

3D aerosol printing technology for filled polyaluminosilicates

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Abstract. Dispersed Al₂O₃ powders with differently distributed particle sizes have been obtained. The most suitable sizes of the dispersed powders for aerosol generation by a pneumatic method have been determined. Viscosity, pH, and Zeta potential of suspensions with different Al₂O₃ concentrations have been studied. The effect of pH, dispersion, and concentration on the suspension viscosity, which affects the ability of aerosol formation in the processes to obtain polyaluminosilicate sol systems (a highly dispersed filler powder), has been determined. Ceramic coatings for printed circuit boards have been obtained by 3D aerosol printing.

1. Introduction

Additive technologies (the technologies to apply materials by 2D and 3D printing) are actively gaining popularity during the past decade. This is caused by the wide capabilities of this technology. Previously manufacturing of devices and products from numerous small parts without their assembling has been unattainable due to the limitations of existing technologies. In addition to new methods to manufacture products, the additive technologies allow obtaining the parts that cannot be manufactured by other methods. If one approaches this subject from the point of view of waste, this technology is practically wasteless in most cases, since all the material immediately falls into its intended place without a surplus.

Aerosol printing is one of 3D printing trends. There is a need to manufacture the parts on the micro and nanoscale in industry, namely in microelectronics and medicine, for example, capacitive and resistive sensors of small thickness, multilayer ceramic printed circuit boards, miniature heating elements, scalpels for neurosurgery, etc. The standard methods to manufacture printed circuit boards do not always provide the required accuracy with low material waste. In some cases these methods cannot be applied at all. Also the traditional methods to apply dielectric and conducting coatings and topologies such as paint and varnish technologies, roller rolling, screen printing, photolithography, milling, laser cutting with a focused ion beam do not always allow obtaining the coatings and topologies necessary to solve technological and design problems in the development and manufacture of microelectronic and medical products and devices. Moreover, the above mentioned methods cannot be used to apply coatings and layers on an already manufactured part or device [1]. Such tasks are successfully implemented by means of 3D aerosol printing technology. Aerosol printing is the cost-effective technology due to the relatively low cost of equipment and virtual absence of material overspending, especially if piece production is required.

Ink-jet printing eliminates many problems encountered when printing layers and topologies on complex-shaped parts. These technologies accelerate manufacturing of a part and then of a device and eliminate the problem of excessive material consumption. The additive printing methods also suit better



for manufacturing parts of a larger area in comparison with the commonly used methods. Thus, 3D printing allows manufacturing printed circuit boards of a large size, antennae, capacitive and resistive sensors, photoelectric and optoelectronic devices and appliances, LEDs, and 3D structures with a high aspect ratio and a printing definition up to 0.5 μm . A printing definition of 0.5 μm clearly shows the importance of 3D printing methods to develop the electronic and medical industries [1].

The 3D aerosol printing method based on additive production of coatings, layers, elements, and interconnects based on dielectric and conducting materials has been chosen in this study. The smallest droplets of the material are applied by an aerodynamically focused jet on a three-dimensional base selectively, and masks are not used. The advantages of 3D aerosol printing are in greater freedom in product design, production flexibility, absence of tooling costs (stencils, templates), and less adverse environmental impact in comparison with the other methods of additive printing, photolithography, and other methods to apply coatings and topologies [1].

Currently, aerosol printers produced by Optomec and Neotech AMT companies are the most available. However, the need to adapt or synthesize new materials is increasingly urgent because sharply large demand for reliability and durability is placed on microelectronic products and devices in the modern industry. Using only the modern 3D printing methods to manufacture layers and topologies is impossible without developing new dielectric and conducting composite materials that specify the necessary physicochemical, thermophysical, and structural properties of end products and microelectronic and medical devices due to the unique opportunity to form structural elements with the phase composition peculiarities.

Thus, to solve the problem of developing new composite materials is only possible with the use of the:

- modern methods to synthesize polymer binders;
- methods to obtain dispersed filler powders;
- modern methods to study material properties.

The research objective is to develop the additive technology for 3D aerosol printing of the ceramic layers of printed circuit boards applied to the polyaluminosilicates containing micro and nanoparticles of the dispersed powders of metal oxides and nitrides.

2. Experiment

The basis of the method to apply a composite material based on the filled polyaluminosilicate by 3D aerosol printing is to obtain an aerosol from it, i.e. a suspension containing finely dispersed powder particles that are suspended in a solvent. According to the research results, the most preferable method is a pneumatic method as an aerosol generator, which allows working with highly viscous materials without destroying the supramolecular structure of the polymer binder, i.e. polyaluminosilicate.

The precipitation of dispersed powder particles and their low concentration is the main problem of the suspension manufacturing. It is necessary to know the dependence of viscosity on temperature, pH, concentration, and Zeta potential to ensure the suspension optimal characteristics, namely high concentration at low viscosity.

Stability is the most important parameter for aerosol printing. The aerosol stability, in its turn, depends on the physicochemical properties of a dispersed filler (the powders based on Al_2O_3 have been studied in this case) and on the polyaluminosilicate physicochemical properties.

One of the problems that arise in the manufacturing of the suspension from the dispersed powders of metal oxides and nitrides is that both the area between the particles of the solid phase and liquid carrier and the number of particles in the given volume significantly increase with the particle size decreasing. This leads to the strong physicochemical interaction between solid particles in the liquid phase and consequently results in the viscosity increase.

The elemental and phase composition of the particles, their size, shape, and Zeta potential are the main parameters of the particles that allow characterizing them in the liquid phase.

One of the ways to increase the stability of the dispersed filler based on Al_2O_3 is to reduce its particle size. However, the problem that arises by the sol manufacturing based on polyaluminosilicate and

smaller Al_2O_3 ceramic powders is that both the boundary area between the particles of the solid phase and a liquid carrier and the number of particles in this volume increase significantly. This leads to the strong physicochemical interaction between the solid particles in the liquid phase and reduces workability, especially by aerosol generating. Therefore, one can expect that the need to reduce the loading volumes in the sol may counteract the advantage of the smaller particles. The shape of the particles also plays an important role, since the sol viscosity strongly depends on the shape.

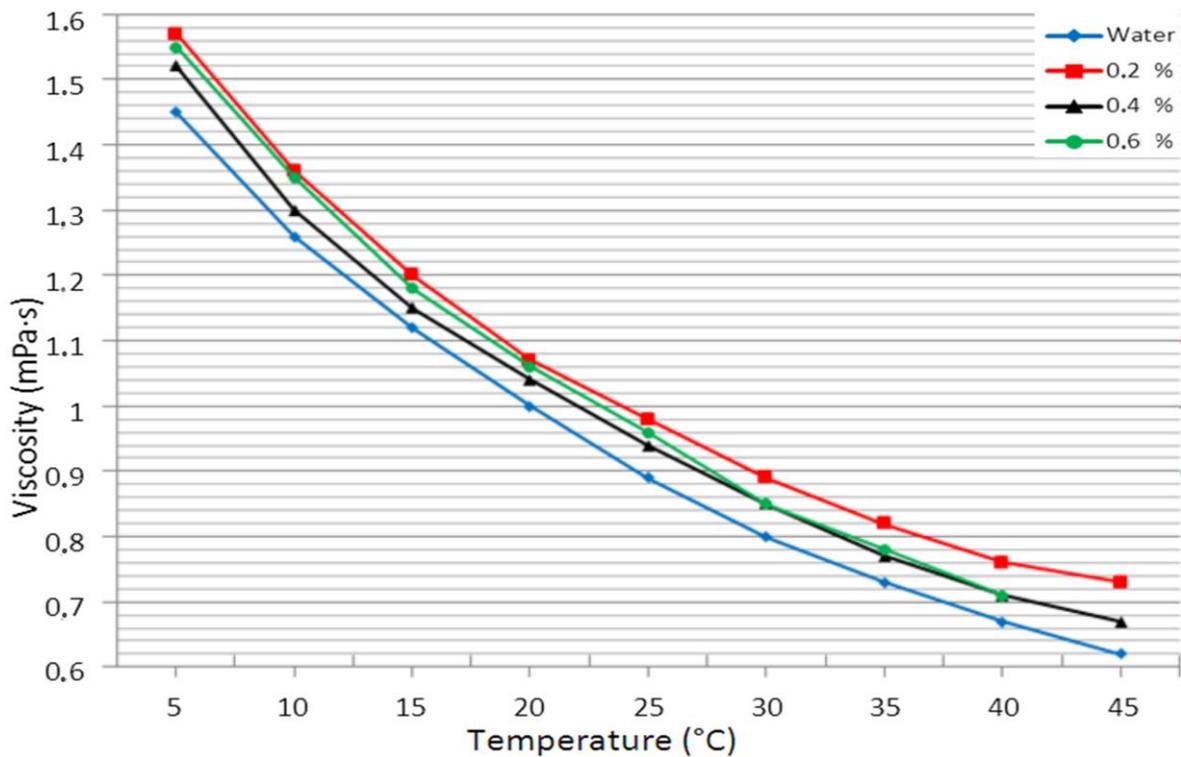


Figure 1. Diagram of viscosity dependence on suspensions temperatures with different Al_2O_3 concentrations

A series of viscosity measurements of the suspensions with different dispersed powder concentrations has been carried out. Al_2O_3 has been chosen as a dispersed powder for the research. Figure 2 shows its particles distribution according to the size. The suspension viscosities (Figure 1) have been measured at various possible operating temperatures by the AND-SV-10 device and Julabo thermostat (Innovative and technological research and educational center of the National Research Tomsk State University, Tomsk, Lenin Avenue, 36.).

The diagram shows (Figure 2) that the suspension viscosity increases sharply with the concentration increase from 0% to 0.2%. The viscosity decreases with a further increase in concentration from 0.2% to 0.4%, but it is still higher than the distilled water viscosity. An increase in the suspension viscosity relatively to 0.4% concentration is observed with an increase in concentration up to 0.6%. This trend can be explained by the fact that the suspension pH and Zeta potential change with an increase in the substance concentration.

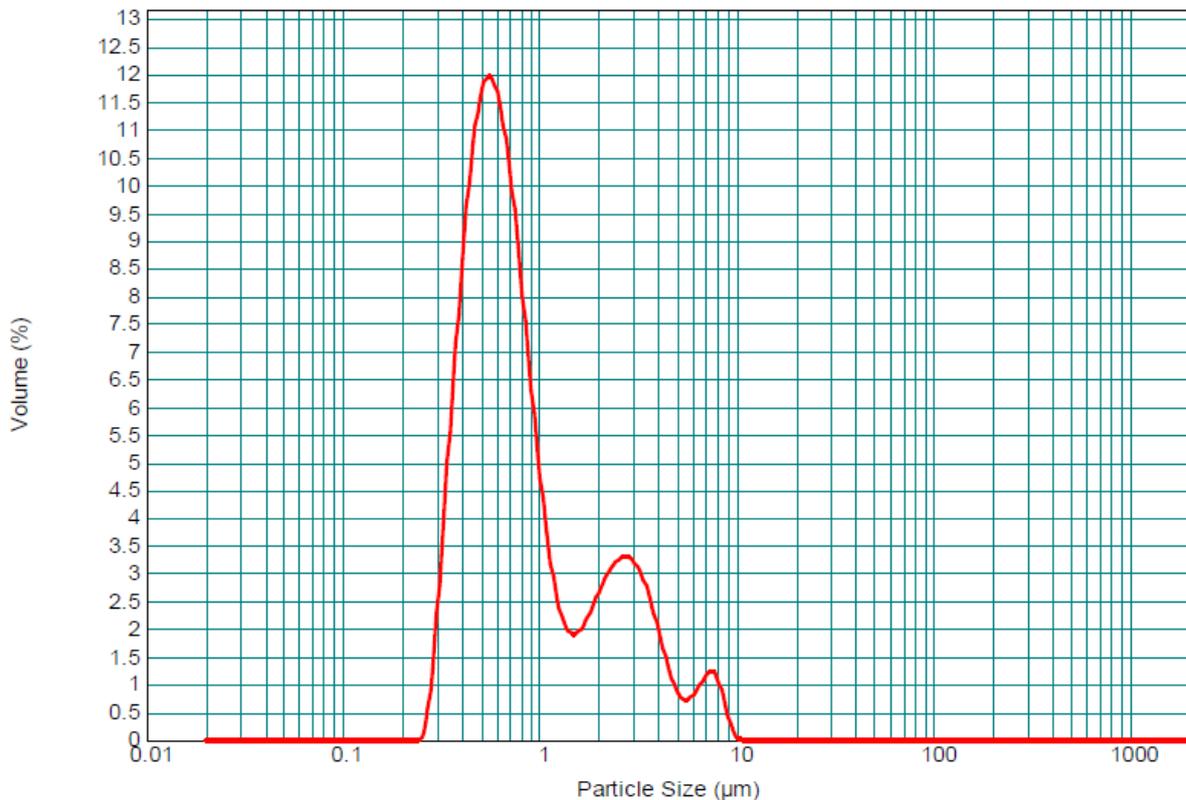


Figure 2. Al₂O₃ powder particles distribution according to sizes

Figure 2 shows that Al₂O₃ particles are mainly 0.5 µm in size, which positively affects aerosol formation by the pneumatic method.

The state stability of the dispersed filler particles in the polyaluminosilicate sol is connected with the Zeta potential ζ that depends on pH and temperature. ζ determines the suspension structure formation, since it affects the aggregation and disaggregation of the particles. In this case, the most preferable value of ζ is in the range from +10 to +40 mV or in the range from -10 to -40 mV. The value of ζ less than ± 10 mV leads to the suspension state, in which electrostatic repulsion is insufficient to prevent the particle agglomeration [2-4]. The particle Zeta potential has been measured with the *Malvern Zetasizer Nano-ZS* (Innovative and technological research and educational center of the National Research Tomsk State University, Tomsk, Lenin Avenue, 36.) device characterizing nanoparticles.

3. Results and discussion

Based on the above-mentioned, it is necessary to measure the pH of the suspensions with 0.1, 0.2, 0.4, and 0.6% Al₂O₃ concentrations that are 6.9, 7.2, 7.6, and 7.8 pH respectively. A series of measurements of the Zeta potential dependence on the pH has been also carried out by the *Malvern Zetasizer Nano-ZS* device. As a result of the measurements, we have obtained a diagram of the Zeta potential dependence on the pH.

The diagram (Figure 3) shows that an isoelectric point of 0.01% suspension is close to 8.5 pH. It indicates a change in the particle polarity and system instability. The diagram shows that the maximum Zeta potential values (more than +30 mV and less than -30 mV) and the largest stability of the suspension with a content of 0.01% of Al₂O₃ are observed at the pH values from 2.5 to 6.5 and from 10 to 11.5. It is recommended to decrease the pH values to use Al₂O₃ in the water suspension, since the isoelectric point is observed at 8.5 pH and agglomerates can form when passing through it.

The bottom line is how the suspension behaves after spraying on a substrate. A series of experiments has been performed to find this out. The images with the morphology of the frozen drops of the

suspensions with different pH values at the same concentration of Al_2O_3 have been obtained by means of microscopy. One may conclude basing on the obtained results that a high level of Zeta potential is required to obtain a relatively uniform and homogeneous surface. This is confirmed by the obtained images presented in Figure 4.

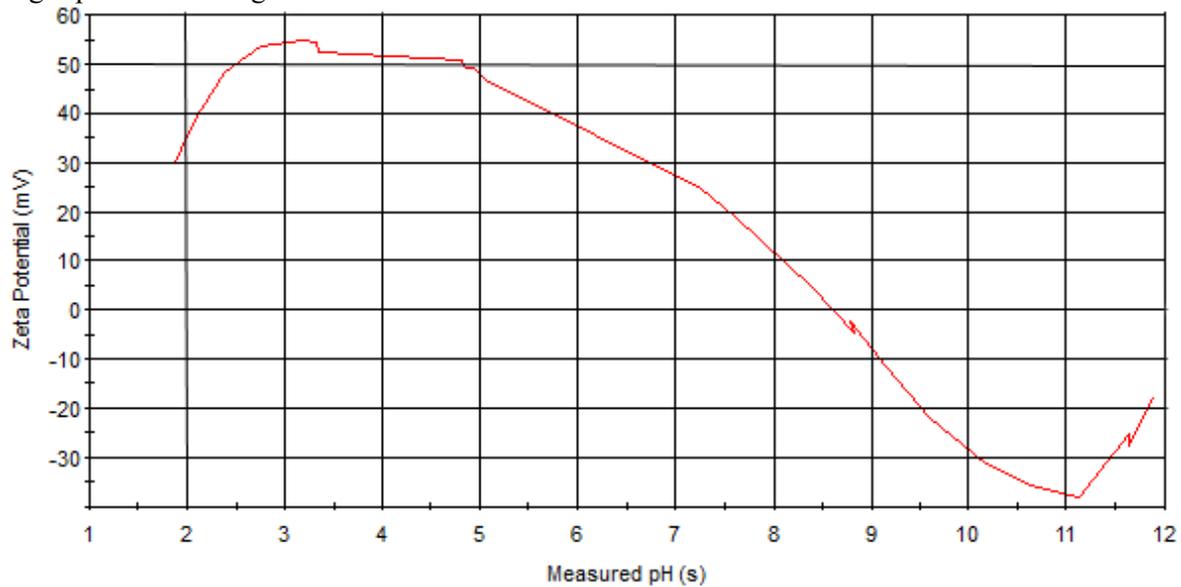


Figure 3. Diagram of Al_2O_3 powder Zeta potential ζ dependence on pH

4. Conclusion

The viscosity, pH, and Zeta potential of the suspensions with different concentrations of Al_2O_3 have been studied in the research. The results have been analytically processed. The effect of pH, dispersion, and concentration on the suspension viscosity that affect the aerosol ability to form in the processes to obtain polyaluminosilicate sol systems (a highly dispersed filler powder) has been determined. Based on the obtained results, it is possible to use temperature and pH as a tool to structure the particles by changing the systemic stability and ultimately to adjust the performance characteristics (thermal conductivity, electrical strength, adhesion, degassing, and so forth) applied by 3D aerosol printing of the ceramic layers of printed circuit boards (figure 5 *a* and *b*).

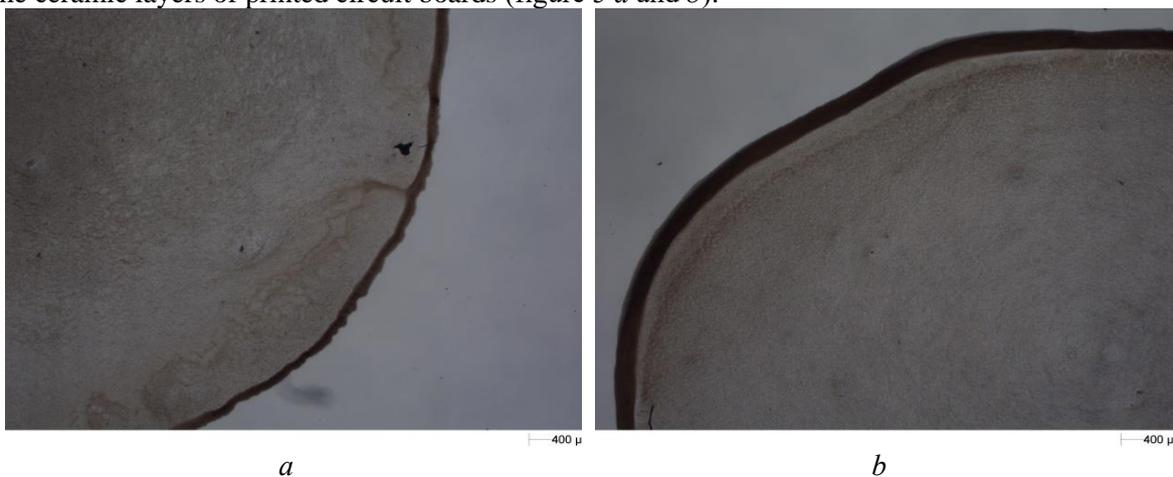


Figure 4. Microphotograph of Al_2O_3 powder suspension in water medium with 7.2 pH (*a*), with 4.8 pH (*b*).

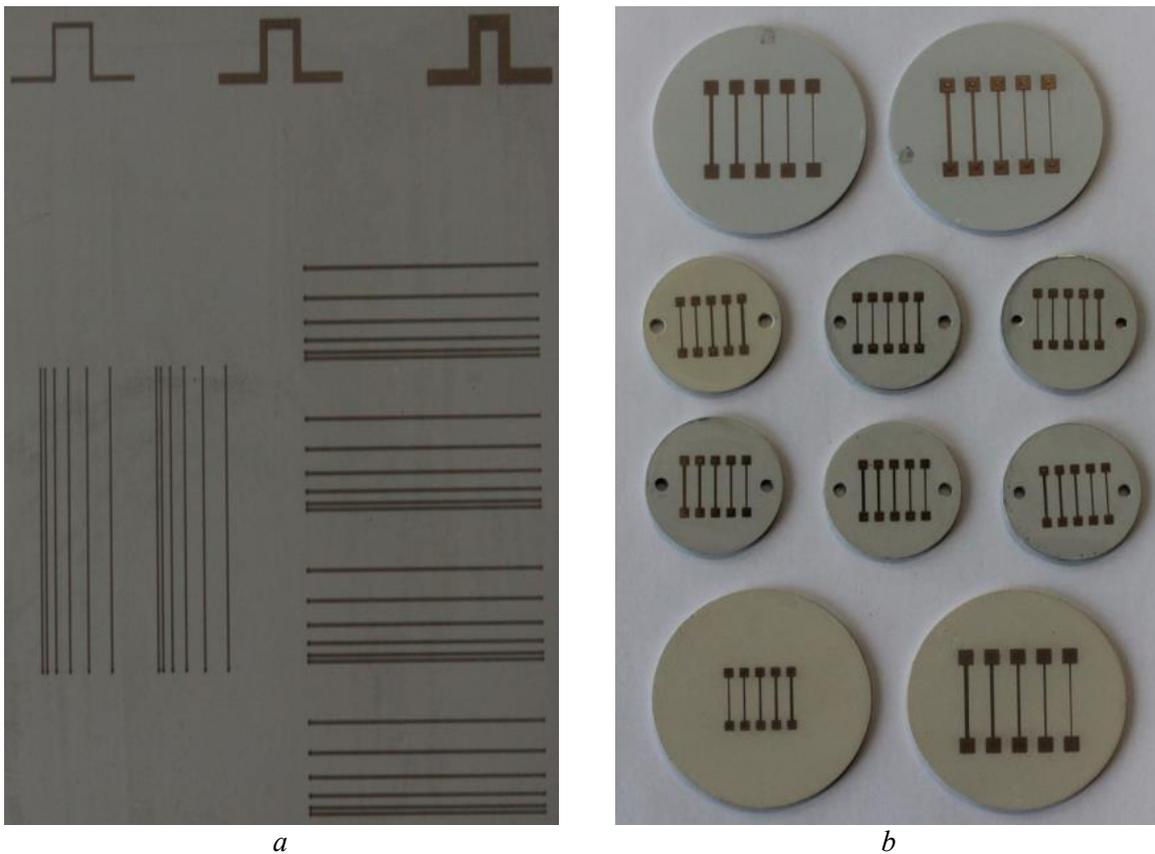


Figure 5. Photo of samples of printed circuit boards on an aluminum base with ceramic layers applied by 3D aerosol printing

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