

## Field-flow fractionation of metallic microparticles in a rotating coiled column

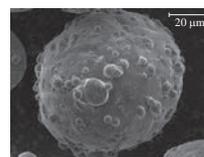
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**The sedimentation field-flow fractionation in a rotating coiled column has been applied to the separation of silumin (aluminum–silicon alloy) microparticles for the first time. The possibility of preparative purification of metallic powders has been estimated.**



An additive manufacturing (AM) technology is one of the rapidly developing advanced manufacturing techniques in the world.<sup>1–3</sup> AM is based on layer by layer shaping and consolidation of particulate feedstock to required 3D-configurations using a computer controlled laser as the energy source. Briefly, a 3D model of produced object is mathematically sliced into thin layers. Then the object is manufactured by the selective consolidation of the deposited material layers with a scanning laser beam. Note that each shaped layer represents a cross-section of the sliced 3D model. AM is also called solid freeform fabrication, digital manufacturing, or e-manufacturing.<sup>4</sup> AM technology, which involves a comprehensive integration of materials science, mechanical engineering, and laser technology, is regarded as an important revolution in manufacturing industry.<sup>5</sup>

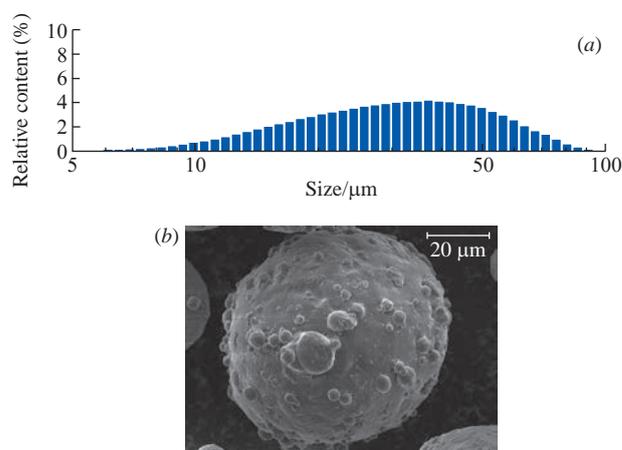
It is known that the complex metallurgical phenomena during AM processing and hence the resultant mechanical properties (strength, hardness, residual stress, *etc.*) of AM final product strongly depend on the material employed. The properties are also governed by such powder characteristics as shape, size, and size distribution of particles.<sup>1</sup> The synthesis of metallic powders with required particle size distribution is a complex and sometimes impossible task. Therefore, a separation (and hence purification) of synthesized powder is urgently required. Unfortunately, the conventional sieving techniques, which are used in powder metallurgy, enable only the particles larger than 40 μm in diameter to be efficiently separated. A challenge is the separation of finer particles.

The sedimentation field-flow fractionation (FFF) in a rotating coiled column (RCC) is a versatile particle separation method covering a size range from about 50–100 nm to 100 μm.<sup>6,7</sup> RCC has been successfully applied to the fractionation of environmental and synthetic samples.<sup>7</sup> The aim of this work was to study the applicability of FFF in RCC to the fractionation of metallic particles on the example of the silumin microparticles,<sup>†</sup> used as a feedstock for AM, and to estimate the possibility of using RCC for their preparative separation.

The planetary centrifuge equipped with RCC was used for the fractionation of particles.<sup>‡</sup> The column was a Teflon tube

with an inner diameter of 1.6 mm and total volume of 25 ml. Because of the hydrophobicity of the synthesized silumin particles, ethanol was used as a carrier fluid. The ultrasound bath (Bandelin Sonorex DT-52, Germany) was used for the dispersion of the initial sample. The initial sample and the fractions of separated silumin were characterized by the scanning electron microscopy (SEM) (TESCAN MIRA3, Czech Republic) and static light scattering (SLS) (Shimadzu SALD-7500nano, Japan).

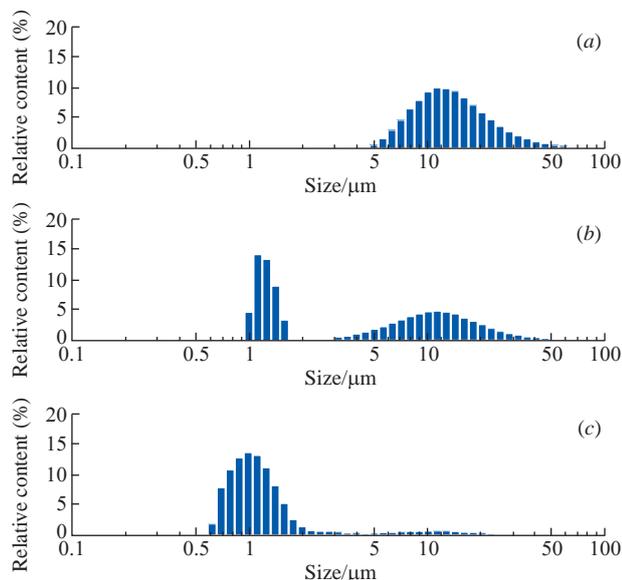
The characteristics of the initial sample obtained by the SLS and SEM are shown in the Figure 1. As it is seen, the initial sample had wide size distribution from about 5 to 80 μm in diameter [Figure 1(a)]. Moreover, the larger particles contain smaller ones (~1–10 μm in diameter) attached to their surface [Figure 1(b)]. The silumin particle fraction required for the application in AM is 20–40 μm. Therefore, our task was to separate particles <20 μm in size (including adhered fine particles from the surface of larger ones) and to recover target >20 μm particle fraction, which may be further separated by dry sieving (con-



**Figure 1** Characterization of the initial sample of silumin by the (a) SLS and (b) SEM.

<sup>†</sup> Silumin microparticles were synthesized in the Division of Powder Metallurgy and Functional Coatings of National University of Science and Technology 'MISIS' (Moscow, Russian Federation).

<sup>‡</sup> The planetary centrifuge equipped with RCC was fabricated at the Institute of Analytical Instrumentation (St. Petersburg, Russian Federation).



**Figure 2** Size distribution (SLS, by particle number) for the initial silumin sample depending on ultrasonication time: (a) 0, (b) 15 and (c) 30 min.

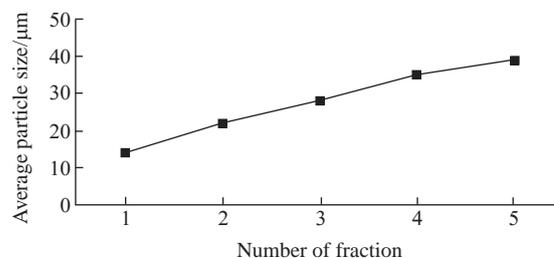
ventional for powder metallurgy). According to the SLS data initial sample contains about 22% of particles <20 μm in size, which should be removed from the sample.

Before the fractionation procedure the initial sample was ultrasonicated for the dispersion and hence for the removal of fine particles from the surface of the coarse ones. The size distribution (by particle number) for the silumin sample before and after ultrasonication (15 and 30 min) was measured by the SLS (Figure 2). After 30 min of the ultrasound treatment the relative content of particles about 1 μm in size is significantly increased as compared to the sample without treatment [Figure 2(c)]. Therefore, 30 min of ultrasonication of the initial silumin suspension preceded all further fractionation experiments.

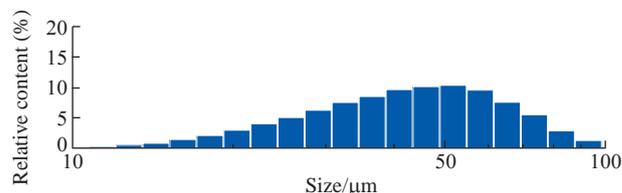
It has been reported earlier that for the fractionation of the microparticles in RCC, it is sufficient to use the rotation speed of 100–300 rpm.<sup>7,8</sup> In this work the applicability of the RCC to the fractionation of the silumin microparticles has been demonstrated. The fractionation of 10 mg of silumin particles in an isocratic mode (at constant flow rate of carrier fluid) was observed. In the course of the process four fractions (50 ml each) were separated at a carrier fluid flow rate of 9 ml min<sup>-1</sup> and a column rotation speed of 200 rpm. The fifth (residual) fraction was recovered from the column afterwards. The SLS data show the increase of average particle size in each subsequent fraction (Figure 3). The relative content of target particles (>20 μm) in the fractions 1–5 was 21, 60, 81, 92, and 95%, respectively.

Hence, the principal applicability of the RCC to the separation of the silumin microparticles has been demonstrated on the loading of 10 mg sample. To attain the aim of preparative separation, the weight of injected sample was further increased up to 100 mg and the further optimization of fractionation conditions was accomplished with 100 mg sample loading.

In fact, the isocratic mode of the fractionation process is not appropriate for further scaling up as it requires the sample injection in a small volume of eluent to achieve the fractions resolution. The fractionation mode that provides the complete retention of one of the fractions (e.g. the target fraction) and the elution of another one (a waste fraction) is optimal for scaling up. Therefore, a decrease in the initial flow rate was necessary to achieve the required fractionation mode. A series of experiments were conducted with the initial flow rate from 3 to 9 ml min<sup>-1</sup> and the column rotation speed of 200 rpm. In each experiment two fractions were separated: the first (waste) fraction was eluted and



**Figure 3** Average particle size of the silumin fractions separated in the RCC at the constant carrier fluid flow rate (in the isocratic mode).



**Figure 4** Size distribution of the silumin target fraction as obtained by SLS.

the second (target) one was separated from the column. It was shown by the SLS that the ‘purest’ target fraction (relative content of target particles 94.5%) was separated in the experiment with the initial flow rate of 9 ml min<sup>-1</sup> (Figure 4), whereas the most impure one was separated in the experiment with the initial flow rate of 3 ml min<sup>-1</sup> (relative content of target particles 81%). The results are not surprising as it has been shown earlier<sup>6</sup> that high sample loading causes a co-precipitation of fine particles with coarse ones. As a result, higher flow rate or column diameter is required for high resolution at increasing sample weight.

Thus, an applicability of analytical RCC to the separation of metallic particles on the example of silumin has been demonstrated. Recent study on the preparative separation of chromatographic sorbent has shown the possibility of scaling up the fractionation process in the preparative RCC of larger volume with the same efficiency.<sup>7</sup> In prospect, the RCC of greater inner capacity may become an appropriate instrumentation for the separation and purification of the feedstock for AM and other powder technologies.

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