Nanoparticle size and zeta potential express analysis in initial material's control at the enterprises of powder industry

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Abstract. The first part of the article describes the current situation in the field of additive technologies, existing international and Russian associations. The problem of lack of uniformity of measurements and imperfection of the regulatory documentation is also identified.
In the second part of the article the problem of particles' agglomeration during the technological processes (creation of adhesive glasses, multilayer films, semiconductor plates, etc.) is revealed and solution is proposed. One of the reasons for this problem is the lack of precise control of the particle zeta potential. The importance of determining the zeta potential is that its value is related to the stability of colloidal systems. Zeta potential determines the degree and nature of the interaction between the particles in dispersion.

1. Introduction
Additive manufacturing (AM), or layer-by-layer synthesis technologies, currently occupy the place of one of the most dynamically developing areas of high-tech manufacturing. The use of AM makes it possible to expedite the research and development work, and in some cases they are used for prototyping and manufacturing of finished products.
Initially, AM were used mainly in science-intensive industries - automotive, aviation and aerospace industries. To date, the determining factor is the ratio of production time to production costs, which contributes to the use of AM in all industries.
Over the past few years in Russia there has been a leapfrog in the development of AM, which radically change manufacturing processes and correspond to the transition to the sixth technological mode. A number of Russian enterprises are currently organizing additive manufacturing of a full cycle, starting with the development and production of powder compositions and ending with the certification of finished goods. Today, serial parts are already manufactured in an additive way, for example, gas- turbine engines. A large number of different products made by the method of 3-D printing are already being tested and being prepared for use in aircraft and rocket engineering.

2. Analysis methods of powders' particle size distribution and morphology in AM
In the world practice, all issues related to the development of advanced industries and innovative tasks are solved within the framework of international associations. To date, the largest corporations and research institutes in the world, leading their activities in the field of AM, united under the aegis of the alliance GARPA (Global Alliance of Rapid Prototyping Associations). Within the framework of the
activities of the international Committee, normative documents are approved, cooperation in the field of development and innovation is carried out.

To solve the problems of standardization in the field of AM since 2011 there is an international Committee ISO/TC 261 "Additive manufacturing", which includes 22 permanent members and more than 30 working groups. In the process of this Committee's activity 8 standards have been issued, 17 are under development.

In the Russian Federation on September 1, 2015 it was decided to create TC 182 "Additive technologies" by the order of the Federal Agency for Technical Regulation and Metrology of Russia № 1013. The Committee is based on FSUE "VIAM" and works on the development and implementation of national standards in the field of AM in Russia. The committee consists of more than 60 leading Russian enterprises and institutions. Within the framework of the committee's activities, about 10 standards have been developed that establish requirements in the field of technologies in the Russian Federation. TC 182 contains the subcommittee "Materials for additive technologies". This subcommittee has developed requirements for the raw materials used in the AM. One of the most important controlled parameters is particle size and morphology. Unfortunately, the regulatory documentation provides for the use of only electron microscopy to solve this task. This method, with its undoubted advantages, is not suitable for rapid analysis of particle sizes in large batches of raw materials due to the high cost of the equipment used, long measurement time and strict requirements for the operation of the measuring equipment. An alternative is the use of other modern control methods that meet the requirements dictated by manufacturing processes:

- relative cheapness of equipment
- short measurement time (less than 10 minutes)
- easy operation
- no need for consumables

The following methods meet the criteria:

- static light scattering (laser diffraction)
- dynamic light scattering
- diffusion spectrometry
- differential mobility

These methods can be divided into groups, depending on the conditions of their usage and the test sample (table 1).

| Method                  | Measurement range, μm | Medium | State Standard          | Traceability |
|------------------------|-----------------------|--------|-------------------------|--------------|
| Laser diffraction      | from 0.05 to 2000     | L/G/S  | GOST R 8.777-2011       | GET 163      |
| Dynamic light scattering| from 0.001 to 5000    | L      | GOST R 8.774-2011       | GET 163      |
| Diffusion spectrometry | from 0.002 to 200     | G      | GOST R 8.755-2011       | GET 163      |
| Differential mobility  | from 0.001 to 1000    | G      | GOST R 8.775-2011       | GET 163      |

Another important parameter of the raw materials is their stability, which can be estimated numerically by measuring the particle electrophoretic mobility and zeta potential. At the current stage of development of AM, zeta potential measurements are not provided and are not regulated by
specialized standards, although in materials science such methods of control are used to improve the quality and purity of products [1].

Zeta potential applicable to AM can be used to assess the physical and chemical properties of raw materials and improve their quality (reducing the number of agglomerated particles, sample caking, preservation of bulk density, etc.).

The zeta potential applicable to AM can be used as assessment of raw materials' physico-chemical properties and increasing their quality (decreasing particle agglomeration, sample caking, preservation of bulk density, etc.).

3. metrological assurance for AM in Russia

There are three main groups of methods: electrokinetic, optical and acoustic, as well as various combinations of methods.

3.1 electrokinetic methods of zeta potential determination

The most common electrokinetic method is electrophoresis (microelectrophoresis). The essence of the method is that most colloidal particles have a surface charge and when the potential difference in the cell is applied, they begin to move to the cathode or anode, depending on the sign of their surface charge. [2]

This method is primary as it allows direct measurement of particle electrophoretic mobility, which is related to zeta potential by the Smoluchowski equation (1) [3]:

$$\mu = \frac{\varepsilon \zeta \epsilon_0}{\eta}$$

where

- $\varepsilon$ – relative permittivity of the medium
- $\epsilon_0$ – vacuum permittivity
- $\eta$ – dynamic viscosity
- $\zeta$ – zeta-potential

Also, it should be noted that with a large number of advantages (simplicity and low cost of technical implementations, visibility), the microelectrophoresis method has one significant drawback - it is applicable only in a limited range of particle sizes (not less than 0.5 microns).

3.2 optical methods of zeta potential determination

Optical methods include methods based on the analysis of scattered light by particles and determination of electrophoretic mobility by frequency or phase shift of scattered light – electrophoretic light scattering (ELS) and phase analysis of light scattering (PALS) [4].

ELS and PALS are indirect methods for measuring electrophoretic mobility $\mu$ based on Doppler shift (ELS) of light scattered by particles and measurement of phase shift (PALS) [5].

Coherent light illuminates particles dispersed in a liquid and located in an electric field. Charged particles move to the anode or cathode depending on the sign of the charge, and the frequency of the scattered light depends on their speed and changes in accordance with the Doppler effect. Thus, the Doppler frequency shift is used to determine electrophoretic mobility [6].

The electrophoretic mobility of some particles in a non-polar solvent is very small, resulting in very small differences between the modulator frequency and the Doppler frequency shifts from electrophoretic motion. Such frequency differences can be less than 1 Hz [4]. For particles suspended in a solution of high ion concentration, only a very small field can be applied between the electrodes before the Joule–Thompson heating affects measurement. Therefore, again, very small Doppler frequency shifts requires PALS [7] detection.

The dependence of electrophoretic mobility on the frequency shift is determined by the design features of the equipment that implements optical methods for determining the zeta potential. For example, in instruments with reference beam, the electrophoretic mobility $\mu$ is calculated by the
equation (2). In case of cross-correlation devices, the mobility $\mu$ is calculated by the equation (3) [5, 6]:

$$\mu = \frac{\Delta \omega \lambda_0}{4 \pi n E \sin(\theta/2) \sin \left(\frac{\theta}{2} + \xi\right)}$$

(2)

$$\mu = \frac{\Delta \omega \lambda_0}{4 \pi n E \sin(\theta/2)}$$

(3)

where $\Delta \omega$ – Doppler phase shift

$\lambda_0$ – wavelength in vacuum

$n$ – medium refractive index

$E$ – electric field strength

$\theta$ – angle between incident light and scattered light

$\xi$ – angle between scattered light and electric field direction

$\theta'$ – angle between two cross-beams

The relationship of electrophoretic mobility and electrokinetic potential in most cases is determined by Henry’s equation (4) [5, 8]:

$$\mu = \frac{2 \xi e \varepsilon_0}{3 \eta f(\kappa a)}$$

(4)

where $\eta$ – medium viscosity

$\kappa$ – reciprocal Debye length

$\varepsilon$ – medium permittivity

$a$ - sphere radius

$f(ka)$ – a monotonic function varying from $f(ka)_{ka \to 0} = 1$ to $f(ka)_{ka \to \infty} = 3/2$.

This equation is quite limited, because it does not take into account many factors. It is also assumed that:

- the total electric field a particle experiences is a superposition of the applied field and the field due to the charge on the particle
- the distortion of the field induced by particle movement (i.e. the relaxation effect) can be ignored
- the inertial terms in the hydrodynamic equation are negligible
- the surface potential is much smaller than $k_BT/e$

Most of the samples are polydisperse and have different values of $ka$, so receiving a complete distribution of the zeta potential is a complex task.

1. When $ka >> 1$, typical for large particles in aqueous suspension, $f(ka)$ takes the value of 3/2 in formula 4, leading to the Smoluchowski equation.
2. When $ka << 1$, typical for small particles in organic liquids, $f(ka)$ takes the value of 1 in formula 4. The equation is then called the Hückel equation.

3.1.1 Electroacoustic methods of zeta potential determination

Electroacoustic theory, following electrophoretic theory, operates with a notion that it is closely related to electrophoretic mobility. This so-called dynamic electrophoretic mobility, $\mu_d$, is the generalization of the electrophoretic mobility concept for high-frequency oscillating particle motion.

The relationship between dynamic electrophoretic mobility and experimental electroacoustic data is not as trivial as that in the case of electrophoretic mobility. The additional theoretical step has been made through the O’Brien electroacoustic theory [8, 9], which is valid for concentrated systems as well as
dilute ones. According to the O’Brien relationship, the average dynamic electrophoretic mobility, $\mu_d$, is defined as:

$$
\begin{align*}
\mu_d &= A_{ESA} \frac{\rho_m}{\varphi(\rho_p - \rho_m)} A(\omega) F(Z) \\
\mu_d &= I_{CVI} \frac{1}{\varphi(\rho_p - \rho_m)} A(\omega) F(Z)
\end{align*}
$$

(5)

where $A_{ESA}$ – electrokinetic sonic amplitude
$I_{CVI}$ – colloid vibration current
$A(\omega)$ – instrument constant found by calibration
$F(Z)$ – function of the acoustic impedances of the transducer and the dispersion under investigation
$\rho_m$ – medium density
$\rho_p$ – particle density
$\varphi$ – volume fraction

4. References

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