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Suspension medium’s impact on the EPD of nano-YSZ on Fecralloy

O. Khanali∗†, M. Rajabi ‡1, S. Baghshahi‡1 and S. Ariaee‡2†

Electrophoretic deposition (EPD) was employed to coat yttria-stabilised zirconia (YSZ) on Fecralloy. Various non-aqueous solvents were utilised to achieve smooth crack-free YSZ coatings. The EPD parameters, including solvent type, sedimentation height, zeta potential, particle size, pH and deposition weight, were studied. The micro-structural evolution and mechanical properties of the coatings were studied by the field emission scanning electron microscopy and micro-hardness, respectively. It was found that coatings obtained from 0.4 g L⁻¹ I₂ acetyl-acetone were uniform, smooth and crack free. Also they had narrow particle size distributions and higher zeta potential in the suspension. The experimental results revealed that suspension stability was a requirement for obtaining high-quality coatings and deposition yield for stable suspensions was higher; however, particle coagulation resulted in coatings with low green density and poor sinter ability. A transition in deposition mechanism from linear to parabolic was observed during EPD where deposition rate was decreased by time.
Introduction

Thermal barrier coatings (TBCs) are widely used in gas turbines and aircrafts in order to protect the components, such as vanes and blades, from harsh environments and high temperatures during their service. The most common TBCs consist of a zirconium oxide that is partially stabilised by the addition of an appropriate amount of yttrium oxide which has a low thermal conductivity and a high thermal expansion coefficient close to that of the super alloys. Plasma spraying or electron beam vapour deposition techniques are of great interest and importance in achieving this type of TBCs. Although several technical processes were developed in order to obtain this type of ceramic coatings, many of them require expensive equipment and complicated process control. Electro-phoretic deposition (EPD) process, on the other hand, has some exceptional advantages which distinguish it as one of the promising coating methods. Also its compatibility for large-scale coatings of simple pieces and ability to be employed for some complex and near net-shape pieces (with accurate dimensions both for micro- and nano-structure) draw significant technical attention to EPD.

Aqueous mediums electrolyse in relatively low applied electric fields and release \( \text{H}_2 \) gas during the process. Accordingly, using them as aqueous solvents for suspension preparation in EPD has a limitation. Therefore, non-aqueous mediums can be used to serve as the suspensions in EPD. Besra and Liu reported that the stability of particles in the suspension has a great influence on the quality of the coatings. The stability of the particles in non-aqueous solvent is much lower than that of water. Xiao and Liu reported some advantages of the usage of tri-ethanolamine as the dispersant agent for giving better stability for the suspension of hydroxide apatite (HA) nanoparticles in butanol for EPD. In an investigation by Fengqiu et al., it was concluded that pHs of 8–11 affect the agglomeration of zirconia particles in aqueous suspensions owing to hydrogen bonding. Aruna and Rajam utilised iodine as an additive to charge YSZ particles in the EPD of the coating in a mixture of acetone (AC) and ethanol (ET) solvents.

Essentially, EPD is a two-step process. First, particles are deflocculated in a solvent to be forced and moved on the electrode surface by applying an electric field to the suspension. Second, particles are collected on cathode and uniformly deposited on the surface. Recently, several reports have been published on the EPD process. However, they gave little attention to the kinetics of the deposition in it. So, there is an absence of a thorough understanding of the mechanism up to now. The charging mechanism in non-aqueous suspensions is a subtle process which depends on the physical parameters of the solvent, such as zeta potential, pH, type of dispersed particles, conduction, dielectric coefficient, viscosity, boiling point and also vapour pressure.

Kinetics models are of essence in better understanding of the deposition process. Figure 1 shows a schematic view of the model proposed by the present authors.

Potential drop \( (V_a) \) in a EPD cell consisting of two flat surface electrodes is given by the following equation:

\[
V_a = \Delta V_{c1} + I_1. R_0. d_1 + I_1. R_s. (d - d_1) + \Delta V_{c2}
\]

where \( \Delta V_{c1} \) and \( \Delta V_{c2} \) are the potential drops of the cathode/working electrode (WE) and anode/counter electrode (CE) in volts, respectively; \( I \) is the electrical current in Amperes; \( R_0 \) and \( R_s \) are the electrical resistance per unit length of the deposit and the suspension (in Ohm/meter), respectively, \( d \) is the electrode distance (in metre) and \( d_1 \) is the thickness of the deposit. Electrical field \( (E) \) in the suspension can be shown by the following equation:

\[
E = \frac{\Delta V_{c1} + I_1. R_0. d_1 + I_1. R_s. (d - d_1) + \Delta V_{c2}}{d}
\]

The potential drops in each of the electrodes can be negligible, and it can be assumed that the specific resistance of the cell in the same order as of the suspension. The fundamental driving force for EPD is the charges on the surfaces of particles and the mobility of particles in the suspension and investigation on the motion of these particles provides very useful information about EPD.
The mobility of particles can be considered by Henry equation (equation (3)) where electrophoretic mobility ($\mu$) depends on the zeta potential of the particles, constant dielectric and the viscosity of the solution:\(^{21}\)

$$\mu = \frac{2\varepsilon_0\varepsilon\zeta}{3\eta f(\kappa r)}$$  \hspace{1cm} (3)

where $\varepsilon$ is the dielectric constant of the suspending medium, $\varepsilon_0$ is the vacuum dielectric permittivity (F m$^{-1}$), $\zeta$ is the zeta potential (V), $\eta$ is the viscosity of the liquid (Pa s) and $f(\kappa r)$ is Henry coefficient, which relates the thickness of the double layer to the radius of the suspended particle in suspensions. For a situation where the double layer is thin in comparison with the particle size, it can be approximated as equation (4):\(^{22}\)

$$\mu = \frac{\varepsilon \varepsilon_0 \zeta}{3\eta}$$  \hspace{1cm} (4)

The kinetics of EPD can be studied by employing several formulas. The most simple model describing the kinetics of EPD is known as the Hamaker model (equation (5)):\(^{23,24}\)

$$m(t) = C_0 \mu S E t$$  \hspace{1cm} (5)

Another model by Sakar and Nicholson (equation (6)) considered the decrease in the solid loading with time: \(^{25}\)

$$m(t) = m_0 (1 - e^{-t/\tau}), \quad \tau = \frac{\nu \mu S E}{m_0}$$  \hspace{1cm} (6)

Moreover, Ferrari et al.\(^{26}\) (equation (7)) considered the linear relationship of the suspension resistivity and solid loading and their variation with time: \(^{26}\)

$$m(t) = m_0 \left(1 - \frac{1}{1 + \frac{\rho m_0}{\rho_{S,\infty}} (e^{t/\tau} - 1)}\right)$$  \hspace{1cm} (7)

The sticking factor represents the percentage of the depositing particles among the total arrived particles to the work electrode by electrophoresis.\(^{29}\)

### Materials, characterisation and methods

YSZ powder (3YSZ > 99%, from Jiaozuo Huasu Chemical Co., Ltd, China) was used as the coating material. Figure 2 shows the morphology and the XRD pattern of the tetragonal powders.

The average particle size is about 50 nm. Acetone (AC > 99%, Merck, Germany), acetyl acetone (ACAC > 99%, Merck, Germany) and ethanol (Et-OH > 99%, Merck, Germany). Table 1 lists common formulas that were proposed by different authors. Further explanation of this subject is beyond the scope of the present study.\(^{28}\)

### Table 1 Summary of kinetic formulas and experimental expressions

<table>
<thead>
<tr>
<th>Ref</th>
<th>Authors</th>
<th>Kinetic milestones</th>
<th>Models or experimental expressions</th>
<th>Equation no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[24]</td>
<td>Hamaker</td>
<td>Basic equation</td>
<td>$m(t) = C_0 \mu S E t$</td>
<td>5</td>
</tr>
<tr>
<td>[25]</td>
<td>Sarkar and Nicholson</td>
<td>Considering the decrease of solid loading with time</td>
<td>$m(t) = m_0 (1 - e^{-t/\tau}), \quad \tau = \frac{\nu \mu S E}{m_0}$</td>
<td>6</td>
</tr>
<tr>
<td>[26]</td>
<td>Anne and et al.</td>
<td>Considering suspension resistivity variation with time</td>
<td>$m(t) = m_0 \left(1 - \frac{1}{1 + \frac{\rho m_0}{\rho_{S,\infty}} (e^{t/\tau} - 1)}\right)$</td>
<td>7</td>
</tr>
<tr>
<td>[27]</td>
<td>Ferrari et al.</td>
<td>Considering the linear relationship of the suspension resistivity and solid loading</td>
<td>$m(t) = m_0 \left(1 - \frac{1}{1 + \frac{\rho m_0}{\rho_{S,\infty}} (e^{t/\tau} - 1)}\right)$</td>
<td>8</td>
</tr>
</tbody>
</table>

$m_0$: initial mass of powder in suspension (g); $\tau$: characteristic time (s); $V$: volume of the suspension considered constant (cm$^3$); $f$: sticking factor ($0 < f < 1$); $E$: applied electric field strength; $I$: current intensity (A); $C_s$: suspension concentration (g cm$^{-3}$); $\mu$: electrophoretic mobility (cm$^2$ s$^{-1}$ V$^{-1}$); $S$: deposition area (cm$^2$); $t$:deposition time (s); $\rho$:suspension resistivity variation (Ω cm).

The sticking factor represents the percentage of the depositing particles among the total arrived particles to the work electrode by electrophoresis.\(^{29}\)
Germany) were used as solvents. Iodine (Merck, Germany) was added to adjust the particle surface charge in suspensions. Three suspensions were prepared using 25 g L\(^{-1}\) of dispersed YSZ powder in each solvent and iodine was added as dispersant. Table 2 summarises starting conditions of the prepared suspensions.

0.08 g L\(^{-1}\) Fe\(_2\)O\(_3\) was added to the solution as the sintering aid.\(^{30-32}\) Suspensions were stirred by a magnetic stirrer apparatus for 30 min in order to de-agglomerate the particles. Then, they were sonicated for 30 min by an ultrasonic probe (35 kHz). EPD process was conducted utilising a constant DC current. Particle size measurements and zeta potential determination of the suspensions were evaluated by means of electrophoretic light scattering technique (via Zeta seizer 3000 HAS, Malvern Instruments Ltd, UK). The EPD process was performed in a (50 mL) cell with two vertically located electrodes of Fecralloy and stainless steel sheets (25 × 10 × 2.5 mm\(^3\)). Fecralloy substrate sheet composition was (Fe72.8wt-%, Cr22wt-%, Al5wt-%, Y0.1wt-%, Zr0.1wt-%). Distance between the electrodes was fixed at 200 mm. After EPD, the samples were slowly dried at room temperature for 24 h in order to eliminate the organic solvent. Then, they were sintered at 1150°C for 5 h in a furnace (heating rate \(= 2^\circ\text{C min}^{-1}\)). Surface morphology evaluation was done using FE-SEM (XL30 Philips, Netherlands). The XRD pattern analysis was performed to all 3 YSZ powders. The micro-hardness results were obtained using Vickers micro-hardness tester. The measurements were carried out under the load of 100N (=1000 g) for 10 s on the top of the each surface of the coatings. Three samples were analysed for each deposition condition and five hardness measurements were taken for each of the samples and the averages were reported.

### Result and discussion

#### Characterisation of the suspensions

Iodine was added to YSZ particles in non-aqueous solvents in order to create positive charges (protons) on the particle surfaces. Figure 3 shows pH of the suspensions as a function of iodine concentration in non-aqueous solvents. It can be seen that increasing iodine content results in lower pHs. The changes were almost in linear mode. The positive charging of YSZ particles is attributed to H\(^+\) ions which were produced in the suspension by the reaction of iodine with AC, ACAC and ET:

\[
\text{CH}_3\text{COCH}_3 + 2\text{I}_2 \rightleftharpoons \text{ICH}_2\text{COCH}_2\text{I} + 2\text{H}^+ + 2\text{I}^- \quad (9)
\]
It can be seen that the zeta potential for AC and ACAC is relatively higher than that of ET. Proton (H⁺) adsorption on particle surfaces causes higher zeta potentials which, in turn, led to well-dispersed suspension. With 0.4 g L⁻¹ I₂ concentration, ACAC-based suspension has the maximum zeta potential. Hence, this suspension is the optimised one for the EPD process compared to ET and AC. Figure 5 illustrates particle size distributions of ACAC, AC and ET solutions.

Their particle size ranges from 30 to 400, 120 to 2000 and 250 to 7000 nm for ACAC, AC and ET, respectively. The ACAC suspension containing 0.4 g L⁻¹ I₂ has a finer and a narrower particle size distribution in comparison to the others. Figure 6 illustrates relative sedimentation heights (R.S.H = ratio of the sediment height to the whole suspension height) of the suspension as a function of time for ACAC, AC and ET (with 25 g L⁻¹ YSZ and 0.4 g L⁻¹ I₂).

Suspension heights were measured by optical methods utilising 100 mL cylinders after being settled for 200 h (Fig. 6). R.S.H ratios of cylinders were measured about %3.32, %37.64 and %89.41 for ACAC, AC and ET, respectively. It was obvious that sediment volume of ACAC was much lower than those of the others, which, in turn, indicates that the ACAC is a better solvent because of enhancing the suspension stability.

**EPD process**

For acidic suspensions, deposition takes place on the cathode. Figure 7 shows the schematic model proposed by the authors for the EPD mechanism of the YSZ particle charged by adsorbing H⁺, while released H⁺ ions can lead to H₂ gas formation.

During the formation of the deposit, when the particles become closer to each other, with increasing attraction forces, they tend to agglomerate. If the particles are high surface charged ones, they will repel each other during the deposition and by occupying their positions, high
particle packing density is achieved. On the contrary, if the particles are low surface charged ones, they will agglomerate even for relatively large interparticle distances which, in turn, can lead to porous, sponge-like deposits.\textsuperscript{17} Based on zeta potential data, more cracks are expected for the suspension based on ET than the other ones, while ACAC-based one has the least crack content expectancy.\textsuperscript{38,39} As seen in equation (4), increasing zeta potential and dielectric constant of the solution causes an increase in the mobility and the stability of the particles. The evaluations of the results are shown in Table 3.

Dielectric constants of these liquids follow the order: ACAC > ET > AC; therefore, AC has the lowest dielectric constant due to a lower polarity and intermolecular forces. Also, according to equation (4), increasing suspension viscosity causes a reduction in electrophoretic particle mobility, because the viscous fluid decreases the motion of the particles. The values shown in Table 3 compare the electrophoretic mobility of the particles in various solutions. The electrophoretic mobility of YSZ particles in ET, ACAC and AC was 409, 1164 and 7762 \( (10^{-7} \text{m}^2 \text{V}^{-1} \text{s}^{-1}) \), respectively. Electrophoretic mobility in AC is higher than the others due to its lower viscosity. As a result, it is expected that AC containing suspension has a higher speed of coating. The relation between the current density (mA cm\(^{-2}\)) and EPD time (s) is shown in Fig. 8.

For all cases, current density decreases with time. ACAC diminishes less than the others. In the case of AC, its starting current density was higher than the others. This phenomenon can be attributed to high electrophoretic mobility in AC suspension. The drift velocity of charged particles in AC is higher than that of others. The AC curve also has much more fluctuations, because with the continuation of the process, deposit is segregated and deposited particles fill the formed vacancies and the repetition of this leads to the turbulence in current density.\textsuperscript{40} Moreover, possible current agitation and severe collisions of the particles can form larger masses of deposits on the electrode surface.\textsuperscript{41} Experimental and calculated values of the deposition weight with time are plotted in Fig. 9.

Figure 9 shows that the calculated data fit well with the experimental values at least for low deposition times; however, they fail to fit accurately for higher deposition times. The slope of the experimental curves changes and the deposition rate starts to diminish after 55, 45 and 20 min for ACAC, AC and ET, respectively. After 100 min, the yields of deposited weights were 0.66, 0.60 and 0.15 wt.% for ACAC, AC and ET, respectively. High deposition mass could not be obtained because gravity made some of the particles fall and settle down at the bottom of the container. High mobility of the particles in suspensions led to rapid deposition on the substrate and created pores and cracks in the coatings. However, the coatings were found to be smooth at low current densities and became rougher with an increase in it.\textsuperscript{42} Also cracks were produced in higher applied current densities and deposition rates.\textsuperscript{43}

### Table 3  Some properties of as-prepared YSZ suspensions

<table>
<thead>
<tr>
<th>Solution Characters</th>
<th>AC</th>
<th>ACAC</th>
<th>ET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C(_3)H(_6)O</td>
<td>C(_3)H(_6)O(_2)</td>
<td>C(_2)H(_6)O</td>
</tr>
<tr>
<td>Zeta potential (\zeta) (mV)</td>
<td>40</td>
<td>45</td>
<td>18</td>
</tr>
<tr>
<td>Pure solution conductivity ((\mu\text{cm}))</td>
<td>0.305</td>
<td>1</td>
<td>4.25</td>
</tr>
<tr>
<td>Suspension conductivity ((\mu\text{cm}))</td>
<td>57.9</td>
<td>31.2</td>
<td>19.3</td>
</tr>
<tr>
<td>pH of suspension contained</td>
<td>1.68</td>
<td>1.98</td>
<td>3.91</td>
</tr>
<tr>
<td>(I_0) and nanoparticles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution viscosity ((\times 10^{-3}) Ns\text{m}^{-2})</td>
<td>0.3</td>
<td>1.09</td>
<td>1.088</td>
</tr>
<tr>
<td>Vapour pressure of solution (kPa)</td>
<td>24</td>
<td>0.8</td>
<td>5.8</td>
</tr>
<tr>
<td>Constant dielectric permittivity (F m(^{-1}))</td>
<td>20.7</td>
<td>25.7</td>
<td>24.3</td>
</tr>
<tr>
<td>Electrophoretic mobility ((10^{-7} \text{s}^2 \text{m}^{-1} \text{V}^{-1}))</td>
<td>7762</td>
<td>1164</td>
<td>409</td>
</tr>
</tbody>
</table>

**Morphology and hardness of YSZ coating**

Figure 10 shows FE-SEM images of the surface morphology of the YSZ films on Fecralloy substrate before and after sintering.

![Figure 9](image-url)  
Relation between current density and time for different solutions at the constant electric potential of 50 V
Deposition weight in 50 V as a function of time for a ACAC, b AC, b ET

FE-SEM images of YSZ film using three suspensions containing a ACAC, b AC and c ET before and after sintering
11 Micro-hardness values of the coatings

Figure 10a shows homogeneously packed YSZ deposits before sintering. Also it can be seen that, in the case of ACAC, the post-sintered coatings were uniform, smooth and without any crack. Poorly packed coatings were resulted from AC and ET suspensions, where the post-sintered ones were non-uniform and rough with vivid cracks resulted from AC and ET suspensions, where the post-sintered coatings were uniform, smooth and without any crack. Poorly packed coatings were caused by lower sediment volume and enhanced suspension stability.

The average hardness was 1.907, 1.187 and 0.96 GPa for ACAC, AC and ET, respectively. It can be seen that there is an apparent connection between the qualities of the coatings with the obtained micro-hardness values. A relatively large scatterband of the hardness data is also expected for the suspension based on ET than ACAC, the post-sintered coatings were uniform, smooth and without any crack. Poorly packed coatings were resulted from AC and ET suspensions, where the post-sintered ones were non-uniform and rough with vivid cracks resulted from AC and ET suspensions, where the post-sintered coatings were uniform, smooth and without any crack. Poorly packed coatings were caused by lower sediment volume and enhanced suspension stability.

Conclusions

YSZ deposits were coated on Fecralloy by EPD. Conclusions are the followings:

(i) Electrophoretic mobility of nano-YSZ particles in ET, ACAC and AC was 409, 1164 and 7762 (10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}), respectively. Electrophoretic mobility in AC was higher due to its lower viscosity.

(ii) R.S.H ratios were measured %3.32, %37.64 and %89.41 for ACAC, AC and ET, respectively. So, ACAC was considered as the best solvent due to lower sediment volume and enhanced suspension stability.

(iii) 0.4 g L^{-1}iodine additions caused a controlled destabilisation of the particles in suspensions. In the case, zeta potentials of the YSZ nanoparticles in the suspensions were higher and the suspensions had finer and narrower particle size distributions. Particle size ranged from 30 to 400, 120 to 2000 and 250 to 7000 nm for ACAC, AC and ET, respectively. Hence, more cracks were expected for the suspension based on ET than the others, while ACAC-based one had the least crack content expectancy.

(iv) Deposition rates started to diminish after 55, 45 and 20 min for ACAC, AC and ET, respectively. After 100 min, the yields of deposited weights were 0.66, 0.60 and 0.15 wt-% for ACAC, AC and ET, respectively.

(v) Micro-structural studies suggested that ACAC suspension produced the most reproducible and homogeneously packed films without significant post-sintering cracks. However, poorly packed green deposits resulted from large agglomerates formed in AC and ET suspensions were recognised as the responsible factor in the generation of large cracks during sintering.

(vi) The average hardness was measured 1.907, 1.187 and 0.96 GPa for ACAC, AC and ET, respectively.

References


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