Precision measurements of the particle size distribution of powder materials based on state primary standard for the units of disperse parameters of aerosols, suspensions and powder materials GET-163

T M Magomedov, D I Belenkii

All-Russian Scientific Research Institute of Physical-Technical and Radiotechnical Measurements

Abstract. In this article the problem of lack of specialized reference base and national standards in the sphere of additive technologies, particularly for the equipment and methods used in production, control of properties and the quality of powder materials is designated. The existing methods and instruments for measurement of particle size distribution and morphology of powders are considered and also the solution of this problem with use of the technical realization applied in the State primary standard for the units of disperse parameters of aerosols, suspensions and the powder materials GET-163 is proposed. Get-163 provides reproduction, storage and transmission of particle size units in aerosols, suspensions and powdery materials in the range from 0.001 to 2000 µm, counting concentration of particles in aerosols and suspensions in the range from $10^3$ to $10^{12}$ m$^{-3}$, mass concentration of aerosol particles in the range from 0.001 to 10,000 mg/m$^3$, electrophoretic mobility of particles in the range from $-2 \times 10^{-7}$ to $+2 \times 10^{-7}$ m$^2$/(V·s), zeta potential of particles in the range from -150 to +150 mV.

1. Introduction

Today additive manufacturing (AM) are actively developing, the leading positions in the development and practical use of AM are occupied by industrialized countries. The most dynamically this direction is developing in the USA (38% of world production), Germany (about 9%), and also China (8.7%). In general, the global market of AM, according to Wohlers Associates, is more than 6 billion dollars. By 2020, experts believe that it will reach 21 billion dollars [1]. Russia is not an exception to this list and is also conducts research in this direction, and a number of companies have already implemented and use AM in their production.

According to the head of the Ministry of industry and trade Denis Manturov, 3D-printing is beginning to spread in the world, and Russia should not lag behind in this area. The use of these technologies can reduce the cost of the product, accelerate its design and production.

An important role in AM is played by the materials used, the properties of which directly determine the quality and reliability of the products obtained. Among them, a large share is occupied by powder materials.
The powder technology [2] describes methods for obtaining dispersions used in a variety of industries – powder metallurgy, ceramic industry, food and pharmaceutical industry, fertilizers, fuel, building materials, etc. Key properties of these materials are flowability, bulk density, particle size and surface morphology. Control of these parameters is an integral part of the technological process. And if there are no significant problems in measurement of first two parameters, using standard calibrated devices, other measurements are much more difficult.

2. Analysis methods of powders’ particle size distribution and morphology in AM

There are a number of the most common methods for measuring the particle size distribution of powdered materials:

- Sieve analysis
- Microscopy
- Laser diffraction method
- Dynamic light scattering method

The sieve analysis [3] is a traditional method for controlling the dispersity of bulk and powdery materials. The essence of the method is that the powder is sieved on a vibration bench through a sieve analyzer, in which sieves with different cell sizes are installed sequentially above each other, at the top of the sieve with the largest cell and downwards the sieve cell size decreases. Sieve analysis allows to determine the particle size, separate particles of different sizes from each other and calculate the quantitative ratio of particles of different dispersion. This method requires considerable time and quite a large number of samples, does not provide high accuracy, and does not allow to control particles smaller than 50 microns.

Microscopy is one of the oldest methods for particles' size and morphology analysis. It is divided into optical and electron microscopy.

Optical microscopes allow to estimate the size and shape of particles starting from 0.5 microns.

Electron microscopes are used to study smaller particles. The scanning electron microscope uses an electron beam, which is focused by a system of lenses into a spot of 1-10 nm in diameter located on the surface of the test sample. The focused beam scans the surface of the sample using a system of deflecting coils. The image obtained in this way is processed using specialized software, which allows to evaluate the morphology of the particles in addition to the particle size.

With the development of high-tech production, microelectronics and aviation industry, the time spent on analyzing the parameters of the initial materials in the AM has become very important. Express methods of control began to develop actively.

One of the most common rapid methods of particle size measurements is the laser diffraction method, which allows to study particles in the size range from 0.05 to 2000 microns. It is based on the measurement of the light scattering indicatrix arising from the scattering of a plane monochromatic electromagnetic wave by an ensemble of aerosol or suspension particles. The scattered light is measured by a multi-element photodetector in a wide range of angles. Then, solving the inverse scattering problem within the framework of certain model representations (for example, representations that the particles have a spherical shape) are determined the particle size distribution function and concentration. Depending on the size of the particles (but rather from the relationship \( \pi d/\lambda \), where \( \lambda \) is the wavelength of the electromagnetic radiation, \( d \) is the radius of the particles), the scattering phase function is changing, it becomes more symmetric with the smaller the value of \( d \).

Dynamic light scattering method is used to measure the size of nanoparticles. In this method, the diffusion coefficient of dispersed particles in a liquid is determined by analyzing the characteristic time of fluctuations measured in the intensity of scattered light. The diffusion coefficient is used to calculate the hydrodynamic radius of nanoparticles. Thermal (Brownian) motion of particles causes fluctuations of their local concentration. In turn, these fluctuations lead to local inhomogeneities of the refractive index of the medium. When a laser beam passes through such a medium, part of the light is
scattered on these inhomogeneities. The fluctuations of the scattered light intensity correspond to the fluctuations of the local concentration of dispersed particles. Information on the particle diffusion coefficient is contained in the time-dependent correlation function of the intensity fluctuations.

3. Metrological assurance for AM in Russia
Today in Russia there are about ten standards in the field of AM and in accordance with them only the method of electron microscopy can be used to control the size and morphology of the particles of the raw materials. This method makes it possible to determine the size and morphology of particles with high accuracy, although it has some disadvantages such as high cost of equipment, long (up to day) measurement time, the need to have highly qualified personnel.

Another problem in the field of AM is the lack of metrological assurance and absence of a reference base [4], which undoubtedly prevents the improvement of the quality and competitiveness of domestic products in the market of high technologies and reduction of production costs.

The solution to these problems is the creation of a reference base, optimization and updating of existing regulatory documentation in accordance with current realities. The creation of a reference base is an extremely long and expensive process, an alternative to it is the use of existing standards. The State primary standard for units of dispersed parameters of aerosols, suspensions and powder materials [5], has been applied in this field since 1997 (revisited in 2017) and providing reproduction, storage and transmission of units specified in table 1.

Table 1. Metrological characteristics of the State primary standard for units of dispersed parameters of aerosols, suspensions and powder materials GET 163.

| Value                        | Measurement range | $u_A, \%$ | $u_B, \%$ | $u_C, \%$ | $U(k=2), \%$ |
|------------------------------|-------------------|----------|----------|----------|-------------|
| Particle size                | from 0,001 to 0,03 μm | 1,2...1,8 | 0,7      | 1,3...1,9 | 2,7...3,8   |
|                              | from 0,03 to 2000 μm | 1,0...1,1 | 0,6...0,7 | 1,2      | 2,4         |
| Particle number concentration| from $10^7$ to $10^{12}$ m$^3$ | 1,5...1,7 | 0,7      | 1,6...1,8 | 3,2...3,6   |
|                              | from 0,001 to 10 mg/m$^3$ | 0,9...1,7 | 0,6...0,7 | 1,1...1,9 | 2,2...3,7   |
| Particle mass concentration  | from 1 to 2000 mg/m$^3$ | 0,4      | 0,6      | 0,7      | 1,3         |
|                              | from 1 to 10000 mg/m$^3$ | 0,4...1,2 | 0,6...0,8 | 0,7...1,5 | 1,3...2,9   |
| Particle electrophoretic mobility | from $-2 \cdot 10^{-7}$ to $+2 \cdot 10^{-7}$ m$^2$/(V∙s) | 1,4...1,6 | 0,...0,8 | 1,5...1,7 | 3,0...3,5   |
| Particle zeta potential      | from -150 to +150 mV | 2,0...2,2 | 0,9...1,0 | 2,2...2,4 | 4,4...4,8   |

3.1 Measurement methods of particle size, realized in GET 163
As can be seen from table 1, the standard allows to solve any problems in the field of at related to the control of particle size distribution and morphology with high accuracy. The set of equipment for reproduction, storage and transmission of particle size units, which is part of the standard, is based on the application of various physical principles and mathematical models and consists of four main parts that implement different methods for measuring particles in aerosols, suspensions and powder materials.
3.1.1 Reference device based on laser diffraction method

One of the standard parts is a device based on the laser diffraction method is described above. Particle size determination from the measured scattering indicatrix [6] is reduced to the solution of the Fredholm integral equation of the first kind with one or another nucleus depending on the diffraction parameter:

\[ p = \frac{\pi d}{\lambda} \]  

where \( d \) - particle diameter;
\( \lambda \) - wavelength of the probing radiation.

In this case, the integral equation will have the form:

\[ l(\theta) = l_0 \int_{0}^{\infty} f(p) \cdot k(p, \theta) dp \]  

where \( \theta \) - scattering angle;
\( l_0 \) - intensity of scattered light;
\( f(p) \) - particle distribution function by \( p \);
\( k(p, \theta) \) - nucleus of integral equation.

3.1.2 Reference device based on diffusion aerosol spectrometry method

The diffusion aerosol spectrometer is an integral part of the standard for determining the size of nanoparticles and is based on determining the diffusion coefficient of particles by the measured value of the particle slip coefficient through the diffusion battery, and by the found value of the diffusion coefficient the particle size is estimated [7]. During the measurement process, nanoparticles are enlarged by condensing vapors of the evaporated liquid on them, and then registered by a laser particle counter.

The diffusion coefficient is related to the slip coefficient by the formula:

\[ D = 2Vr \left[ \frac{\ln P(n)}{An} \right]^{3/2} \]  

where \( V \)- linear velocity of aerosol through the diffusion battery;
\( r \) - radius of the wire from which the mesh is made;
\( P(n) \) - slip coefficient equal to \( C/ C_0 \), where \( C_0 \) and \( C \) are number concentration of particles in the aerosol, respectively, before and after its passage through the diffusion battery;
\( n \) - number of meshes;
\( A \) - empirical constant.

Relationship between the diffusion coefficient and the size of the aerosol particle is described by the Cunningham-Millikan equation:

\[ D = kT \frac{1 + a_1 \left( \frac{2l}{d} \right) + a_2 \left( \frac{2l}{d} \right)^2 \cdot e^{-a_3 \left( \frac{2l}{d} \right)^3}}{3\pi\mu d} \]  

где \( k \) - Boltzmann constant;
\( T \) - aerosol temperature;
\( \mu \) - coefficient of dynamic viscosity of dispersion medium;
\( d \) - aerosol particle diameter;
\( l \) - mean particle' free path length;
\( a_1,a_2,a_3 \) - semi-empirical constants, equal, respectively, 1,25; 0,42; 0,87.
3.1.3 Reference device based on differential mobility method
The main set of equipment for determining of particle size and number concentration implements the
method of differential electric mobility, based on the separation of aerosol particles by size when they
pass through an electric field, where charged aerosol particles change their trajectory depending on
their size, velocity of aerosol flow, electric field strength and geometry of the classifier, which acts as
a cylindrical capacitor, to which the voltage is applied. The particles entering into the classifier are
affected by the electric field force, Stokes force and the aerodynamic force of clean air [8]. When the
force of the electric field and the Stokes force are equal, the particles are affected only by the
aerodynamic force that drags them down. After the classifier, the particles enter the condensation
counter. In this case, the aerosol particles act as condensation nuclei of superheated liquid vapor, and
after growing, are counted by the optical particle counter.

The relationship between differential electric mobility and particle size for spherical particles is
described by the equation:

\[ Z = \frac{NeS_C}{3\pi\mu d} \]  \hspace{1cm} (5)

where \( N \) - number of elementary charges per particle;
\( e \) - elementary charge \((1.6 \times 10^{-19} \text{ C})\);
\( \mu \) - gas dynamic viscosity;
\( d \) - particle diameter;
\( S_C \) - Cunningham correction factor on the gas slide.

3.1.4 Reference device based on dynamic light scattering method
To determine the particle size in the liquid, a dynamic light scattering device, described above, was
included in the standard.

The change of scattered light intensity is a stochastic stationary process expressed by the
autocorrelation function:

\[ G(\tau) = \langle l(t)l(t-\tau) \rangle = \lim_{\Delta t \to \infty} \frac{1}{\Delta t} \int_{0}^{\Delta t} l(t)l(t-\tau)dt \]  \hspace{1cm} (6)

where \( \Delta t \) - averaging (integration) time;
\( \tau \) - correlation time;
\( l(t-\tau) \) scattered light intensity over time \((t-\tau)\).

In the case of Brownian motion in suspension, the autocorrelation function \( G(\tau) \) has the form:

\[ G(\tau) = a \exp \left( -\frac{2\tau}{\tau_0} \right) + b \]  \hspace{1cm} (7)

where \( a = \langle l^2(t) \rangle \) \( b = \langle l(t) \rangle^2 \) - experimentally determined constant (the angular brackets \( \langle \rangle \)
denote the average value over time);
\( \tau \) - correlation time;
\( \tau_0 \) - characteristic relaxation time.

For a known characteristic relaxation time \( \tau_0 \), the value of the diffusion coefficient \( D \) is calculated
from the analysis of the autocorrelation function. The size of the nanoparticles \( d \) is calculated
according to the Stokes-Einstein equation [9]:

\[ d = \frac{k_B T}{3\pi\eta D} \]  \hspace{1cm} (8)

where \( k_B \) - Boltzmann constant;
\( T \) - absolute temperature;
\( \eta \) - dynamic viscosity of liquid.
4. References

[1] Kablov E N 2017 Eurasian Metals 3 2-6
[2] Andrievsky R A 1991 Poroshkovoe materialovedenie 1 (Moscow) p 4
[3] Naumov S V 2012 Вестник ПНИПУ 14 76-84
[4] Yakovleva M et al 2017 Tsifrovoe proizvodstvo 1 38-44
[5] Lesnikov E V et al 2013 Measurement Techniques 56 pp 1-7
[6] Shifrin K S, Kolmakov I B 1967 Fiz. Atm. Okeana 3 1271 – 1279
[7] Zagainov V A 2006 Nanotekhnika 1 141-146
[8] Fuchs N A 1963 Geophys. Appl. 56 185-193
[9] Berne J, Pecora R 1963 Dynamic Light Scattering: With Applications to Chemistry, Biology, and Physics vol 1 (New York)