Amorphous Superhard and Functionally Unique Materials Developed on Granulation Using Controlled Film Flow Decay

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Abstract—The specific granulation problem is presented, which has concern to the controlled liquid metal jet and film flows for a production of the uniform by size and form particles (granules) cooled with a high rate, to be amorphous or close to the amorphous materials. Basics of the developed theory of the controlled jet and film flow disintegration with further rapid cooling of the drops after disintegration of film flow are presented together with the new patented granulation devices developed and tested. The original methods and devices can be used for production of the amorphous granules in a wide range of the given sizes, with a very narrow (plus-minus 50%) deviation in size.

Keywords—Film flow, disintegration, drops, high cooling rate, granulation, amorphous material.

I. THE FINE PRECISE METALS’ GRANULATION

In a contrast to the known works by amorphous materials and granulation of the metals and alloys, we deal with a granulation of the middle-temperature metals (Cu, Al, Pb, Mg, etc.), with the substantial request of the spherical form of particles and strictly uniform size (mainly below 1 mm). The methods and devices for production the spherical granules (particles) of metals of a given size, with a high cooling rate by solidification are presented.

The cooling rate of the drops during their solidification has been achieved up to $10^4$ °C/s! Such fine structure metals are amorphous or close to amorphous ones. The idea of their creation appeared on the assessment of the iron’s hardness by Ya.L. Frenkel (1925) [1]: theoretically the iron’s strength differs from the real one up to thousand times in some of its properties. This results excited many scientists and engineers to produce rapidly cooled amorphous materials with superhard properties, which would be amazing being able to do revolution in material science and industry: decrease of the weight and metal consumption, creation of the marvelous airplanes and diverse engineering constructions, etc.

The conventional methods of the metallurgy lead to a deterioration of all properties of the metals due to slow cooling of a metal and a forming of the crystals due to this. Granular technology in the material science requires amorphous particles of nearly the same size (uniform properties) cooling rapidly to avoid development of the crystals, which decrease the quality of a metal dramatically. The uniform particles (uniform properties) fit the best to production of new materials. Granular technology is a contrast to the powder metallurgy, where cooling of particles of different size is usually going with a comparably low cooling rate. Therefore granules of a small size are normally required, except some special applications other than the ones of the material science.

Our creation of the highly efficient processes and perspective technological devices was based on the earlier developed theory of the parametric control of film flows, as well as on the discovered new phenomena of the controlled disintegration of film flow into the drops with their further rapid solidification [2-5]. The theory of the parametrically controlled jet and film flows has been developed [2-16]. Technological processes based on the discovered phenomena and the invented methods and devices [6-10] were patented and implemented into metallurgical and space industry. Here we present a description of the film flow granulation for Zn, Al, Mg and their alloys, which has no analogs in the world.

II. THE PARAMETRICALLY CONTROLLED FILM FLOW DECAY

The most important results obtained, which have been created a base for the perspective granulation machines, are as follows:

1. The parametric excitation and suppression of oscillations in the film flow under an action of the electromagnetic fields and vibrations.
2. Theoretically predicted and experimentally tested 3 new phenomena of the disintegration of the liquid film flow into the drops using the alternating electromagnetic fields and vibration:
   - the resonant electromagnetic decay of a film flow into drops of strictly given size,
   - soliton-like film disintegration into the drops by vibration, in a narrow range (50% of average),
   - the shock-wave regime for the film flow’s disintegration into the micro size drops.
3. The experimental facilities for a rapid cooling of the drops (up to $10^4$ °C/s) during solidification, which allow producing the amorphous nanostructured granules for the new materials.

The results are new in the metals’ granulation, which may serve for production of the new amorphous materials and for development of some materials with the unique complex structure by application of the electromagnetic control of a flow inside the drops before their solidification.
III. OPERATION PRINCIPLE OF THE JET AND FILM FLOW GRANULATION

The principle of the machines for electromagnetic batching of metal alloys [11-13] with a melting temperature approximately no more than 10³ °C is based on a controlled disintegration of free the jet flow on the first mode of its Eigen oscillations. It is producing the metallic granules of the size from 2 mm using the metal melts and alloys. Applying the crossed electric and magnetic fields at the exit from the channel (nozzle) delivering a melt leads to the resonant regime. A frequency of the alternating ponderomotive electromagnetic force is chosen equal to a frequency of the jet’s Eigen oscillations.

The magnetic field is created by a permanent magnet as the simplest way but can be arranged any other. A current in a melt at the nozzle has the industrial frequency 50 Hz. The crystallizer is done depending on the granulating melt and requirements to a size of particles and cooling rate. Coolants were air, water, water-cooled copper plate, etc. As a jet’s disperser it was also applied for creation of the liquid metal protection of experimental tokamak.

The electromagnetic batcher implements the controlling capillary disintegration of the liquid metal jet in the range 100...400 Hz. The diameter of the metal spherical granules is determined by the resonant frequency of a jet at the first harmonics, which is approximately \( \omega = 0.23 u/d \) for the low viscous melts [2,11,13]. Here \( u \) is the flow velocity and \( d \) is the nozzle’s diameter. A diameter of the particles producing due to a jet’s decay is roughly estimated as \( d_0 = 1.88 d \).

Because the capillary forces are growing inversely proportional with a decrease of the nozzle’s diameter, the control of a jet’s disintegration is available up to the nozzle’s diameter of about 1 mm. Afterward, the Coanda effect makes the jet chaotically directed flow from the nozzle. The jet’s type granulators produce particles of a size over about 2 mm. Despite their advantage in getting nearly ideal spherical granules of the same size, there is limitation to the size.

The granular technology requires particles sometimes substantially below 1 mm. Therefore the theory of parametrically controlled disintegration of the liquid metal film flow has been developed [2, 4], and the methods and devices for film granulation were invented [7-11], to produce granules in the range of 0.5-1.5 from the average size, but they practically do not have any limitations on a size of the producing granules up to the micrometer scale.

A. Phenomenon of jet flow transformation into film flow

Forming the thin film flow is the following fascinating phenomenon (Fig. 1). Vertical jet transforms into a horizontal thin film flow. For the shock of a jet on horizontal disk, the momentum conservation law must be considered.

The mass of amount of jet’s liquid, which is abruptly decelerated from the velocity of a jet to a zero velocity of a disk, during small shock time \( \Delta t \), is \( \rho c \Delta t S \), where \( \rho \) is density of liquid, \( c \) is the speed of sound in this liquid medium (e.g. for water about 1500 m/s), \( S \) - the cross-section of a jet. This mass multiplied by a jet’s velocity yields a momentum of the decelerated part of a jet due to a shock on disk. Momentum of the decelerated part of a jet is equal to the impulse of force created by jet on the disk due to a shock: \( PS \Delta t \). Then \( P \) is computed as the pressure in collision. The momentum conservation for the shock is \( P \cdot b \cdot \Delta t = \rho \cdot c \cdot \Delta t \cdot b \cdot u_{00} \), where \( S = b \cdot 1 \). Then \( P = \rho \cdot c \cdot u_{00} \), so that it is much higher than a normal action of the jet on a plate by a smooth flow equal to a kinetic energy of the jet, \( P = 0.5 \rho \cdot u_{00}^2 \). For instance, for water jet 1 m/s the pressure in a shock is about 1.5*10⁶ N/m², which is 3000 times higher than the normal pressure from the same jet flow caused on a plate (500 N/m²) by a smooth flow.

![Fig. 1 film flow formation on a disk due to shock of a jet on a disk](image)

The momentum conservation for the film flow is:

\[ \rho \cdot c \cdot u_{00} = 0.5 \rho \cdot u_{0}^2, \]

where follows

\[ u_{0} = \sqrt{\frac{2 \rho \cdot c \cdot u_{00}}{a \cdot b \cdot u_{00}}}, \quad a = b \cdot u_{00} / u_{0}. \]  

In the above conditions \( u_{00} = 55 \text{ m/s}, \ a = 0.018 \cdot b \) is computed, where from yields \( a = 0.09 \) mm for \( b = 5 \) mm (a jet of 1 mm width, with velocity 1 m/s creates less than 0.1 mm thick film flow with a speed 55 m/s!). The viscous dissipation was neglected; therefore, these values are slightly overestimated.

B. Parametric control of the film flow decay

The moving liquid film can be disintegrated into the drops of given size depending on a frequency of the parametric excitation, with the comparably low energy consumption. In the other case, the system of solitons throws off drops like a series of the unit jets do in a phase of vibration modulation. The third case is available with a shock wave on a jet, at the high vibration Euler numbers (10-100).

Controlled fragmentation of the jet and film flows and the drops’ formation due to this is of interest for metallurgy, chemical technology, new material science, etc. These phenomena must be considered altogether because the real processes are complex, e.g. solidification of the drops, form of the solidified granules and their distribution by sizes in the range stated. Examples of parametric decay of the jet and film flow using the vibration and/or electromagnetic field (current) are shown in Fig. 2. The multiple series of the drops are being produced through controlled disintegration of the jet or film flow on a vibrating plate or under electromagnetic forces:
By the low vibration Euler numbers, the film flow decay is ineffectively controlled (Fig. 2b). The drops are produced from the edges of the vibrating film flow. Under such conditions, only some regularization of the process is available, e.g. twice narrowing the drops’ sizes distribution.

Radial film flow is formed from vertical jet 1 transforming into a film flow on a horizontal plate as shown in Figs 2, 3. Film flow is under control of an electromagnetic field, e.g. organized by the electromagnetic wave in the form:

$$h=h_m(r,\varphi)\exp(i(kr+m\varphi-\Omega t)),$$

created by the inductor 2 in Fig. 3c installed both over the film flow and below the disk. The wave numbers $k, m$ by coordinates $r, \varphi$ and a frequency $\Omega$ of the electromagnetic field can be regulated, $h$ is a vertical component of a strength of the magnetic field, $h_m$ is its amplitude.

Also, the vertical harmonic vibration of the horizontal plate is considered as:

$$\ddot{z} = g_v \cos \Omega t,$$

where $g_v$ - acceleration of vibration, $\Omega$ - frequency.

Parametrically controlled disintegration of the film flows into the drops of given size was studied on the mathematical models and experimentally. Control was performed by the electromagnetic field and vibrations and by their combination. The film granulation machines invented [6-16] are unique. They are distinguished by simplicity, the developed specific surfaces of a melt and an intensive cooling of the granules in the liquid nitrogen film flows.

These machines allow producing particles of the strictly given sizes in the different regimes depending on a frequency of the parametric action, a flow velocity at the nozzle and a diameter of the nozzle. It is possible to produce the amorphous identical particles due to a high cooling rate, in a narrow range of particles’ distribution by the sizes. In contrast to the earlier developed jet granulation machines, the film granulators allow obtaining granules practically of any desired size, with a narrow distribution by sizes (deviation ~50%).

Actually, the film flow devices considerably surpass the traditional ones with a working liquid body being ecologically clean too. What is more, much high-efficient withdrawal, heat- and mass-transport, and the other processes and installations can be constructed on a basis of the film flows, especially in case of parametric film flow control.

C. Film flow dispersators and granulators

Inside view in a chamber and schematic of the film granulator with vibration control [16] are shown in Fig. 4, where: 1- vertical channel for liquid metal, 2- nozzle, 3- disk, 4- bar to vibrator, 5- membrane of vibrator, 6- vibrator, 12- box in chamber with liquid nitrogen, 13- cooling system.

Experimental study of the controlled film flow disintegration has been done using the invented and constructed facilities. Two have electromagnetic control devices, while another two had the vibration type controlling devices (with deep vacuuming of the chamber and with controlled nitrogen atmosphere in the chamber).

The uniqueness of the granulation machine includes the special vibration type control unit, which can work using the standard low-power vibrator modified by application of the resonance membranes for different vibration frequencies. Granulation machine was built on the principle of the parametrically controlled disintegration of film flow in the optimal modes of parametric oscillations, which were revealed.

Nitrogen atmosphere in a chamber and liquid nitrogen cooling system for the granules in the form of a series of
liquid nitrogen film flows below the liquid metal film flow to avoid the heat transfer crisis. The highest intensity of cooling rate $10^6$°C/s has been achieved.

After disintegration of a film flow into the drops, in a narrow range of the given size, the drops are moving through a series of the film flows of liquid nitrogen (the bell-type film flows). The cooling rate for the drops and particles was achieved (the world record for such case!), to have the amorphous structure of the metal.

D. Rapid solidification, the highest cooling rate

The cooling rate $10^6$°C/s was achieved for the flakes in the USA (the Al drops were shot with a high speed on the water-cooled Cu plate). But the flakes are not as good as the uniform granules of a nearly spherical form are for a production of the amorphous materials. Erwin Mayer invented a novel method, which was later called "Hyperquenching" [17], and then developed it during about 25 years.

This was a breakthrough in solving the problem, which the Royal Swedish Academy of Sciences emphasized as the key role of the hyperquenching method for the 2017 chemistry Nobel prize (E. Mayer has often interacted with J. Dubochet starting from the first work [17]). This method allowed achieving the cooling rate of up to $10^6$°C/s, sufficient to beat a formation of the ice crystal for pure water, and for all aqueous solutions.

E. Three new phenomena of the controlled film flow decay

We discovered in detail the 3 new phenomena of the resonant, soliton-like and shock-wave disintegration of a film flow experimentally and theoretically. The vibration type control of a disintegration of the liquid metal film applied in the facility in Fig. 4. The soliton-like disintegration of a film flow and the shock-wave disintegration of a film flow have been implemented in this granulation machine. The first one is observed in Fig. 5, where the drops are levitating over the vibrating plate.

Fig. 5 start of the vibrational spraying of film flow: $r_0 = 3.75 \times 10^{-3}$ m, $0.2 m/s$, $\Omega = 1880 Hz$, $We = 342$, $Fr = 13.6$, $Re = 7.44 \times 10^3$ (upper) and partial vibro-spraying: $\Omega = 1750 Hz$, $g_0 = 160 g$ (lower)

It looks like a chaotic process but it is not chaotic indeed. A process is regularly controlled, and the drops are produced from a series of the solitons, which all are nearly uniform on the plate vibrating in a vertical direction. In this regime, there were also cavitations on the vibrating plate, not studied yet.

The shock-wave regime was got at ten times higher vibration Euler number and looked as conical shock-wave on the vertical jet, producing the fine particles (mkm size). The film flow does not exist in this case. This regime may be used for production of ultra-small particles or for the spraying. The results in Figs 5, 6 were obtained using water because illustration of the controlled disintegration of the liquid metal film flow is not available.

Spraying is going directly from the surface of a disk but there is also some short flow on a disk. By $u_0 = 2.8 m/s$ results: $\Omega = 490, 805, 1610, 3100 Hz$, and $\Omega = 1610Hz$ yields nearly total spraying, while the other regimes give just spray at the edge of film. The regimes of soft loosing of instability show a gradual increase of oscillations’ amplitude of a disk, which leads to a monotonous growing of amplitude of the film flow perturbations. At $Eu_s \approx 1$, monotonous increase of vibration acceleration $g_0$ leads to an explosive collapse of a film, its spraying into the smallest droplets invisible to eyes [4, 15].

The conic shock wave is passing to a jet head from a film: the jet turns out with the sharp nose (forming lines of a shock wave) touching a disk surface (Fig. 6 to the right). The drops are in a cone formed around the jet by the shock wave.

Fig. 6 vibration soliton-like (left) and the shock-wave film decay (right): $r_0 = 0.8 \cdot 10^{-3}$ m, $u_0 = 0.2 m/s$, $\Omega = 450 Hz$, $v = 250 g$

The vibration accelerations providing $Eu_s \approx 1$ correspond to a case of soliton-like solutions. At $Eu_s \approx 1$ there is a shock wave passing to a vertical jet, and the film disappears, there is a rigid mode of stability loss (explosive transition of a film to small drops, spraying from a disk surface in a jet contact place). Emergence of solitons at $Eu_s \approx 1$ leads to that dispersion of waves in radially spreading film disappears and separate solitons under the influence of vibrations work as separate vertical jets, from which crests the drops break.

IV. THE DISTRIBUTION OF GRANULES BY SIZES

For checks of uniformity of disperse structure on the above device with the nitric atmosphere, the Gallium granules were produced (Fig. 7). The equivalent diameter is

$$d_{eq} = \sum n d_i / \sum n_i \approx 0.88$$

The particle size distribution is given in the Table 2:

<table>
<thead>
<tr>
<th>n</th>
<th>12</th>
<th>24</th>
<th>25</th>
<th>19</th>
<th>15</th>
<th>15</th>
<th>9</th>
<th>14</th>
<th>8</th>
<th>3</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>d</td>
<td>0.5</td>
<td>0.6</td>
<td>0.7</td>
<td>0.8</td>
<td>0.9</td>
<td>1.0</td>
<td>1.1</td>
<td>1.2</td>
<td>1.3</td>
<td>1.4</td>
<td>1.5</td>
</tr>
</tbody>
</table>
where: 15 sets of granules by 10 pieces were three times considered, $n$- quantity of granules, $d$- diameter (in mm).

The dispersive structure is uniform. The developed new principles of a granulation allowed constructing the film MHD- and electrodynamic granulators [11-13]. They don't have analogs in the world, considerable wider range of the produced mono-granules, and simplicity of a design and low-energy consumption. Semi-industrial granulator was successfully tested [15, 16]. This direction is perspective for many technologies [2-4, 16, 18, 19].

In electromagnetically controlled Gallium film flow disintegration [4, 14], the drops were nearly uniform by sizes as seen from the Fig. 8. Granules were prepared for production of the new materials. Distribution of the granules by sizes was narrow, deviation about 50% (Figs 9-11):

For comparison, the distribution of the granules by sizes in the process of free film flow decay like the ones shown in Figs 1, 2, was broader than the given value (10 times and even more). Granules from jet granulator are nearly ideally spherical (Fig. 12). The centrifugal granulators produce also very wide range of particles, which is shown in Fig. 13 (granules are after separation by size, which is wider than shown in figure).

The electromagnetic disintegration of the film flows shown in Fig. 8 (to the right) was done in a vacuumed chamber with the nitrogen atmosphere. The weak vacuum in a chamber (e.g. 1
mbar) did not allow working with some melts due to strong thin oxide film on a surface of the liquid metal (Fig. 14):  

![Fig. 14. Gallium film flow with oxidation of the melt](image)

Granulation technologies have specific applications, one of which is production of the new materials from the uniform particles having the amorphous structure. Powder metallurgy has its own specific application where the particles’ uniformity and structure are not among the main requirements.

In case the granules of over 2 mm are needed, the best are the jet-type granulators [11-13, 16], which produce spherical particles with a deviation in sizes less than 5%. The price of such granules is nearly the same as for example from the centrifugal granulation machines, where the size distribution is wide (over 10 times in both sides from the required).

This film granulator has refrigerating conditions and solidification of the drops into granules, at which their adhesion is excluded. These conditions are defined by the corresponding choice of level of coolant (liquid nitrogen) in a cooling system and its continuous circulation. Besides, the creation of the film flows of coolant is provided improving conditions for rapid solidification of drops into granules.

V. CONCLUDING REMARKS

The theoretical and experimental studies of parametric film flow decay showed that in case of flows of such melts as Gallium, Aluminum, etc. the oxide film formed on a free surface of melt is of great importance even in the presence of small amount of oxygen. Such oxide film creates so strong capillary forces that only electromagnetic fields with induction over 1T or vibrations with acceleration over 100g (10^3 m/s^2) could fight it. Oxide film is non-uniformly distributed on a melt surface, therefore the Marangoni effect is prevailing. The controlled atmosphere (nitric, for example) or vacuuming the device excludes a randomization of a system.

The physical modeling of disintegration of the film flow under electromagnetic fields and vibrations proved correctness of the basic theoretical results and possibility for revealing the new exciting valuable phenomena. The developed granulation technology based on the controlled film flow phenomena allow obtaining the unique amorphous and special particles (e.g. with internal filling oriented in an electromagnetic field) for a production of the super hard metals, as well as the materials with the functionally unique properties.

REFERENCES


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