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Abstract—ElectroHydroDynamic Atomization (EHDA) is a physical process of liquid dispersion to fine droplets by electrical force and shear stress on the liquid surface. Under these forces, the jet at a capillary nozzle outlet elongates and breaks up into fine droplets at its end. EHDA technique allows production of micron-sized droplets, which can be used for the deposition of thin solid films on substrate. Because the droplets are electrically charged, they disperse uniformly within the space between the nozzle and the substrate that facilitates thin and uniform film deposition. Film morphology can be controlled, to some extent, via controlling charge and size of the droplets, by steering the flow rate of the liquid and voltage applied to the nozzle, and also substrate temperature. Thin solid film can be produced from a solution or colloidal suspension of deposited material after solvent evaporation or from a precursor after chemical reactions occurring at the substrate. By changing the kind of liquid and operational parameters of EHDA system, nanocomposite film can be deposited by a simple way. The paper discusses practical aspects of the applications of EHDA to thin film deposition.

Keywords-ElectroHydroDynamic Atomization, electrospraying, thin film deposition

I. INTRODUCTION

ElectroHydroDynamic Atomization (EHDA, also electrohydrodynamic spraying or electrospraying) is a physical process of liquid atomization due to electric forces and stresses on liquid jet flowing from a capillary nozzle. The process is usually accomplished by maintaining the nozzle at high electric potential. The electric field causes the liquid to form a conical meniscus and the shear stress expels fine liquid jet from the apex of this meniscus. Due to mechanical instabilities and electrostatic repulsion, this jet disperses into fine droplets at its end [1]-[3]. EHDA technique allows production micron-sized droplets, which can be used for the deposition of thin solid film on a substrate [4], [5]. Thin solid film can be produced from a solution or colloidal suspension of deposited material, after solvent evaporation, or from a precursor, after chemical reactions occurring at the substrate or in the aerosol phase. Films produced by EHDA are homogeneous and composed of small agglomerates built of particles smaller than 1 μ m, which are the particles of dry powder used for preparing suspension, or crystallites smaller than 1 μ m, resulting from precursor decomposition.

Due to many advantages over other physical or chemical methods, EHDA has successfully been used for thin film deposition in many areas. One of these advantages is that all droplets are of nearly the same size and can be controlled within the range from tens of nanometer to tens of micrometers via adjusting capillary voltage (usually in the range from 5 kV to about 25 kV) and liquid flow rate (typically in the range from 0.1 to 10 ml/h). The electric charge on the droplets causes that they are self-dispersing in the interelectrode space due to their mutual Coulomb repulsion, resulting in more uniform distribution on the substrate, that facilitates deposition

of thin and even film, and at the same time, their deposition efficiency on the substrate is higher than for uncharged spray. EHDA can be considered as simple, flexible and cheap "ondemand" technology. "On-demand", in this case, means that the properties of deposited film, for example, its density, porosity, crystallinity, or morphology, can be tailored to some extent by proper selection of process parameters such as liquid flow rate, capillary voltage, capillary-substrate distance, nozzle diameter, substrate temperature, precursor and solvent used, and also electrosprayed liquid properties: surface tension, electric conductivity, viscosity, mass density and permittivity.

When viscosity of liquid is higher than a certain critical value, the jet does not disperse into droplets but continues to move off the nozzle forming a long nanofiber. Such a process is called electrospinning. Both of these processes used simultaneously allow formation of nanocomposite films or materials.

The present paper reviews the practical aspects of applications of EHDA for thin film deposition.

II. EHDA THEORETICAL BACKGROUND

The volume density of bulk electrodynamic force (\vec{F}_e) on a fragment of liquid jet is proportional to the resultant electric field \vec{E} at this point:

$$\vec{L}_l = \rho_q \vec{E} + \frac{1}{2} \left[\vec{D} \nabla^T \vec{E} - \vec{E} \nabla^T \vec{D} \right]$$
(1)

where: ρ_q is the local volume charge density, \vec{D} is the electric flux density, and \vec{E} is the electric field due to the voltage on capillary nozzle and space charge of previously emitted droplets.

Electrodynamic stress tensor results from a dyadic product of surface charge density vector (\vec{q}) at the liquid-air interface and local electric field (\vec{E}) , and from the stresses caused by difference in liquid and gas permittivities:

$$\underline{\underline{\Lambda}}_{l} = \vec{q} \otimes \vec{E} + \underline{\underline{I}} * \frac{1}{2} \left[\vec{D} (\vec{E}_{l} - \vec{E}_{g}) - \vec{E} (\vec{D}_{l} - \vec{D}_{g}) \right]$$
(2)

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Presented at the 2014 International Symposium on Electrohydrodynamics (ISEHD 2014), in June 2014



Fig. 1. Stresses and forces on the electrohydrodynamic liquid jet (a). Photograph of cone-jet mode of EHDA (b) (MgO suspension in methanol, electrode distance: 20 mm, voltage 5.1 kV, flow rate 20 mL/h).

These active bulk forces and stresses are in dynamic equilibrium with inertial, viscose and differential pressure forces opposing jet deformation, and are given by the following equations (cf. schematic in Fig. 1):

$$\frac{\partial \rho_{l} \vec{v}_{l}}{\partial t} = \rho_{l} \vec{g} + \vec{L}_{l} - \vec{\Phi}_{St} - \nabla \cdot \left(\underline{\underline{\Pi}}_{\Delta p} + \underline{\underline{\Pi}}_{\eta} + \underline{\underline{\Pi}}_{\rho} \right) (3)$$

$$\nabla \times \underline{\underline{\Xi}} = \underline{\underline{\Pi}}_{\Delta p} + \underline{\underline{\Pi}}_{\eta} + \underline{\underline{\Pi}}_{\rho} + \underline{\underline{\Lambda}}_{l} \tag{4}$$

where $\underline{\Xi}_{i}$ is the stress tensor due to liquid surface tension.

Stress tensor due to pressure difference on both sides of liquid boundary surface is:

$$\underline{\underline{\Pi}}_{\Delta p} = \underline{\underline{I}} \left(p_l - p_g \right) \tag{5}$$

Stress tensor due to dynamic viscosity of liquid is proportional to the gradient of liquid velocity perpendicular to the interphase surface:

$$\underline{\Pi}_{n} = \eta_{l} \nabla \vec{v}_{l} \tag{6}$$

Stress tensor due to inertia of flowing liquid is proportional to the dyadic product of local liquid velocity at the interphase surface:

$$\underline{\underline{\Pi}}_{o} = \rho_{i} \vec{v}_{l} \otimes \vec{v}_{l} \tag{7}$$

The drag force $(\vec{\Phi}_{St})$ due to the motion of liquid jet in air depends on the air viscosity (η_g) , but general form of equation describing this process is unknown. In these equations ρ_l , η_l and σ_l are the mass density, viscosity and surface tension of the liquid, respectively.

For water liquid jet electrosprayed in cone-jet mode, the electric field distribution has been determined using a commercial code COMSOL 3.5 (Fig. 2). Mesh creation was performed using the built-in mesh generator, which produced 1.22×10^6 elements. In the vicinity of high-curvature surfaces tetrahedral volume elements were generated. Physical properties of air, water and stainless steel forming the boundary surfaces were taken from COMSOL material library. Gas ionization and field generated by charged droplets were neglected in these simulations.

Fig. 3 presents distribution of electric field component normal to the liquid surface along liquid meniscus and jet.



Fig. 2. Magnitude of electric field distribution on the cone and jet.



Fig. 3. Normal component of electric field along the jet surface for highly conducting liquid (water).

The highest magnitude of electric field is at the tip of the jet. The Maxwell stress due to this electric field causes stretching the jet downwards.

Mode of electrospraying plays a crucial role in the quality of thin solid film. Many modes of spraying have been reported in the literature [1]–[3], [6]–[14], however, for the process of thin film deposition, cone-jet and multijet modes are the most preferable. By cone-jet mode, the liquid meniscus assumes the form of regular, axisymmetric cone with a thin jet, < 100 μ m in diameter, at its apex. The jet disperses to fine droplets due to varicose or kink instabilities. By multi-jet mode, several skewed cones are regularly distributed at the rim of capillary nozzle. From each cone, a jet thinner than in the case of conejet mode (< 10 μ m) issues. The droplets are much smaller than those produced by cone-jet mode.

The size of droplets generated in cone-jet mode depends on liquid physical properties and liquid flow rate following the equation [15], [16]:

$$d = \alpha \left(\frac{Q^{\frac{3}{2}} \varepsilon_0^{\frac{1}{2}} \rho_l^{\frac{1}{2}}}{\sigma_l^{\frac{1}{2}} \kappa_l^{\frac{1}{2}}} \right)^{\frac{1}{3}}$$
(8)

where κ_l is the liquid conductivity. The constant α depends on liquid permittivity.

Similar scaling laws were formulated by Fernandez de la Mora and Loscertales [17], [18], Hartman et al. [19], Lopez-Herrera et al. [20] and Barrero et al. [21]. Eq. (8) does not take into consideration liquid viscosity because, in certain range, the droplet size only weakly depends on this parameter [22]. For liquids of high viscosity more energy is required to drive the liquid from meniscus, and, therefore, the droplets are generated with lower frequency than for liquids of low viscosity [23]. The size of capillary also has an effect on droplet diameter. Similar model for multi-jet mode has been developed by Yoon et al. [24] and for pulsed drop generation by Chen et al. [25]. From Eq. (8) results that droplet size can be decreased via decreasing liquid flow rate and increasing liquid conductivity or surface tension.

The dependence of droplet diameter on the voltage at capillary nozzle is given by the following equation [26]

$$d(U) = d_0 \left(1 - \left(\frac{U}{U_{crit}}\right)^2 \right)^{\frac{1}{3}}$$
(9)

where d_0 is droplet diameter for U = 0, and U_{crit} is the critical voltage at which the cone-jet mode of spraying becomes unstable.

III. EHDA DEPOSITION SYSTEM

Thin solid films are produced from solution or colloidal suspension of a film material or from a precursor. When a solution or suspension is used, the solid film is obtained after solvent evaporation without chemical reactions. When a precursor is electrosprayed, it decomposes at high temperatures in the aerosol phase or on the substrate, or due to chemical reactions with additional gaseous agent, and a product of decomposition of the precursor is forming the film. Metal chlorides, nitrates, or acetates dissolved in water, methanol, ethanol, or their mixtures, or metal-organic salts dissolved in organic solvents are usually used as precursors [5]. Chlorides are of low cost, good solubility in ethanol, but are corrosive. Nitrates are also of low cost but less soluble in ethanol than chlorides. Metal-organic salts are more costly than chlorides and nitrates but are of high solubility in organic solvents [27].

EHDA system usually comprises of stainless steel or quartz glass capillary nozzle faced at a substrate. The substrate is usually electrically heated in order to facilitate solvent evaporation or promote chemical reactions, in the case a precursor is used. Schematic showing two EHDA methods of thin film deposition is shown in Fig. 4. The distance between the nozzle tip and the collector is typically between 10 mm and 50 mm, and the voltage ranges from 5 to 25 kV of positive polarity. AC up to kHz superimposed on DC voltage is frequently also used in order to stabilize cone-jet mode of spraying.

EHDA is also used for nanocomposite film deposition, i.e., film composed of nano-sized, chemically non-reacting components (nanoparticles, nanofibers) differing in mechanical, electrical, thermal, physical and chemical properties, which have bulk properties different from their building blocks. Nanocomposite film is produced either by simultaneous or



Fig. 4. EHDA systems for thin film deposition; left: from a solution or suspension, right: from a precursor.



Fig. 5. EHDA system for two-step nanocomposite thin film deposition.

consecutive spraying or spinning of two or more materials onto a substrate [5], [28], or by using two co-axial nozzles [29]–[31]. Schematic of such a process is shown in Fig. 5.

IV. EHDA-DEPOSITED FILM PROPERTIES

Formation of thin solid film from charged-aerosol phase is a complex and multi-step process. First, the liquid jet is dispersed to fine droplets, which flow towards the substrate under gravitational and electrostatic forces. During the droplets flow, solvent evaporates and the solution or suspension densifies (Fig. 4). When droplet approaches the substrate, the evaporation/condensation processes become more intense due to higher gas temperature close to the heated substrate. When a solution or colloidal suspension is electrosprayed, semidry particles impact on the substrate and next they solidify or crystallize forming solid film. In case a precursor is sprayed, the semidry particles or condensed solution impinge the substrate, where the precursor is decomposed, and the products of these reactions are forming the film. These processes can proceed via various paths depending on time the droplet remains in the space between capillary nozzle and the substrate, the temperature gradient in this space, the boiling point of solvent used for EHDA, and the substrate temperature.

Film morphology and its quality depend on evaporation, solidification and crystallization processes or on precursor decomposition, size of droplets and resulting particles, gas and substrate temperature, precursor or suspension flow rate, time of droplet flight to the substrate, deposition time, and the rate of solvent evaporation from the substrate. Some of these parameters can be controlled by varying voltage, flow rate, solvent chemical composition, concentration of deposited



Fig. 6. Morphology of thin films produced by electrospraying: dense (a), porous (b) [32].



Fig. 7. Examples of various structures of EHDA deposited films: crystalline $CaCO_3$ (a), fractal-like Al_2O_3 (b), grainy Al_2O_3 (c), reticular TiO_2 (d).

material, distance between spray nozzle and substrate, and substrate heating.

Depending on electrospray conditions, dense or porous films can be formed (Fig. 6). Dense film can be amorphous (homogeneous or with crystalline intrusions) or crystalline (monoor polycrystalline). Porous films can have various structures: reticular (cells confined by nanowalls), grainy (separate packed grains), or fractal-like (dendrites formed by crystallites or particles). Examples of those structures are shown in Fig. 7. Sometimes, the fractal-like structures assume a regular form, resembling flower, and such structures are called flower-like (Fig. 8).

For longer time of deposition, couple of hours, film morphology changes with the film height as an effect of changing evaporation and solidification conditions during the film growth [33]–[38]. This effect is caused by the fact that only the first layer of a thickness of tens of nanometers has direct contact with heated substrate. The droplets, which are further landing, impinge onto the layers deposited previously, but the contact angle is different from that on the substrate, and the temperature of the surface of layer is also lower than the previous one that slows down the evaporation process. Due to different contact angles, spreading of the droplets is also different and the morphology of the new layers changes.

An example of such effect is schematically illustrated in



Fig. 8. Flower-like structure of Al₂O₃ on stainless steel.



Fig. 9. Film morphology evolution with increasing time of deposition [32].

Fig. 9. After a time of deposition t_1 , the film remaining in direct contact with the substrate is dense due to small contact angle and fast spreading of the liquid over the substrate. In the time interval $t_2 - t_1$, porous reticular structure grows as an effect of high contact angle of precursor solution to the first layer that facilitates cage-like structure formation. Because surface becomes uneven with many protrusions, the electric field deforms, and points of small radius and higher electric field become centers of preferential landing for the incident droplets [33]. As an effect, fractal-like structure is growing. The preferential landing is the dominant mechanism when the droplets are nearly dry or completely dried and the droplet cannot spread over the surface to fill the pores between dendrites [39].

Increased flow rate of liquid can facilitate formation of more dense and smooth surface because larger droplets are difficult to evaporate, and they can spread over the surface filling the pores. However, if the surface is too wet, cracks and voids can occur on it because of layer shrinkage during solvent evaporation. The number and size of voids, flaws, and cracks in the film are smaller for finer particles of narrow size distribution.

To obtain good adhesion of a film to substrate, semidry particles should land on the substrate and spread on it. This occurs when the substrate temperature is slightly higher than the boiling point of solvent, and the evaporation rate of solvent at the surface is equal to the deposition rate of droplets [40]–[43]. For too low temperature, only droplets splash on the substrate, but solvent evaporates too slow and the film is dense but cracked due to mechanical stresses. At too high temperatures, solvent completely evaporates from droplets before they reach the substrate, and only dry solid particles are deposited, which very weakly adhere to the substrate [27], [34], [35], [42].

Porous, for example, fractal-like structure is also formed when colloidal suspension or solute of low solubility is



Fig. 10. Process of thin film formation from evaporating droplet for various contact angles: (a) $\theta < 90^{\circ}$, (b) $\theta > 90^{\circ}$.

sprayed. In the later case, the solute can crystallize and precipitate within the droplet due to solvent evaporation in aerosol phase, and after impingement of such droplet onto the substrate, these fine crystallites cannot be spread over the surface before ultimate drying [27].

The rate of solvent evaporation can be tuned by using a mixture of two liquids of various boiling points, for example, a mixture of ethanol and butyl carbitol, or ethanol and glycol [35], [36]. Liquid of lower boiling point evaporates faster that makes the droplet smaller and the concentration of precursor or solute increases. The remaining solvent of higher boiling point still constitutes the droplet, which can be spread on the surface after impingement, forming a dense amorphous film. After the impingement, this solvent evaporates at higher temperature, and only solid film of low porosity remains on the substrate.

Film morphology depends also on substrate material, i.e. on the contact angle to the solvent and differences in surface energy of the substrate, which also depends on substrate temperature. The contact angle between the droplet and the substrate is:

$$\cos\theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{lg}} \tag{10}$$

where σ is a surface tension, and the indices *s*, *l*, *g* refer to solid, liquid and gas phases, respectively. The effect of contact angle on thin film formation is schematically illustrated in Fig. 10.

For substrates of high surface energy, $\theta < 90^{\circ}$ ($0 < \cos \theta < 1$), surface is easily wet and entirely covered with solvent in a short time, and next evaporates quickly. The thickness of liquid film is smaller at the circumference of spread droplet than in the middle, and the local temperature of liquid increases faster causing faster solvent evaporation that initiates nucleation and precipitation processes of the solute. The liquid flows from the middle towards the edge of spread droplet, and solute concentration increases at the edge. After complete evaporation of the solvent, thick ring-deposit remains at the edge of splash and thin layer in-between. Topography of such a film is shown in Fig. 11(a).

For substrates of low surface energy, $\theta > 90^{\circ}$ (-1 < $\cos \theta < 0$), surface is not completely wet, and each droplet evaporates independently. The temperature is higher at the

Fig. 11. Effect of contact angle on film morphology. MgO in methanol (0.6%) on stainless steel (a), Ag on Al (precursor: $AgNO_3 20\%$ in water+methanol 1:1 by vol.).

point of contact of droplet with the substrate, and solvent evaporates in this point leading to nucleation process of the solute. The solution circulates from the contact point upwards, and returns downwards alongside the droplet surface due to temperature gradient in the droplet. The circulating liquid bears the crystallites upwards. As a result, large agglomerates with free space between them are formed (Fig. 11(b)). For low solute concentration also a cage-like round particles with many voids can be formed after complete solvent evaporation.

The droplet size has also an effect on properties of the film due to different dynamic processes of solvent evaporation during droplet flight and different times of spreading over the substrate. The time of spreading of droplets generated by EHDA ranges from 10 μ s to 1 ms [44]. Spreading of large droplet is faster than its heating and boiling, whereas small droplet evaporates almost immediately during its spreading.

Decreasing the surface tension of solvent by the addition of low surface tension agent (for example, poly(ethylene) glycol), results in breaking the spread droplet onto a number of smaller droplets and finer morphology of the film is obtained.

V. SUMMARY

It was shown in this paper that EHDA allows the production of thin solid film, which can be crack-free and more homogeneous than those obtained by other methods. The process is simple, cheap, flexible, and easy to control. Compared to other methods such as chemical vapor deposition (CVD) or physical vapor deposition (PVD), the growth rate is relatively high. The EHDA process can be carried out in ambient atmosphere, in air or other gas, and at low temperature, without the need for complex reactors and high-vacuum systems. EHDA method is also a very efficient because at least 80-90% of base material can be deposited onto the substrate. The production rate of particles of the size of 10 μ m is of the order of magnitudes of 10^5 do 10^4 #/s or 10^{10} do 10^{11} #/s for particles of 10 nm.

This technique can be applied for the production of thin solid films and nanocomposite materials or materials having on-demand properties, or as a low-cost tool for composing small and complex structures via spray forming or direct writing.

ACKNOWLEDGMENT

is The paper supported by the Project No. 2011/03/B/ST8/05643 "The elaboration of coatings of heat resistant properties deposited be means of electrohydrodynamic method" financed by Polish National Science Center.

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