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[54] **METHOD OF PRODUCING METAL PARTICLES**

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[51] **Int. Cl.** **B01j 2/02**

[58] **Field of Search** .... 264/8; 18/2.5 RR; 425/8

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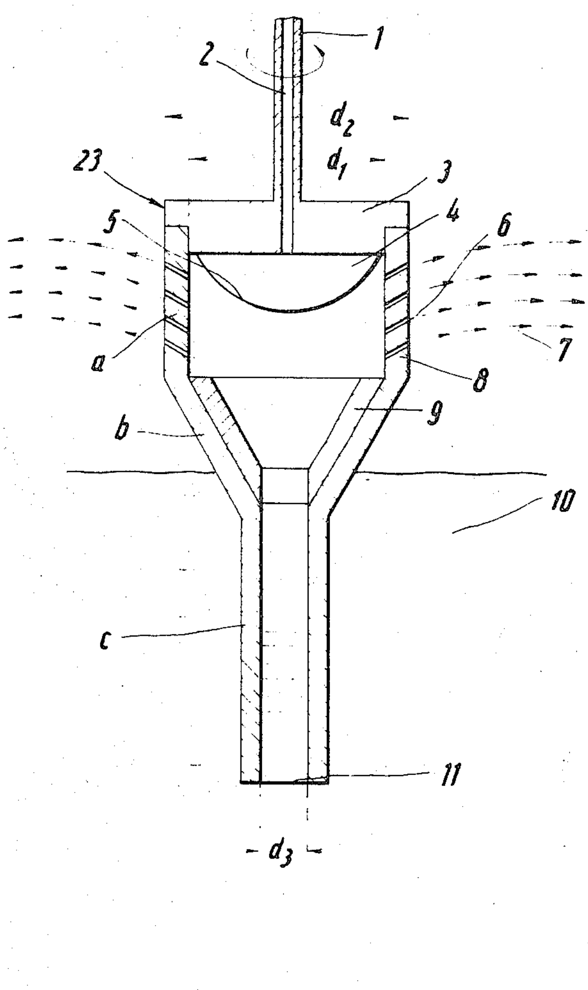
[57] **ABSTRACT**

A method of producing metal particles and especially smooth-surfaced round or elongated metal particles having a low surface-volume ratio whereby a rotating cylinder with perforated parts has a riser reaching into a bath of the liquid and is rotated at a speed such that molten metal cast from the perforations of the cylinder is replaced by a rising current of the molten metal.

1 Claim, 4 Drawing Figures



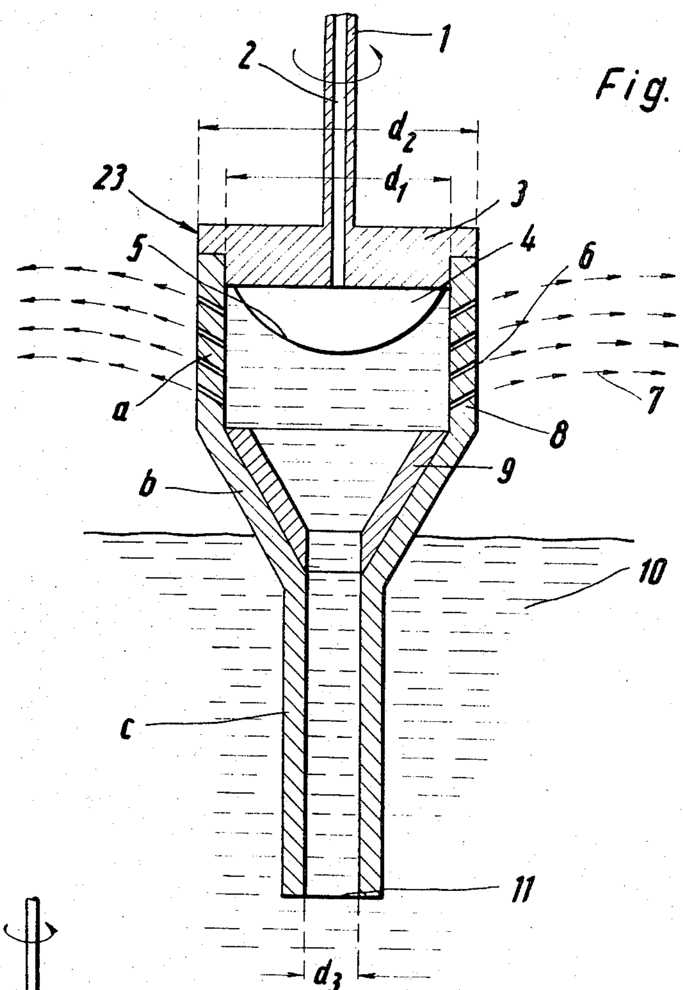


Fig. 1

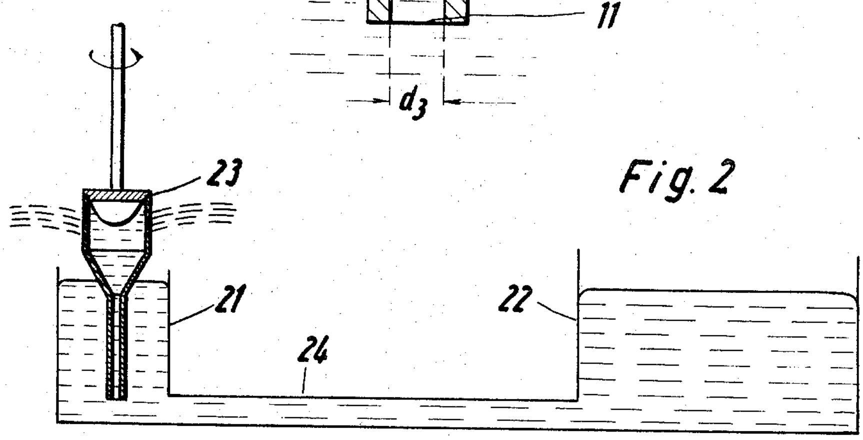


Fig. 2

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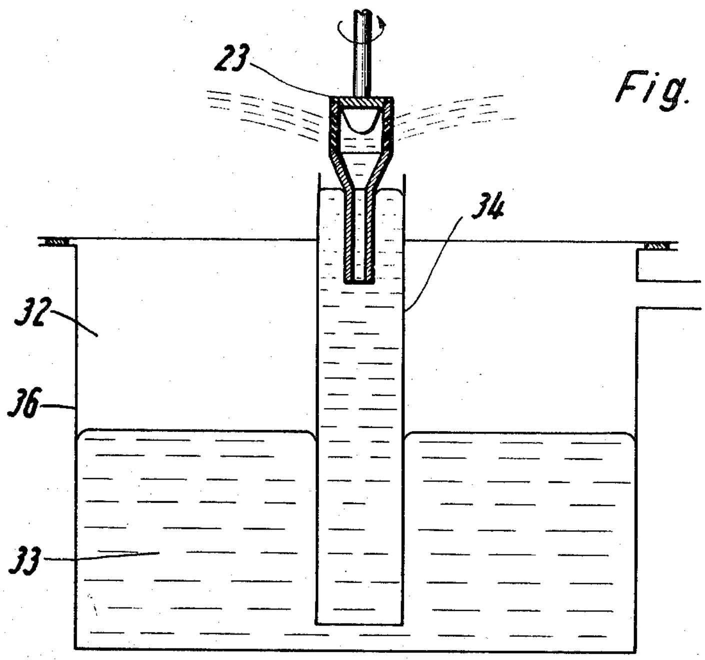

Fig. 3

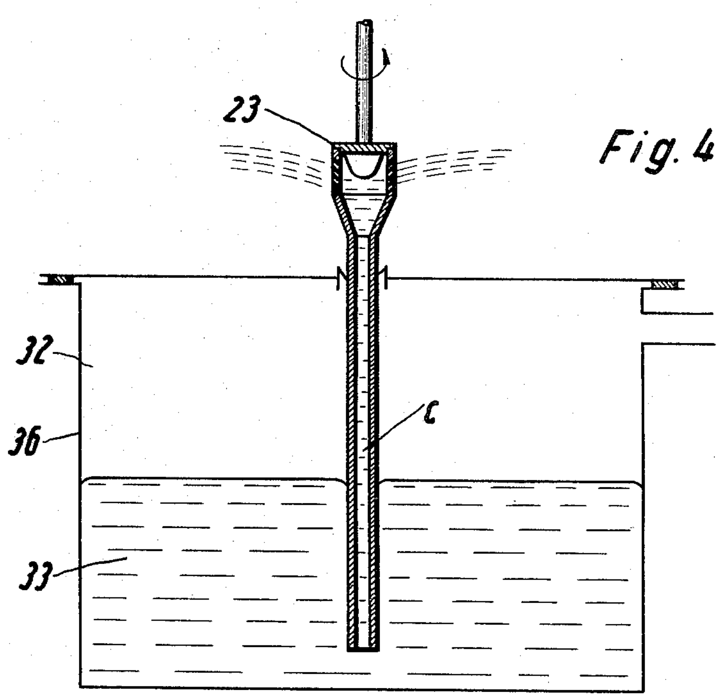

Fig. 4

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METHOD OF PRODUCING METAL PARTICLES

FIELD OF THE INVENTION

Our present invention relates to a method of producing metal particles; more particularly the invention relates to a system for producing metal particles with improved topography and physical properties and to the production of metal particles from metals which have not hitherto been used for such purposes.

BACKGROUND OF THE INVENTION

The production of metal shot, pellets and granules has long been carried out using various techniques and there are also a number of processes in which metal shot is used effectively. Most of these techniques required the controlled dispensing of droplets of the molting metal and the passage of these droplets through a gaseous or liquid environment which also serves for cooling. As a result of surface tension, the metal particles tend to form globules. Conventional processes of this type have not always yielded satisfactory results and, indeed, commercially economical shotting techniques may give rise to particles with poor topography (i.e., surfaces having crevices, angular portions, rough texture, pitting) or configurations which are not desirable for the particular task for which the shot is to be employed.

Also conventional shotting techniques cannot make use of certain metals which react readily with the surrounding atmosphere for which the production of small particles or granules, especially particles with a low specific surface (ratio of surface area to mass or volume) would be advantageous. For example magnesium shot cannot be produced by the conventional techniques but has a ready market, because the product is particularly desirable for chemical reactions (e.g., Grignard-reagent reactions). Magnesium shot of high purity and good mechanical characteristics is suitable for use in the production of sphaerolitic cast iron. Furthermore, modern techniques can be employed with metals which are available in a granular or shot form, especially if such metals can be produced in excellent quality and large quantities in an economical manner. Typical of these techniques are the direct rolling of sheets and/or the roll or die extrusion from high-purity granules, e.g., of magnesium, aluminum, lead, copper and zinc.

One of the known systems for producing metal granules with a limited specific surface area (ratio of surface area to volume or of surface area to mass) has made use of a centrifugal basket or crucible into which the molten metal is filled from above. The crucible may be provided with openings through which streams of the molten metal are ejected by centrifugal force as the crucible is rotated rapidly. The technique exploits the principle that a free falling stream of liquid is broken up by the surface tension into droplets. The problems with this method, however, were manifold. For example, the characteristics of the granular product were dependent upon the level of the melt within the crucible or centrifugal vessel and it was difficult to control this level or maintain the level sufficiently constant to produce consistently large quantities of metal granules of a uniform character. The melt in the rotating crucible has the tendency to freeze and to clog the openings or borings, since the required amount of heat is delivered to the crucible with the incoming melt, any interruptions or unregularities in the flow of the melt lead to the interruption of the production. Perhaps of greater importance is the fact that with higher melting metals and alloys the crucibles were required to be of ceramic and were relatively brittle, but had to be rotated at high speed. Attempts to reduce the angular velocity of the crucible, either failed to yield the desired quantity and quality of the particles, or required the use of larger crucibles with increased problems of structural stability. Frequently, it was not possible to control the flow of molten metal into the rotating crucible and the melt level therewithin often rose to the point that quantities of the molten metal were cast over the edge of the crucible and ruined the product. Moreover, since ceramic rotating vessels of massive construction were required, the openings in the wall of the crucible were relatively long (corresponding to the wall thickness) and often cooling of outermost portions of the melt within these openings lead to complete blockage of the system. As a practical matter, the rotating-crucible technique has not found success in the art of granulating highly reactive or higher melting metals, especially where high-quality, narrow-size range and readily contaminated particulate products are to be obtained.

It is, therefore, the principal object of the present invention, to provide an improved method of producing metal granules and particularly particles of metals which have not hitherto been economically produced in the form of shot.

Another object of this invention is to provide an improved method of producing metal particles of the character described, which will obviate the aforementioned disadvantages.

It is a further object of this invention to provide a method of producing high-purity metal granules or particles with a high surface quality in a narrow-size range at relatively low cost and high rates.

SUMMARY OF THE INVENTION

These objects and others which will become apparent hereinafter are attained, in accordance with the present invention, by a method of producing particles from a melt of molten metal which comprises rotating a cylindrical perforated spray head about its axis to centrifugally discharge a molten-metal melt from the interior of the cylinder through the openings or perforations, while drawing further quantities of the melt from a bath thereof the level of which may be variable as long as a dip tube remains immersed in the larger bath. We have discovered, most surprisingly, that when certain relationships of the diameters of the generally cylindrical dip tube or riser and the coaxial metal-dispersing cylinder are adhered to, and the top of the cylinder is closed so that a flow of metal can be induced upwardly through the dip tube without coming in contact with the surrounding atmosphere at a rate determined by the discharge through the perforations, all of the problems of control of the system are eliminated and uniform granules of a low-surface area/mass or surface area/volume ratio can be obtained. In effect, therefore, the molten metal discharged through the perforations draws a continuous stream of metal from the supply bath into which the free lower end of the dip tube is immersed. We have found it to be advantageous to introduce an inert gas into the head of the cylinder at a small pressure above ambient to avoid reactions of the melt with the surrounding atmosphere inside the perforations.

According to the principles of this method invention, the apparatus used to carry it out comprises a hollow lower cylinder intended to extend below the surface of the melt as contained in a receptacle which may be upwardly open or may have a free surface which may vary. Above the hollow lower cylinder and, advantageously, formed in one piece therewith, is a perforated hollow upper cylinder having its free upper end sealed by a plug, cap or cover. The apparatus carrying out the method is rotatable about the axis of the coaxial cylinders to draw metal from the melt into the cylinder and eject it from the hollow upper cylinder radially and/or tangentially by centrifugal force. As noted, there are certain essential relationships which must be provided for the system to operate in accordance with our principles and these critical dimensions relate the internal diameter d_1 of the hollow upper cylinder, the external diameter d_2, of the hollow upper cylinder and the internal diameter d_3 of the hollow-lower cylinder. It will be evident that $d_2 - d_1 = 2t$, where t is the thickness of the upper cylinder and the minimum length of the passage which must be traversed by the molten metal as it is centrifugally discharged from the perforations of the hollow upper cylinder. These critical relationships are $d_1/d_2 > 0.33$ and $d_3 < d_1$. Preferably $d_1/d_2 > 0.66$ and $d_3 \leq 0.5\ d_1$ and $d_3 \geq 0.2\ d_1$. Best results have been obtained wherein d_1 ranges between 3 and 15 cm while the perforation diameter lies between 0.3 and 2.5 mm. More specifically, we prefer an arrangement in which d_1 is between 5 and 10 cm and, better still, below 7.5 cm while the diameter of the perforations lies between 0.8 and 1.8 mm, preferably less than 1.2 mm and, even better, less than 0.6 mm.

The cylinder may, according to the invention, comprise a perforated sheet, sieve, net or screen or may be formed from a solid cylinder through which the perforations are drilled. When the axis of the apparatus is vertical, we prefer to orient the perforations with an upwardly outward inclination of, say, 1° to 45° to the horizontal.

Moreover, it has been found to be advantageous to off-set the perforations from radial planes through the system whereby the channels are generally tangential to circles centered on the axis of rotation of the device. The inner surface of the hollow upper cylinder or hollow lower cylinder, or both, may be roughened or provided with fins to promote rotative entrainment of the molten metal with the cylinders and the latter may be driven by a shaft fixed to the cover of the cylinders. The shaft may be hollow to permit the inert gas to be introduced as described earlier.

When reference is made to an "inert gas," we intend to so define any gas which is nonreactive with the melt. Such gases include the rare gases, nitrogen, hydrogen, other reducing atmospheres (e.g., carbon monoxide), etc.

The vessel receiving the bath may be connected with a reservoir adapted to feed additional molten metal to the vessel substantially at the rate at which the melt is discharged by the rotating cylinder or drum. Furthermore, we may provide means for pressurizing the melt and driving it upwardly through the hollow lower cylinder to augment the upward inducement of the melt resulting from the pump effect of the rotating upper cylinder. The hollow lower cylinder and the hollow upper cylinder may be composed of or lined with iron, cast iron, steel, refractory metals and alloys, graphite or a ceramic material such as alumina, magnesia or zirconia to which may be added particles of metal selected, for example, from the group which consists of chromium, molybdenum and tungsten.

With respect to further aspects of this method invention, we may point out that the preferred rotational speed of the cylinder is 600 to 9,000 rpm when d_1 ranges between 3 and 15cm and when the diameter of the perforations is between 0.3 and 2.5mm. Within this range, the sub-range of 1,500 to 6,000 rpm provides most effective results, especially when d_1 is held between 5 and 10cm and the perforations have a diameter of 0.8 to 1.8mm. Also, when the speed of rotation is greater than 7,000 rpm, d_1 should be less than 7.5cm and the perforation diameter less than 1.2mm.

We have found that it is possible to operate at speeds from 9,000 to 18,000 rpm if the value of d_1 is made less than 5cm and the perforation diameter is less than 0.6mm. Preferably, the melt into which the hollow lower cylinder extends is covered with a floating layer of a material protecting against atmospheric contamination, e.g., fused salt, and the region surrounding the cylinder may be placed under reduced pressure or vacuum. Most convenient, however, is the use of an inert gas atmosphere (as defined) in the space surrounding the upper cylinder and we may direct jets of inert gas at the cylinder wall from which the droplets are discharged to protect the rapidly solidifying droplets of the melt. The present method is best carried out with molten magnesium alloy, lead, lead alloys, tin, tin alloys, zinc, zinc alloys, alkali metals, alkali metal alloys, aluminum, aluminum alloys, copper and copper alloys.

DESCRIPTION OF THE DRAWING

The invention will be described in greater detail below, reference being made to the accompanying drawing in which:

FIG. 1 is an axial cross-sectional view through an apparatus embodying the present invention;

FIG. 2 is a vertical section illustrating one mode of supplying molten metal to the system; and

FIGS. 3 and 4 are vertical sections diagrammatically illustrating other embodiments of the instant invention.

SPECIFIC DESCRIPTION

The rotating pellet sprayer **23** as shown in FIG. **1**, consists of three main parts, namely, a hollow, perforated upper cylinder *a* as the upper part, a conical middle part *b*, and an elongated hollow lower cylinder *c*, reaching below the surface of the melt **10**, connecting the interior of the upper cylinder *a* with the surrounding melt.

This pellet sprayer **23** can be rotated by a shaft **1** connected to a motor (not shown) at its upper end and to a cover **3** of the hollow cylinder a at the lower end of shaft **1**.

On rotation, the melt inside the conical middle part *b* rises, fills the hollow perforated upper cylinder *a*, and is driven by centrifugal forces through perforations **6**. Exactly the amount of melt thrown off from the perforations **6** is drawn in through the end **11** of the elongated hollow lower cylinder *c* below the surface of the melt **10**. The melt ejected breaks up into droplets **7**.

When the rotation of the pellet sprayer is slowed down or increased, exact equilibrium between the melt sucked in and the melt thrown off is always reached.

Furthermore the pellet sprayer 23, reaching with its hollow lower cylinder c below the melt 10, is always heated up by the heat of the melt 10 even if at a standstill, so that the tendency of the melt to solidify and clog the perforations 6 is minimized.

Experiments have shown that, with constant temperature of the melt 10 and a constant number of rotations per minute of the pellet sprayer 23, the size distribution of the resulting pellets or granules is very narrow. Slags which float on the surface of the melt 10 cannot reach the interior of the pellet sprayer 23 because the melt is sucked in from below its surface; therefore long periods of operation free of trouble can be expected.

Once in rotation the pellet sprayer 23 empties each melt-containing vessel as far as the hollow lower cylinder c reaches down into the melt. Therefore small differences in the level of the melt have nearly no influence on the performance of the device.

Experiments have further shown that the wall thickness of the perforations hollow upper cylinder a with its perforations 6 should be limited, to avoid disintegration of melt in the passages 8 forming the perforations due to the difference of centrifugal forces in the parts near the axis of rotation and the parts at a greater distance from it. Each time a short strand of disintegrated melt leaves the perforation 6 of a relatively long passage 8, the following evacuated part is filled with the surrounding atmosphere, which causes reactions with the melt inside the channel 8 and gives rise to clogging. In short passages 8 the continuous intensive stream of melt keeps the passages 8 and their perforations 6 clean.

Good results have been reached too with a perforated hollow upper cylinder a consisting of a net or sieve made of a heat- and corrosion-resistant material, such as niobium alloys for copper melts, stainless steels for aluminum melts, or nickel for lead melts.

Generally it has been found that the ratio d_1/d_2, where d_1 is the inner diameter and d_2 the outer diameter of the perforated hollow upper cylinder a, should be greater than 0.33, preferably greater than 0.66.

To assure an even flow of the liquid melt through the pellet sprayer, the inner diameter d_3 of the hollow lower cylinder *c* should be smaller than d_1, preferably between 0.5 d_1 and 0.2d_1.

On the other hand it has been found that the size of the pellet sprayer 23 should be related to the rotational speed and to the diameter of the passages 8, if output and size distribution for a given size of the resulting product are to be optimal.

For the production of spherical or elongated portioles with a diameter betwen 0.1 mm and 3 mm, preferably 0.3 to 1.5 mm, the inner diameter d_1 of the perforated upper cylinder a should be more than 3 cm and less than 15 cm, preferably between 5 and 10 cm, while the number of revolutions per minute should be more than 600 and less than 9,000 rpm. The diameter of the passages 8 or perforations 6 should be between 0.3 and 2.5 mm, preferably 0.8 to 1.8 mm.

If the spherical or elongated granules are to have a diameter below 0.3 mm, preferably below 0.1 mm, the inner diameter d_1 of the hollow upper cylinder a should be below 7.5 cm, preferably less than 5 cm. The speed of rotation should be more than 7,000 rpm, preferably between 9,000 and 10,000 rpm. The diameter of the passages 8 should be less than 1.2 mm, preferably less than 0.6 mm.

An upward direction of the passages 8 is of advantage, as the particles should travel as long a way as possible, for instance to assure solidification, in free flight.

It was found that a non-radial direction of the passages 8 loads to elongated particles; if the passages leave the surface of the hollow upper cylinder *a* nearly tangentially, thread-like or wool-like products can be obtained from metallic melts. In the case of lead, it was found that these whisker-like threads consist of long single-crystalline parts.

An improved reliability over a longer time can be reached if an inert gas, such as argon, is forced in small amounts through a bore 2 in the shaft 1 into the space 4 above the rotating melt surface 5. Only a small amount of gas is needed to keep the perforations 6 clean.

Furthermore an improved production rate can be achieved if the inner surface of the conical middle part *b* is rather rough, or bears fins 9 to bring the melt into fast rotation.

The even and continuous flow of the melt can be improved further if the feeding vessel 21 for the pellet sprayer 23 is connected with a large melting vessel 2, so that the fluctuation in the level of the melt in the feeding vessel 21 is kept small (FIG. 2).

Another method can be applied if a continuous production is not necessary and only the contents of a rather large feeding vessel has to be emptied. According to FIGS. 3 and 4, by means of gas pressure in a closed space 32 above the melt 33, the melt can be forced into the pellet sprayer 23. Once in action the gas pressure can be lowered; in FIG. 3 the level of the melt 33 in a fixed cylinder 34 put into the feeding vessel can be lifted by gas pressure so that the pellet sprayer 23 can stay in continuous production. A regulation system, for instance coupled with an electrical contact in the upper part of fixed cylinder 34, can vary the gas pressure in order to keep the level of melt inside the fixed cylinder 34 nearly constant. However, the cylinder 34 is not absolutely necessary. It can be replaced by an appropriately sized hollow lower cylinder *c* of the pellet sprayer 23.

By the above method even molten magnesium and its alloys, sodium, and other reactive metals, can be granulated in large volumes.

In the feeding vessel, the melt of such a reactive metal is covered with salt mixtures well known in the art. The hollow lower cylinder *c* reaches through the salt cover floating on the surface of the melt and sucks the melt in below the surface. The melt contacts the surrounding atmosphere only when it leaves the perforations 6 in form of a liquid, disintegrating into droplets which solidify so fast that, below a certain diameter of about 0.7mm, the granules do not burn while on their flight through the air.

The fabrication of granules of highly reactive metals and alloys is made possible, and the surface quality, for instance, of lead and aluminum pellets or granules is improved, which is of great advantage for the production of sheet by direct rolling or of intermediate products by extrusion.

Granulated lead particles made by the above method have a shining surface and can be used for the fabrication of leaded steels.

It is also possible to produce commercially steel shot and shot of cast iron by the above method. Formerly great difficulties arised using the method of a rotating open crucible, because the larger crucibles of ceramic materials needed for a volume production had a tendency to break, and the feeding and warming up of the crucible had to be mastered.

If the melt is of magnesium, a magnesium alloy, lead, a lead alloy, tin, a tin alloy, an alkali metal, or an alkali metal alloy, the pellet sprayer should preferably be of iron, case iron, or steel. If the melt is of aluminum or an aluminum alloy, it may be of iron, cast iron, steel, graphite, or a ceramic material. In the case of copper or a copper alloy, the pellet sprayer should be of graphite or a ceramic material. If the melt is of iron or steel, the pellet sprayer should be of ceramic material such as Al_2O_3, MgO, or ZrO_2, preferably with metallic additions such as Cr, Mo, and W.

It is found that with the present method the diameter of the pellet sprayer shown in FIG. **1** can be much reduced compared with an open rotating crucible of the same production capacity. So the danger of breaking for the pellet sprayer is much reduced compared with an open rotating crucible. This feature is even more pronounced because the closed construction of the pellet sprayer is more rigid and the pellet sprayer suspended on its axis **1** runs in a very stable position nearly without vibration and even better stability with increasing rotations per minute. Furthermore the hollow lower cylinder *c* submerged under the melt proves to be an additional vibration-damping element.

Pellet sprayers with a small diameter and a surprising production rate can be made while increasing the speed of rotation up to the limit the material used can endure. With pellet sprayers of a diameter d_2 of about 3.5cm and a hollow perforated upper cylinder a made of perforated sheet or net, commercial production of 3 tons of lead powder per hour is feasible, if the speed of rotation is raised to 18,000 r.p.m.

To produce particles of high purity, the melt ejected from the hollow perforated upper cylinder *a* should not be allowed to come into contact with the air. This can be achieved by surrounding the whole apparatus with an inert atmosphere, or by directing jets of inert gas at the hollow perforated upper cylinder *a*. Alternatively, the pellet sprayer **23** can be situated in a compartment held at a reduced pressure or in a vacuum; if the feeding vessel is closed from this compartment and is at atmospheric pressure, flow of the melt through the pellet sprayer will be enhanced.

SPECIFIC EXAMPLES

EXAMPLE I

Using the apparatus illustrated in FIG. **1** with the feed arrangement shown in FIG. **2** to the vessel **21** and a fused-salt layer atop the exposed surface of the bath, molten lead was granulated with a pellet sprayer having the configuration of FIG. **1** and composed of perforated sheet iron. The internal diameter d_1 of the cylinder was 2.8cm the external diameter d_2 thereof was 3.5cm and the internal diameter d_3 of the hollow lower cylinder *c* was 9.75mm. The aperture diameter was 0.3mm and the bath was 90° C above the melting point of lead. The head was rotated at 18,000 r.p.m. to cast lead into an environment of pure nitrogen at room temperature and at a pressure of 0.0 atmospheres gauge. Three tons per hour of lead powder with a particle size in the range of 0.07mm was obtained. The same system with essentially the same parameters, but at the respective melting points, was used to granulate molten magnesium, tin and elemental sodium. In all cases, similar powders or granules were obtained. The granules were found, for the most part, to be elongated ovoids with smooth topography.

EXAMPLE II

The device illustrated in FIG. **1**, supplied with molten metal using the arrangement illustrated in FIG. **4** by the application of gas pressure at least sufficient to maintain a uniform flow into the cylinder, was used to produce aluminum granules. The cylinder was composed of graphite and had an internal diameter d_1 of 6.4cm, an external diameter d_2 of 8cm and a hollow lower cylinder with an internal diameter d_3 of 2.2cm. The perforations had a diameter of 1.2mm and the system was rotated at 3,500 r.p.m. to produce 1.4 tons per hour of the granules with a diameter of about 0.5mm. The same system was used with equivalent results to granulate molten copper. The enveloping gas at 1 atmosphere absolute was argon.

EXAMPLE III

Using the dimensions of the sprayer of Example II, but an upper cylinder and hollow lower cylinder consisting of fired ceramic composed in equal parts by weight of ZrO_2 and molybdenum powder, about 5 tons per hour of cast iron granules were obtained.

The improvement described and illustrated is believed to admit of many modifications within the ability of persons skilled in the art, all such modifications being considered within the spirit and scope of the invention except as limited by the appended claims.

We claim:

1. A method of forming solid metal particles of a metal reactive with surrounding atmosphere and selected from the group which consists of iron, cobalt, nickel, copper, aluminum, magnesium, lead, tin, zinc and alkali metals and alloys thereof, comprising the steps of:

a. forming a bath of the molten metal covered by slag;

b. immersing downwardly an open hollow lower cylinder vertically into said bath past said slag, said hollow lower cylinder communicating at its upper end with a closed-top perforated hollow upper cylinder, said cylinders consisting essentially of at least one substance selected from the group which consists of iron, nickel, cobalt, steel, refractory metals, graphite and ceramic, provided that said cylinders are composed of iron or steel when the molten metal is magnesium, lead, tin or an alkali metal or alloy thereof, said cylinders are composed of iron, steel, graphite or ceramic when the molten metal is aluminum or an alloy thereof, the cylinders are composed of graphite or ceramic when the molten metal is copper or an alloy thereof, and the cylinders are composed of ceramic when the molten metal is iron or an alloy thereof;

c. spinning said cylinders about a common vertical axis at a speed of 600 to 18,000 RPM and with sufficient centrifugal force to impel discrete droplets of molten metal from the individual perforations of said cylinder and to draw a replenishing flow of molten metal into the latter, said hollow upper cylinder having an internal diameter d_1 and an external diameter d_2 while said hollow lower cylinder has an internal diameter d_3, d_1/d_2 being greater than

0.66, d_3 being between $0.5d_1$ and $0.2d_1$, d_1 ranging between 3 and 15 cm, the perforations of said cylinder having a diameter p ranging between 0.3 and 2.5 cm, the speed S, the internal diameter d_1 and p being related by the following table:

S	d_1	p
1,500 to 6,000 rpm	5 to 10 cm	0.8 to 1.8 mm

upwards of 7000 rpm	less than 7.5 cm	less than 1.2 mm
9,000 to 18,000 rpm	less than 5 cm	less than 0.6 mm

and

d. cooling and solidifying the droplets of molten metal cast from said hollow upper cylinder in said atmosphere.

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