than iso-butyl methyl ketone. Comparatively, under the same deposition condition, a much better deposit yield (1.8099 mg/cm^2) was obtained in case of mixture of acetone and butan-1-ol (1:1 ratio). Highest deposit yields (5.7887 mg/cm^2) were obtained in the case of alumina suspension in butan-1-ol under same condition. Therefore, subsequently butane-1-ol was used as the medium for detail optimisation studies.

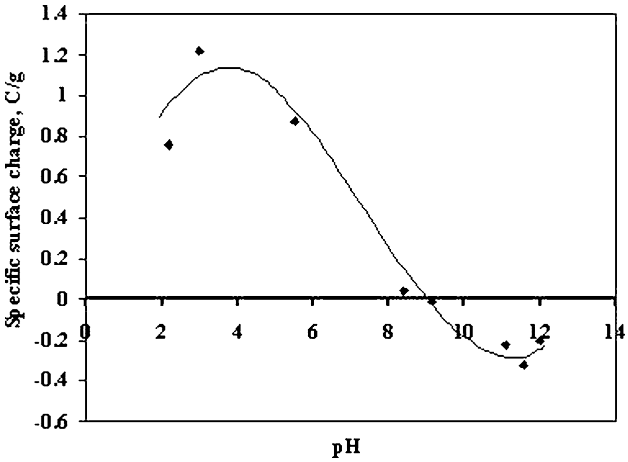

Fig. 3 Effect of pH on the specific surface charge of alumina in aqueous (Millipore milli-Q deionised water) suspension

The reason for poor deposition in the case of iso butyl methyl ketone but highest deposit yield for butan-1-ol can be explained from the magnitude of charge on the alumina particles in different solvents. The surface charge data of alumina in different solvents are also presented in Table 1. It clearly shows lowest surface charge of 0.1668 C/g in iso butyl methyl ketone and highest surface charge (0.5367 C/g) in butan-1-ol. On account of high surface charge, the electrophoretic mobility in butan-1-ol is expected to be high compared to iso butyl methyl ketone for which the deposit yield is also very high in butan-1-ol. The surface charge of alumina in acetone and 1:1 mixture of acetone and butan-1-ol was in between iso butyl methyl ketone and butan-1-ol. Accordingly, the deposit yield was also in between those two solvents. Our observations are not completely in line with the hypothesis forwarded by Gonzalez-Cuenca et al. [18] who proposed by equations derived from first principle (i.e. Maxwell equation for electrostatics) that deposits with uniform thickness (i.e. smooth surface) can result during EPD when the permittivity of particle ε_p is less than permittivity of liquid ε_L ($\varepsilon_p < \varepsilon_L$). In addition, it suggested that any slight variation in deposit thickness will result in an extremely rough surface, with particles only depositing on the highest peaks which may lead to collapse of the deposit as the particles drips off the electrode. Since, the permittivity (dielecetric constant) of each of the solvents used in the present investigation (Table 1) are more than the permittivity of alumina ($\varepsilon_p = 9.34$) [19], smooth deposit is expected from each of them. However, best

Table 2 Specific surface charge of alumina in different organic solvents

Solvent	Surface charge (C/g)
Iso butyl methyl ketone	+0.1668
Acetone	+0.2054
Acetone + butan-1-ol (1:1)	+0.3243
Butan-1-ol	+0.5367

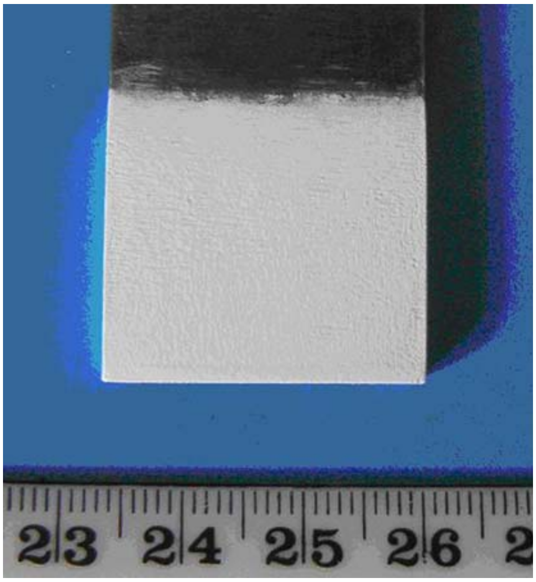

Fig. 4 Photograph of alumina deposited on stainless steel from its suspension (20 wt%) in butan-1-ol at 250 V, 5 min

quality (i.e. most smooth) deposit and hence maximum deposit will be obtained from alumina suspension in acetone because it has the highest permittivity/dielectric constant value from among all the solvents used in this investigation (Table 1). Our observations do not completely obey this rule. This may be because their hypothesis was advocated based on the assumption that the charge is zero in the entire system. On the other hand the EPD system in the present investigation contains charged alumina particles. Since, we observed maximum deposit yield from system with highest magnitude of surface charge, it indicates that the influence of surface charge is more dominant than permittivity in the EPD process.

Effect of suspension concentration

The yield of alumina films electrophoretically deposited on stainless steel substrate with varying concentration of suspension (10–30 wt%) in butan-1-ol deposited at a constant applied voltage of 250 V for 5 min is shown in Fig. 5.

The EPD yield is low at lower solid concentration and high at higher solid concentration. The increase in EPD yield of alumina and with increasing concentration of suspension is linear and in accordance with the following equation which is a solution of a differential equation (obtained from Hamaker's equation), according to which the weight (w) of charged particles deposited per unit area of electrode in the initial period, ignoring the charge carried by the free ions is [20, 21]:

$$w = \frac{2}{3} C \varepsilon_o \varepsilon_r \xi \left(\frac{1}{\eta}\right)\left(\frac{E}{L}\right) t \tag{1}$$

In the above equation, C is the suspension concentration, ε_o is the permittivity of vacuum, ε_r is the relative permittivity of the solvent, ξ is the zeta potential of the particles, η is the viscosity of the solvent, E is the applied potential, L is the distance between the electrodes and t is the deposition time. The above equations, suggests that the deposition weight of the charged particles under ideal electrophoretic deposition depends on a variety of parameters. However, since the factors ξ, ε_r, η and L in the above equation are constants, for a given solvent, particle and apparatus, the weight of the deposited particles (w) in the EPD method is a function of E, t and C. Therefore, the mass of the deposited particles can be readily controlled by the concentration of the suspension, applied potential, and deposition time in the EPD method.

In the present case, higher EPD yield could be achieved when the suspension concentration was high. However, the surface morphology of deposited film made from the higher suspension concentration was less smooth compared to those obtained from the lower concentration suspension. This may possibly be because of the high deposition rates at higher concentrations at which the particles do not get sufficient time to sit at closest possible packing positions before deposition of incoming particles.

Table 3 Effect of solvent on deposit yield by EPD from 20 wt% suspension at 250 V for 5 min deposition time

Solvent	Deposition (mg/cm^2)
Iso butyl methyl ketone	No deposition
Acetone	0.2951
Acetone + butan-1-ol (1:1)	1.8099
Butan-1-ol	5.7887

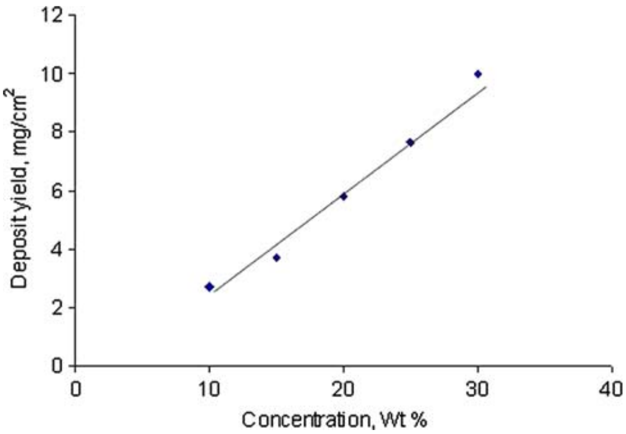

Fig. 5 Deposit yield of alumina on stainless steel substrate at 250 V, 5 min from a suspension in butan-1-ol with increasing concentration

Effect of applied voltage

The EPD yield of alumina film by varying voltage (150–300 V) for 30-wt% suspensions in butan-1-ol, deposited for 5 min again followed similar trend as predicted by the solution of Eq. 1 and is shown in Fig. 6. The amount of deposition was found to increase linearly with increase in applied voltage.

Effect of deposition time

The deposition yield of alumina film with varying deposition time (2–20 min) from 30-wt% suspension in butan-1-ol at a constant applied voltage of 250 V is shown in Fig. 7. It is apparent from the Fig. 7 that the deposition yield of alumina increases with increasing time. But in contrast to the linear prediction of deposit yield with time from Eq. 1, a non-linear increase in deposit has occurred right after start of the experiment. Such deviation from linearity is possible in a constant voltage EPD because of several factors. The most commonly attributed factor is that due to shielding effect of the electrically resistive deposited layer and accumulation of ions at the electrode [22–24]. The deposited layers can act as insulating layer thereby decreasing deposition rate. It is also suggested that a decrease in deposition can result due to the depletion of powder from the suspension with the progress of deposition [18, 25]. In addition, as the thickness of deposit increased at high deposition times, the adhesion of deposit to the substrate deteriorated. This was more significant at very high deposition times of 45 min and 1 h at which the deposits tend to fall off the substrate while taking it out from the suspension and thus making it extremely difficult to collect yield data. Studies on use of binders to improve adhesion to the substrate for thick film deposition are under progress and will be communicated in our future communications.

The non-linearity of deposit growth with time has been modelled by several authors [12, 18, 24, 26] who have also attributed the decrease in deposit growth rate with time to the resistance of the deposit and to depletion of the suspension. But these models err with respect to the Kynch theory since they were based on the assumption that the volumetric particle concentration in the suspension (ϕ_s) is much lower than deposit packing factor (ϕ_d) which is equal to unity minus porosity ($\phi_s << \phi_d$). In addition, they also assumed that neither the particle mobility (μ) nor the suspension volume (V) change in time. The model developed by Gonzalez-Cuenca et al. [18] tried to relate the resistance to the more fundamental properties such as permittivity of particle and liquid and system geometry. The numerical model and explicit equations developed by Gonzalez-Cuenca et al. [18] produced moderate fit at low zeta potential of 4.45 mV and seemingly very large electrode surface area of 520 cm^2. Much better fit could be obtained for high zeta potential value of 56 mV and more reasonable electrode surface area of 84 cm^2. The better fit in the later case was because the suspension concentration and final deposit thickness was extremely low. It will be of interest to investigate and develop models for suspensions with high solids loading considering the dilution effect of the suspension during deposition for better fit of the experimental data from any suspension.

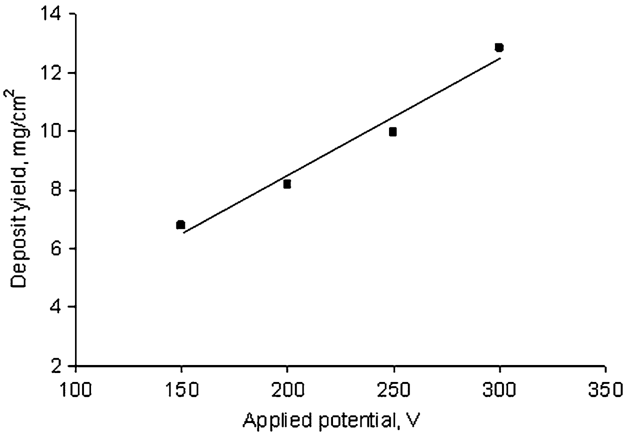

Fig. 6 EPD yield of alumina on stainless steel from 30 wt% suspension in butan-1-ol with varying applied voltage [deposition time = 5 min]

Conclusion

The broad objective of this investigation was to choose a suitable medium to obtain maximum deposition of alumina on stainless steel substrate by Electrophoretic deposition

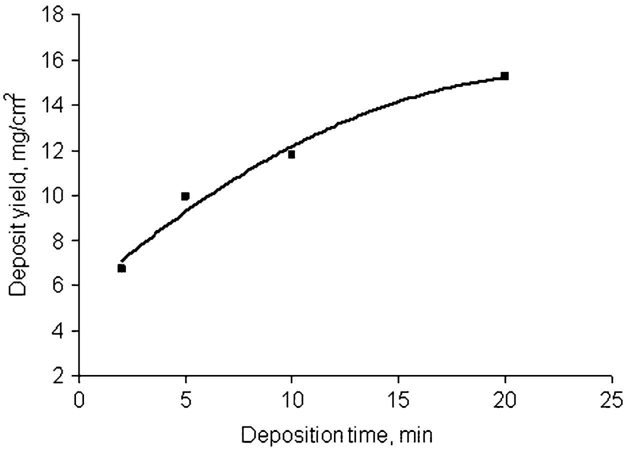

Fig. 7 EPD yield of alumina deposited films against various time of deposition. [The deposit increases but is non-linear in nature. The curve fitting the data points is only a guide to the eye]

(EPD). Another objective was to study the influence of different operating parameters such as solid concentration, applied voltage and deposition time to obtain maximum deposit yield. The following conclusions can be drawn based on the results obtained in the investigation:

i. It has been found that success of EPD from a suspension depend on the magnitude of surface charge developed on alumina particles in the media. A higher magnitude of surface charge enabled in obtaining a high deposition yield and vice versa.
ii. No deposition was possible from a suspension in isobutyl methyl ketone in which the magnitude of alumina surface charge and stability of suspension was very low.
iii. In the range of present investigation, there is a linear increase in deposit yield with increasing concentration of alumina in suspension, and applied voltage following solution of the Hamaker's equation.
iv. The deposit yield was found to increase with time. But a non-linear increase in deposit yield was observed right after start of the experiment. This is due to two primary reasons: (a) because of the shielding effect of the deposited layers and accumulation of ions at the electrode, and (b) because of the depletion of powder from the suspension with increasing deposition time. At deposition times beyond 45 min, the adhesion of deposit to the substrate was found to be poor.

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