Production and Use of the Amorphous Granules and Powders

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***Abstract*—**The problem of granulation is very wide by the granulated materials, as well as by their application. In the paper, some history of the granulation problem during over century and modern applications of the metallic granulates and amorphous materials are given at the beginning. Then the specific own 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. Such granules of the given size and form are needed for the new material science. The basics of developed theory of the controlled jet and film flow disintegration with further rapid cooling of the drops obtained after flow disintegration are presented together with the new patented granulation devices. The developed methods and devices can be used for production of the amorphous or close to amorphous granules in a wide range of the given sizes, with very narrow (plus-minus 50% deviation of size from the average one).

***Keywords*—**Granules, powders, amorphous, methods, rapid quenching, industrial applications.

I. The Problem Statement and History

Granulation of materials is widely used in a number of applications such as agriculture (fertilizers), metallurgy, chemical technology, pharmacy, etc. In many industries, granulation represents important preliminary stage in a manufacturing of a product. In some cases, the granules are intended for a direct sale as a final product. The reasons for transforming the powders or dust into granules are: improvement of flow properties (agglomeration of filter dust), increase bulk density (agglomeration microsilica), and avoidance of the demixing effects (the ceramic press bodies). Development of amorphous metallic granules is perspective direction connected with a production of the new functionally unique materials.

An excellent ratio of weight to strength, together with appearance of the high-quality surface, made the *magnesium alloys* particularly suitable for the mobile applications in the consumer goods sector. In automotive, the magnesium die castings are increasingly replacing steel- and aluminium-based components. This is a major factor of the total weight reduction for the vehicles representing a valuable contribution to achieving the agreed climate targets. An improved the weight/strength ratio in a comparison to the aluminium alloys has some new applications: aviation, aerospace and the other industries. Also, the magnesium granules (coated and uncoated, size of particles over 160 μm) are used to reduce sulfur in the pig iron. The sequential process with lime and/or calcium carbide as the desulphurization reagents uses the both, pure magnesium and Mg mixtures. They ensure a highly efficient reduction of sulfur to the lowest ratios in a short time of the running processes. Also, the magnesium powder (size less 160 μm) is used in pyrotechnics and for military purposes, the aluminium-magnesium - for space industry, etc.

Probably the first attempts to use the granulation technology for improvement of the metals were done after the 2nd World war by Forton H.R. (Method and apparatus for forming a powder from metals, 1945), Polysius Gmbh (Vorrichtung zum Granulieren von Pulver- oder Griessfoermigem Gut, 1952), Western Electric Co (Apparatus for making metal pellets, 1953), and US Steel Corp (Disc-type balling device, 1955). Hundreds of patents on the subject appeared starting from 1960-th. The first were Ibm (Amorphous alloys and process therefor, 1964), Matsushita El IndCoLtd (Ferromagnetic materials, Magnetic permeability material, 1966), United Aircraft Corp (Process for filamentary materials, 1966 and Electrostatic coatings, 1967), Monsanto Co (forming fibers and filaments directly from melts of low viscosities, 1969), Uddeholms Ab (Method of making granulate, 1970).

Metglas, Inc. (then Allied Signal, NJ) pioneered (1970s) the development and production of the amorphous metal, a unique structure alloy, in which the metal atoms are randomly distributed. The key to the company's proprietary manufacturing process is the rapid solidification of the molten alloy at a rate of approximately 10^6 ^{0}C/s. Amorphous metals have unique non-crystalline structure, excellent physical and magnetic properties, as well as strength and hardness with the flexibility and toughness.

Then it was continued by: Fuji Photo Film Co., Ltd (Ferromagnetic metal powder comprising lead and method for making the same, 1974), Allied Chemical Corporation (Method of producing amorphous cutting blades, Titanium-beryllium amorphous alloys, 1975; Metallic glasses with high crystallization temperatures and high hardness, 1976), The Research Institute for iron, steel and other metals of the Tohoku University (Iron-chromium series amorphous alloys, 1975), International Business Machines Corp (Method for inducing uniaxial magnetic anisotropy in an amorphous ferromagnetic alloy, 1974; Controlled catalyst for manufacturing magnetic alloy particles with selective coercivity, 1975), University of Pennsylvania (Method of making amorphous metallic alloys with enhanced magnetic properties using the tensile stress, 1976), Bell Telephone Laboratories, Inc. (Electric fuse, 1976).

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Afterward many other companies joined to: Gen. Electric, United Tech. Corporation, Kokusai Westinghouse Electric Corp. Denshin Denwa Kabushiki Kaisha, Western Gold and Platinum Company, Siemens Aktiengesellschaft, Tokyo Shibaura Denki Kabushiki Kaisha, Electric Power Res. Inst., Inc., Tsuyoshi Masumoto, etc.

Recently the next efforts were made: Glassimetal Technology, Inc. (Bulk iron-nickel glasses bearing phosphorus-boron and germanium, 2013), Yale University (Bulk metallic glass nanowires for energy conversion and storage, 2011), Hon Hai Precision Industry Co., Ltd. (Coated article and method for making the same, 2011), Lawrence Livermore National Security, Llc (Amorphous metal formulations and structured coatings for corrosion and wear resistance, 2011).

II. The accomplishments and challenges

For the moment, hundreds of publications and practical achievements were reported by companies in granulation, amorphous materials, and different products of them. Let's shortly mention some of the known results [1-36]. The novel different metal alloy compositions in the amorphous state have been obtained in the world, in the USA, UK, Japan, India, Russia, Ukraine, and other countries.

These new materials were superior to such previously known alloys based on the same metals. The new compositions were quenched to the amorphous state due which they obtained desirable unique physical properties. E.g., a novel of wire of these novel amorphous metal alloys was disclosed, as well as of other compositions of the same type. A limited number the amorphous (noncrystalline, glassy) metal alloys have been prepared by a rapid quenching of molten alloy of a suitable composition. Alternatively, a deposition technique is used when a suitably employed vapor is deposited, sputtered, electrodeposited, or chemically deposited to get the amorphous metal.

Production of the amorphous metal by the known techniques, either through a rapid quench of the melt or through a deposition, severely limits the form in which the amorphous metal is obtained. When the amorphous metal is obtained from the melt, the rapid quench is generally achieved by spreading of the molten alloy in a thin layer against a metal substrate (Cu or Al) held at the room temperature or below it. Typically, the molten metal is spread to a thickness about 0.05 mm, with a cooling rate of about $l0^{6}\ {}^{0}C/s$ [19, 20].

Various methods have been invented for rapid quenching by spreading the molten liquid in a thin layer against a metal substrate [2-5], e.g. a gaseous shock wave propels a drop of molten metal against a substrate of a metal [2], the piston and anvil technique [3]; the casting technique [4] when a molten metal stream impinges on the inner surface of a rapidly rotating hollow cylinder open at one end; and the method of rotating double rolls [5], in which the molten metal is squirted into the nip of a pair of rapidly rotating metal rollers. These methods give small foils or ribbon-shaped samples with one dimension much smaller than the other two, therefore they are not so useful in a practical matter because some important applications are severely limited due to difference in properties in one of the directions (a layered material has weak properties).

Amorphous metals are not formed without sufficient cooling. Typically, they must have at least one size, small enough to allow a rapid heat removal from a solidifying material. To avoid crystallization, the cooling rate necessary to achieve a stable amorphous state, depends on the composition of the alloy. Some alloys are obtained in amorphous state with a lower cooling rate, which in practice can be more easily obtained or can be obtained with a greater thickness during melt quenching. There is a small set of compositions, for which an amorphous state is easily got. A question for research, which alloy is the best glass-forming agent. The problem is obtaining amorphous metal with predetermined processing conditions.

Amorphous and crystalline states differ in the corresponding periodicity of the long-range or its absence. Compositional ordering in alloys is probably different for two states because of differences in their diffraction behavior of x-rays. Their measurements most often distinguish between crystalline and amorphous substance. Amorphous substance exhibits a slowly varying diffracted intensity similar to liquid, while crystalline materials give a much more rapidly varying diffracted intensity.

The physical properties being dependent on the atomic arrangement are unique concerning the crystalline and the amorphous state. Moreover, the physical properties, depending on the arrangement of the atoms, are unique with respect to the crystalline and amorphous states. Mechanical properties are significantly different for the two states; e.g., an amorphous Pd band with 0.005 cm thick is relatively ductile and stronger and will be plastically deformed under a sufficiently strong bend, whereas a similar crystalline strip of the same composition is brittle and weak.

The magnetic and electrical properties of the two states are also different: the amorphous state passes to the crystalline state by heating to a predetermined high temperature with the release of the crystallization heat. Cooling of molten metal to a glass is quite amazing and different from cooling it to a crystalline form: in the first case, the liquid solidifies continuously over a range of temperature without a discontinuous evolution of a heat of fusion, while the crystallization is a thermodynamic first order transition associated with a heat of fusion and a specific temperature.

New interesting compositions were done mainly of Fe, Ni, Cr, Co and V. Although some of them, e.g. Fe PC Fe Co Co PB Fe BC and Ni PB, have previously been described as being quenched from a melt to an amorphous state, it has been found that some new, excellent and useful compositions can be obtained by adding small amounts (0.1 to 15 atom%, but preferably 0.5 to 6 atom%) of some elements, such as Al, Si, Sn, Sb, Ge, In or Be, to alloys.

These alloys become much better glass formers, that is, an amorphous state is easier to obtain and, moreover, is more thermally stable. It was found that the incorporation of small amounts of Al, Si, Sn, Ge, In, Sb or Be to the alloys of the group consisting of Fe, Ni, Co, V and Cr; and Y represents elements from the group consisting of P, B, and C. Excellent glass-forming alloys are obtained. The selected alloys can be relatively more consistent and easily quenched to amorphous state than previously thought with known Fe-Ni-Co based alloys. Moreover, these alloys are more stable.

III. Granules and powders

Powders of amorphous metals containing the particles of 0.001 to 0.025 cm can be obtained by spraying a molten alloy into the drops of this size, and then quenching drops in a liquid coolant (water, chilled brine, nitrogen). These alloys may contain small amounts of the other elements contained in the commercial Fe or Ni alloys as the primary source of metals. Such elements, Mo, Ti, Mn, W, Zr, Hf, and Cu, may be added subsequently. Cooling of the molten stream to form an amorphous metallic wire was achieved by spraying the melt into water or a cooled solution. The cooling rate experienced by the jet of molten metal during the quenching depends on the cooling method used and diameter of a jet.

The method of cooling determines the speed at which the heat is removed from surface of a jet. The diameter determines the surface-to-volume ratio and the amount of heat to be removed per unit area. E.g., it is necessary to meet the requirements by the cooling method, the diameter of the jet and the alloy composition to obtain an amorphous metal wire [23-25, 35] in accordance with the invention [23-25].

These amorphous alloys and wire products have valuable physical properties: high compressive strength, elasticity, good corrosion resistance, unique magnetic properties. In some compositions, it is extremely ductile in the amorphous state. Samples can bend over radii of curvature, less than their thickness, and can be cut with scissors. In addition, using these plastic samples, a tensile strength of up to 350,000 pounds per square inch was obtained under hardening conditions. Thus, thermal treatments often give crystalline materials to obtain high strength, are eliminated by amorphous metal alloys.

Amorphous alloys provide a durable material that is resistant to corrosion; selected compositions of these amorphous alloys are relatively stable to the concentrated sulfuric, hydrochloric or nitric acid. For example, the amorphous Feg Ni P B Al is several orders of magnitude less reactive than the stainless steels with the concentrated hydrochloric acid [29].

The preferred novel compositions are characterized by the formula M Y Z [29] wherein M is a metal from the group of iron, nickel, cobalt, chromium and vanadium and mixtures thereof; Y is an element from the group of phosphorus, boron, and carbon, and mixtures thereof; and Z is an element from the group of aluminum, antimony, beryllium, germanium, indium, tin and silicon and mixtures thereof, and wherein the relative proportions in atomic percentages from about to 80, B from about 19 to 22, and C from 1 to 3.

These amorphous metals may be suitable for a wide range of applications, e.g. alloys with M iron (e.g. Fe P C Si Al) are of particular interest due to low cost and relatively high strength; Ni Fe P B Al are of significance (easy formation in combination with high strength and corrosion resistance); alloys with high chromium content (Cr P B Si) have the exceptional hardness and corrosion resistance. Bulk metallic glasses (BMG) are alloys that can be solidified into a diameter larger than 1 mm without detectable crystallization. The amorphous solid state satisfies the thermodynamic definition of a glass so that heating above a glass transition temperature leads to reaching a metastable super-cooled liquid region before crystallizing. There are many known methods for producing amorphous metals [23-33].

The material properties and the ease of manufacturing amorphous metal specimens depend on the methods used, e.g. the invention [23] relates to a granulating a stream of molten metal, which falls from a launder down into a liquid cooling bath contained in a tank. The melt divides into droplets in the liquid cooling bath and the droplets solidify in solid granules. The flow of cooling liquid has a velocity below 0.1 m/sec. The distance from the outlets of the launder to the surface of the liquid cooling bath is kept less than 100 times the diameter of the metal stream measured as the metal stream leaves the launder.

From the Swedish Pat. No. 439783 it is known to granulate FeCr by allowing a stream to fall down into a water-containing bath wherein the stream is split into granules by means of a concentrated water jet arranged immediately below the surface of the water bath. This method yields a rather high amount of small particles. In addition, the risk of explosion is increased due to the possibility of trapping water inside the molten metal droplets.

The Iscor Saldanha Steel installed the granulator to accommodate an excess iron production from the Corex plant [27]. The granulation of iron has proven the most cost-effective method compared to the traditional such as the sand bed pooling. And the prime metal product showed solid performance as a raw material feed into the steelmaking operations. Also the use of a metallic feedstock with a high level of Si and C and without any content of the gangue or unreduced oxides enhanced the steelmaking operation.

IV. Granulation and use of cobalt

Decrease in the cobalt particle size has a dramatic effect on the processing behavior of submicron WC/Co materials [13]. As finer cobalt powders are utilized, the issues of dust generation and environmental stability (i.e. oxidation resistance) are a concern. Therefore, the cobalt powders were granulated with an organic binder to produce a free-flowing product with a reduced level of dust generation and improved oxidation resistance. The effects of granulated cobalt in the processing of superfine WC powders were examined and compared to nongranulated cobalt powders.

Cobalt is commonly used in the manufacture of WC hard metals for a variety of applications such as cutting tools, drills, seals, mining and masonry tool bits. In order to take advantage of these WC powders, finer cobalt powders must be used to ensure the production of homogeneous, high-quality WC/Co materials. Advantages of finer cobalt powders have been summarized in [13, 14] for the Ultra Fine, Sub Micron, Extra Fine HDFP and 400 mesh powder grades, which correspond to cobalt powders with a size 0.4, 0.8, 1.5, 4.0 mkm, respectively (Table 1).

Many different methods are commercially available to granulate the fine powders [16-18]. During granulation, a force acts on the powder to bond it together into larger granules. The forces bonding the powder together can be classified into three categories:

1) capillary forces generated when a liquid is used to granulate a powder together; the strength of these granules is generally low;

2) adhesive bonding; a solidified binder phase adheres to the surface of the powder bonding particles together into larger granules;

3) the third force for granulation is solid bridging. The binder phase is usually an organic material (paraffin wax, PVA, etc.). The strength of granules depends upon amount and type of the binder phase present.

Table 1. Characteristics of the cobalt powder grades

	Ultrafine	Submicron	Extra Fine HDFP	–400 mesh
FSSS (um)	0.4*	0.8	1.5	4.0
O_2 (%)	0.9	0.6	0.2	0.4
D_{50} (um)	4	5	7	15
AD (g/cc)	0.6	0.8	1.1	2.2
S.A. (m^2/g)	4.5	2	1	< 1

After discovery of the first metallic glass (1960) [1], the amorphous metals were made in a variety of compositions, mostly fabricated as thin ribbons less than a millimeter in thickness because fast cooling rates (up to 10^6 $^0C/s$) have been required to retain the metastable amorphous phase. Recently, a new class of the amorphous metals developed has required the cooling rates of only 1 $^0C/s$ [6]; such alloys, as Zr41.2Ti13.8Cu12.5Ni10Be22.5 (at%), can thus be processed in bulk form.

V. Amorphous metals, large-scale atomization, advantages in industrial use

The amorphous metals generated much interest [10], both in basic research and structural applications, because of their near-theoretical strength to stiffness ratios and extremely low damping characteristics [7]. And a number of amorphous metals revealed high corrosion resistance [8-12], which was explained by their structural homogeneity.

An extraction step to the final refining in the pyrometallurgical smelting process requires melts casted and/or comminuted for further taking up into solution or leaching [22] using mostly the hydrometallurgy. A general practice with a friable material having the properties associated with the higher sulfur, carbon and silicon levels is to granulate and in many cases to mill them, to develop a surface area for the optimal leaching. But in case of the metallic melts, a milling can be unfeasible thanks to the ductility of the granules. Water solidification is applied for producing the fine particles through a process of the granulation or atomization (40 mkm without a milling circuit).

Hydrometallurgy has been used for centuries in the precious metal refining but it is now widely used for the metals like Co,Cu,Ni,Ta,Nb, etc. Maximum powder sizes (250 mkm) and median sizes (40-75 mkm) are normally preferred. Atomization is widely used for processing Al, Zn and Cu alloys at rates of 0.5-3 t/h. The main concept of liquid spraying was known to Agricola who granulated a molten metal already in the 16^{th} century [22].

In XIX century, atomization of tin and solder was introduced for the manufacture of pastes for plumbing. Then 100 years ago Prof. Hall (USA) patented spray nozzles for aluminium, applied in explosives (1915). He used compressed air or the easily accessible steam for spraying. The air is still mainly used for the Al processing, zinc and copper alloys at a rate of 0.5-3 ton/h. Processing of copper alloys and cast iron was carried out using air and water jets during 1930-1940. Dr. Jones was a pioneer in the treatment of Fe, Ni and Co alloys (England, 1940-1950).

A large-scale water atomization (10-30 ton batch) of the carbon steel powders was carried out. There are factories with a capacity up to 50 t/h (world production is about 1 Mt/y) and several factories more than 200000 t/y. This low-cost melt processing technology is now commonly used in the metallurgy, especially for the high-temperature melts. Our methods based on the controlled jet and film flow disintegration are more complex and allow producing the small particles in a strictly defined size range but it is available only approx to 10^3 ^0C. Over this temperature, we did not solve a problem with the durability of materials for our granulation machines, for the moment.

Atomization allows the conversion of the liquid melt to powder in one straightforward operation. Apart from the advantage of having one less step in the process compared to granulation and milling and four less compared to casting, crushing and milling, there is also an advantage of dispensing with all attrition components in the milling process.

Thus, it is attractive considering the atomization to replace milling and grinding when extraction of Cu, Ni, and Co from sulfide ores and to use similar technologies to extract metals from the landfills Cu, Ni, Co, where a slag is processed through smelting. Alloys obtained during this reprocessing are low in sulfur and hence ductile, and are not suitable for processing by crushing and/or milling.

While atomization with high-pressure water is related to water granulation, the much higher water pressure (20-200 bar compared to the 2-6 bar for granulation) significantly affects the design of the equipment.

The granular product has a high bulk density, 3500-4500 kg/m^3, for penetration into the slag layer during the addition, while the shape and size provide for rapid melting and dissolution in a hot metal melt. The generation of fine particles, defined as a material less than 4 mm, formed during the processing, packaging, and loading of FeCr producers, etc., was studied [21]. The comparative data to describe the difference in the fines, from handling and transporting the purchased HC FeCr product by 10-50 mm in comparison with the product of granular HC FeCr was made. These granules were to almost 99% over 4 mm size, no dust generation.

The weight and size, as well as the homogenous and clean analysis of the granulated material, are ideal from logistical and metallurgical points of view. Some large HC FeCr granules were during tumbling broken into two pieces but with no major fines generation. Tumbling of crushed HC FeCr generates fines and losses at some 10 times higher levels compared to granulated HC FeCr. The combined figure of material losses and fines (<4mm) was reported a total of 7% for crushed material as compared to 0.7% for granulated one.

The need for increasingly better steel grade products and higher quality levels requests the raw material, such as granulated ferroalloys which has a homogenous composition, minimum pollutants or oxides and rapid melting properties. As many ferroalloy grades, especially low carbon grades, LC FeNi, LC FeCr, are added at the very final stages of the steelmaking process, then requirements on cleanliness become even more important. The granule size and shape also fit well to rapid and complete dissolution in the melt.

VI. Our Field of Study in Granulation of Middle Temperature Melts for New Materials Science

In a contrast to the above-considered 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 Celsius degrees per second in our experiments! Such fine structure metals are amorphous or close to amorphous metals. The idea of their creation appeared on the assessment of the iron's hardness by Academician Ya.I. Frenkel nearly hundred years ago (1925) [37]: theoretically the iron strength differs from the real one up to thousand times in some of its properties. The conventional production methods of the metallurgy lead to a deterioration of all properties of the metals due to slow cooling of a metal from its liquid to a solid state and a forming of the big crystals due to this instead of the amorphous structure.

The granular technology in the material science requires amorphous particles of nearly the same size (the uniform properties) produced from liquid drops, cooled down with a high cooling rate so that to avoid development of the big crystals, which can decrease the quality of a metal dramatically. The uniform particles fit the best to further production of the new material because from different particles the material produced has nonuniform special properties. This may decrease a lot the advantages of the amorphous final product.

The 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 being. Therefore granules of a small size are normally required, except some special applications other than the ones of the material science. Big spherical granules cannot be produced this way because the big liquid drops have non-spherical form and worse conditions for the rapid cooling during solidification. The capillary forces fall rapidly down by growing of a diameter of particles over 3 mm or so.

Our results in a creation of the highly efficient processes and the perspective technological devices have been 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 a further rapid solidification of the drops [38-43]. Some of these basics are presented in this Journal as a separate paper. The scientific novelty of this work consists in a development of the principles and the optimal regimes in a production of the amorphous granules for the creation of the super hard and the functionally unique composite metals. Different possible technical and technological applications are presented and discussed here for the new methods developed by us.

The new theory of the parametrically controlled jet and film flows has been developed by our team at the Institute of Electrodynamics of Ukrainian Academy of Sciences. The technological processes based on the discovered phenomena and the invented methods and devices for the materials' granulation were patented and implemented into metallurgical and space industry.

This technology and devices have no analogs in the world practice. In a development of this granulation machine the following three important problems have been solved:

- parametric control of a disintegration of the liquid metal film flow (a dispersing knot),
- stabilization of the phase transition boundaries (protection of the channel walls against destruction and, at the same time, protection of a liquid metal in a channel against pollution with particles from the channels' walls),
- selection of an optimum cooling regime for the granules with achievement of a highest cooling rate for the drops during their solidification into granules.

The first one was realized in a film granulation machine, while the other two have got an only theoretical solution for the moment.

One of the semi-industrial granulation machines is presented schematically in Fig. It is applied for the film flow granulation of the alloys of Zink, Aluminum, Magnum (Zn, Al, Mg), etc.

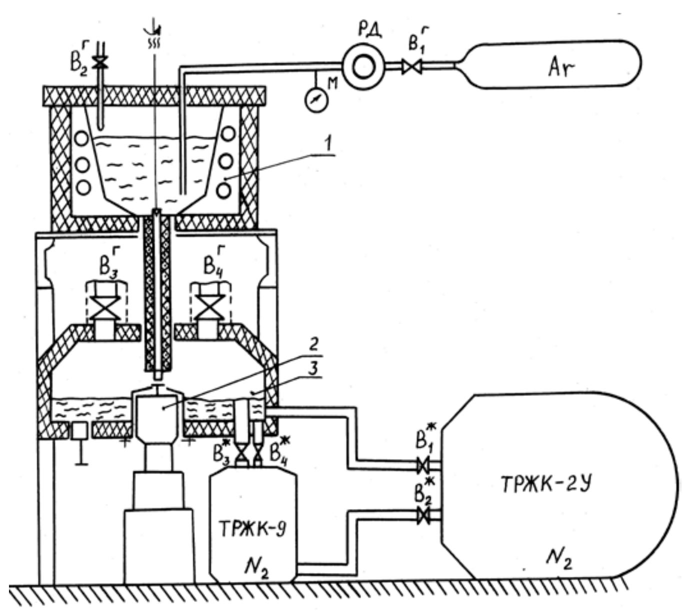

Fig. semi-industrial granulation machine: 1- furnace supplying liquid metal to the chamber 3 filled with liquid nitrogen, 2- vibration stand

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 ring veil of coolant is provided improving conditions for rapid solidification of drops and promoting growing cooling rate.

VII. Concluding remarks

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. The known granulation machines (e.g. centrifugal) produce a wide spectrum of particle sizes and have much below cooling rate so that cannot compete with our technology.

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