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METHOD OF GRANULATING POWDER

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U.S. Cl. 264—.5 **6 Claims**

ABSTRACT OF THE DISCLOSURE

This invention relates to a method of granulating a fine powder. A fine powder is difficult to handle when it is molded by compression. Therefore, this invention provides a method in which a powdery foaming agent, that is, a substance which vaporizes upon heating, is previously mixed with the powder of a grain size smaller than the grain size desired, then this mixture is compressed into shaped pieces; these shaped pieces thus obtained are heated to get the foaming agent to vaporize, the expansion force of this vaporization pulverizes the compressed pieces into grains of the desired grain size. The invention also teaches a method which makes it possible to freely control the grain size distribution of the grains to be obtained by altering the grain size of the foaming agent, the ratio of the foaming agent added and the compression force.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of patent application Ser. No. 876,035 filed Nov. 12, 1969 now abandoned.

This invention relates to a method of granulating powder, or more particularly, to a method of manufacturing grains by compressing a mixture of powder and a foaming agent into shaped pieces and heating these shaped pieces to pulverize them into grains.

When compressing a fine powder of metals, alloys, ceramics, etc. to mold and sinter it into a desired solid, its handling in the compression process is accompanied by difficulty because of its poor fluidity and a marked change in its apparent specific gravity, if the powder is in the condition of a fine powder. It is well known that this difficulty can be removed if the raw material fine powder is converted into coarse grains before the process, and this is referred to as granulation.

The method of granulation heretofore employed was either to dissolve a binding agent in a suitable solvent, mix the solution with the powder to be granulated in order to make it viscous, and then granulate it by tumbling, extrusion, etc., or to compress the powder into bound pieces, pulverize them mechanically by a pulverizer and granulate the powder by sieving the grains thus obtained.

When the method using a binding agent is employed, a binding agent which will become an impurity and the grains obtained cannot be used. Besides, when the compressed pieces are pulverized, a part of the pulverizer finds its way into them as an impurity through wear. Furthermore, when the method using a pulverizer is used, it is often the case that the sizes of the grains are not uniform and the product obtained is of a widely distributed grain size. Thus, the pulverizing method calls for skill, and it is difficult to obtain a product of the desired grain size.

This invention has an object to provide a method of granulating powder which is free from the afore-mentioned drawbacks.

When making a sintered body, if fine powder is used as the raw material for the sintered body, the quantity compressed and molded before sintering varies every time a body is molded, and this great variation gives rise to fluctuation in the quality of the product obtained. Also, there is difficulty in that since it is hard to expel the air among the powder particles out of the compressing vessel, compression has to be done twice. To avoid these difficulties, it is common sense that grains having a larger grain size than powder particles should be used. The grains obtained by the method of this invention as a granular material for making such a sintered body are free from impurities. Such grains can be manufactured by the method of this invention more easily than by the granulating methods already known to the public.

In order to attain the object, according to this invention, a foaming agent or a substance which readily becomes a gas upon heating (hereinafter it will be referred to in this application as a foaming agent) is first added to the fine powder of the raw material (a metal, alloy, ceramics, etc.) and their mixture is compressed and molded. If such compressed and molded pieces are simply heated in a furnace, they spontaneously become pulverized by the evaporation of the foaming agent, and grains of a suitable size can be obtained.

As a foaming agent to be used in this invention, any substance which becomes a gas upon heating will do, provided that it meets the condition that it does not chemically react with the powder to be granulated. As a foaming agent, any of the already-known foaming agents, such inorganic foaming agents as sodium hydrogen carbonate and ammonium carbonate, such organic foaming agents as 1,1′-azobisformamide, 4,4′-oxybisbenzene, sulfonylhydazide, dinitrosopentamethylene-tetramine and α-polyoxymethylene, and organic solvents, naphthalene, etc., which readily becomes gasified or volatized upon heating may be used. Where a problem will be encountered because a particular element will be transferred into the product obtained, it is permissible if a foaming agent which does not contain that particular element is employed.

It is not particularly necessary to restrict the atmospheres for the heating for foaming. However, where the powder to be granulated may be oxidized or may undergo some other unfavorable change at the foaming temperature, it is advisable to carry out the heating in an atmosphere of an inert gas or in a vacuum.

The method of this invention makes it possible to control the grain size distribution of the granulated powder over a wide range by specially using a foaming agent in a solid state and regulating its grain size, the quantity of the foaming agent added and the compressing force on the mixture of the powder and foaming agent.

The inventor has discovered that in this case the greater the diameter of the foaming agent, generally the larger the grains of the granulated powder are, and that the grain size of the grains obtained is in inverse proportion to the ratio of the foaming agent added.

The hardness (strength) and density of the granulated grains can be varied by changing the density of the compressed pieces by altering the compressing force.

In carrying this invention into practice, if the powder is such that it is affected detrimentally in some way or other by temperatures above some degree, it is advisable to add cadmium stearate, lead stearate or zinc stearate as a foaming auxiliary for the purpose of lowering the foaming temperature of the foaming agent. Needless to say, a foaming agent having a foaming gas efficiency of 50 ml./g. or more, for instance, is generally found more effective, and it is preferable to use it in a quantity of about 1–20 weight percent.

It is not especially necessary to limit the size of the compressed and molded pieces. From the viewpoint of production efficiency, the larger they are, the better. For the purpose of making the grain size of the granulated powder uniform, it is preferable to make them smaller. This is so because the larger the compression-molded piece is, the less uniform is the density of the interior of the molded piece. On the other hand, if the molded piece is large, the press has to possess a large capacity commensurate therewith. In the examples of embodiment described hereinafter, the molded piece is given a size of 50 mm. diameter x 70 mm. high. The compression force for such molded pieces is generally 20–40 tons.

The method of this invention has such advantages in that the grain size distribution and hardness of the grains obtained can easily be controlled, that no binding agent is used so that there will be no such agent remaining in the granulated powder as an impurity, and that there is less likelihood of impurities finding their way into the product than is true with mechanical pulverization.

Now I will describe examples in which this invention was actually embodied, from which the advantages and characteristics of this invention will be made clearer.

EXAMPLE 1

To the powder of UO_2 (grain size 44μ or less) was added 5 wt. percent or 7 wt. percent of α-polyoxymethylene having a grain size of 44μ or less or of 100μ–300μ. This mixture was compressed into a piece 30 mm. diameter x 70 mm. by a pressure of 20 tons, and this compressed piece was heated to 250° C. for foaming. The compressed piece then collapsed into grains again, though the grains obtained were of a larger grain size.

The grain size distribution (wt. percent) of the larger grains thus obtained is shown in Table 1.

Grain sizes are classified as shown below according to the grain size of the foaming agent, also in the examples described later.

(i) Instances where a foaming agent of a grain size of 44μ or less was used.

(ii) Instances where a foaming agent of a grain size of 44μ–150μ was used.

(iii) Instances where a foaming agent of a grain size of 100μ–300μ was used.

(iv) Instances where a foaming agent of a grain size of 300μ–1000μ was used.

(v) Instances where a foaming agent of a grain size of 150μ–1000μ was used.

TABLE 1

Grain size (μ) of granulated UO_2	Grain size distribution (wt. percent)			
	With 5 wt. percent foaming agent, Instance		With 7 wt. percent foaming agent, Instance	
	(i)	(iii)	(i)	(iii)
840–150	0	85	0	60
150–70	70	10	20	30
70 or less	30	5	80	10

EXAMPLE 2

Dinitrosopentamethylene-tetramine was used as a foaming agent. 5 wt. percent of this was mixed with UO_2 powder (grain size 20μ or less) and this mixture was pressed into a compressed piece (density of the compressed piece=40% T.D.) by means of a press. Then it was heated to 250° C. in nitrogen gas to decompose the foaming agent. In this case, the under-mentioned five ranges of grain size of the foaming agent were used for the experiment, as a result of which granulated UO_2 powder having the grain size distributions shown in Table 2 was obtained.

TABLE 2

	Grain size distribution (wt. percent)				
Instance	(i)	(ii)	(iii)	(iv)	(v)
Grain size (μ) of granulated UO_2 powder:					
840–300	0	8.1	45.7	77.2	65.8
300–150	1.7	12.2	28.0	5.2	15.3
150–100	6.8	22.7	7.6	0.8	2.7
100–70	15.7	24.0	5.0	0.5	2.0
70–44	42.2	22.0	5.3	2.9	11.0
44 or less	33.6	11.0	8.4	3.0	1.0

EXAMPLE 3

Using the foaming agent of the grain size of 100μ–150μ of the Instance (v) of Example 2, the ratio of its addition to the raw material UO_2 powder (20μ or less) was varied to the under-mentioned three values. Thus, granulated UO_2 powder having grain size distributions shown in Table 3 was obtained.

(a) 5 wt. percent foaming agent added to UO_2 powder.

(b) 7 wt. percent foaming agent added to UO_2 powder.

(c) 10 wt. percent foaming agent added to UO_2 powder.

(d) 20 wt. percent foaming agent added to UO_2 powder.

TABLE 3

	Grain size distribution (wt. percent)			
Instance	(a)	(b)	(c)	(d)
Grain size (μ) of granulated UO_2 powder:				
840–300	65.8	48.0	35.0	13.0
300–150	15.3	17.2	25.2	27.0
150–100	2.7	8.1	8.7	21.8
100–70	2.0	5.3	7.1	11.5
70–44	11.0	14.4	17.6	18.9
44 or less	1.0	7.0	6.4	8.0

EXAMPLE 4

7 wt. percent of a foaming agent of a grain size of 1,000μ–150μ (Instance (b)) was added to UO_2 powder (grain size 20μ or less). This mixture was compressed into two kinds of pieces of different densities, and then granulated by heating to 250° C. in a nitrogen atmosphere. As a result, granulated UO_2 powder of the grain size distributions given in Table 4 was obtained.

In this case, the higher density of the compressed piece brought about a greater strength and higher density of the granulated grains. The results in this connection are also shown in Table 4. As regards the strength, the granulated grains were placed in a vessel and subjected to vibration for a fixed length of time, and the strength was measured by observing the reduction of rough grains (840μ–300μ) into fine grains (ratio of decrease of rough grains). As to the density, the apparent densities of the products sieved to a certain grain size were compared.

TABLE 4

	Density of compressed 34% T.D. piece			Density of compressed 40% T.D. piece		
Grain size (μ) of granulated UO_2 powder	Grain size distribution (wt. percent)	Strength, percent	Density, g./cm.^{3}	Grain size distribution (wt. percent)	Strength, percent	Density, g./cm.^{3}
840–300	48.0	61.5	3.7	67.0	88	4.4
300–150	17.2			13.5		
150–100	8.1			8.1		
100–70	5.3			2.1		
70–44	14.4			9.2		
44 or less	7.0			2.1		

EXAMPLE 5

To WC powder (grain size at 44μ or less) was added 10 wt. percent of ammonium carbonate of a grain size of 840μ or less. After this, the mixture was compressed into a compressed piece and pulverized into rough grains by heating to 200° C. in nitrogen gas. The grain size distribution of the product obtained was such that 83 wt. percent had grain sizes within the range of 840μ–150μ.

EXAMPLE 6

To WC powder (grain size of 40μ or less) were added 8 wt. percent of azodicarbonamide and also 1 wt. percent of zinc stearate as an auxiliary. The mixture was heated to 180° C. in nitrogen gas. (Although the decomposition temperature of azodicarbonamide is 200° C., its decomposition almost completes at about 150° C. when an auxiliary has been added). The grain size distribution of the WC powder obtained in this case was as shown in Table 5. Also shown in the table is the grain size distribution of the product obtained without the addition of the auxiliary. The product for which the auxiliary was used shows a somewhat larger ratio of rough grain. Probably this is because the auxiliary slows down the decomposition speed and weakens the breaking force of the gas.

TABLE 5

Grain size (μ) of granulated WC powder	Grain size distribution	
	Without auxiliary (wt. percent)	With 1 wt. percent auxiliary (wt. percent)
840–300	37.5	40.2
300–150	24.2	29.5
150–100	11.6	12.3
100–70	13.6	7.1
70–44	8.1	7.4
44 or less	5.0	3.5

If an auxiliary is used, some amount of an organic substance is left in the finished granulated powder. (In the case of the example, approximately 0.1%). For some applications, therefore, the use of an auxiliary is not desirable.

The rough grains obtained in the afore-mentioned Examples 1–6 were fed to an ordinary automatic press and sintered, at 1500°–1700° C. for UO_2 and 1400°–1600° C. for WC powder. Sintered pieces of a homogeneous constitution with little variation in weight were obtained.

The fluidity of rough grains was better than that of the raw material powder directly fed into the press. Very little variation in weight took place when the grains were automatically dropped to fill the press mold.

When a granulated powder obtained by the method of this invention was heated to 1500°–1700° C. in an H_2 atmosphere, grains of 90–97% T.D. (theoretical density) were obtained. In this way, a granulated product of a still higher density can be obtained by sintering. This is because the density of granulated powder before sintering can be made high by this method. This is a remarkable feature of this method of granulation.

If these high density sintered grains of different grain size distributions are suitably combined and filled into a pipe by the vibration filling technique or the like to a filling density of 90% or so, a powder-type fuel rod of 81–87% T.D. can be made.

Besides UO_2, ceramics nuclear fuels can also be granulated by the method of this invention. Uranium carbide and uranium nitride are readily oxidized in the air. The method of this invention can, therefore, be applied to them satisfactorily, if a foaming agent which does not contain O_2 in the decomposition gas is used, and an inert gas is used for the heating atmosphere.

Referring to the afore-mentioned examples of embodiment, it is advisable to carry this invention into practice with the under-mentioned conditions taken into consideration as regards the grain size of the foaming agent, the ratio of the foaming agent added and the compression force for molding.

The details concerning this invention which have been described may be summarized as follows:

(a) Grain size of the foaming agent

Since the grain size of the foaming agent determines the grain size of the granule obtained, the limits to the grain size of the foaming agent are to be determined reversely by the desired grain size of the granulated product. As the grain size of the granulated powder for making sintered pieces, a size of 1000μ–44μ as shown herein is preferable. This is because these grain sizes make the fluidity of the powder good and also because these grain sizes are not too large, but keep the apparent density of the powder considerably large. In consequence, the grain sizes of the foaming agents shown in the examples are used in order to obtain grains of a grain size distribution meeting the requirements.

(b) Ratio of addition

The smaller the ratio of addition, the more economical it is. However, if the quantity added is too small, the expanding force for breaking the compressed piece will not be obtained, so that granulation will not take place. This lower limit of the quantity added varies according to the kind of foaming agent used, since it varies according to the volume of gas produced by 1 g. of the foaming agent. For example, the ratio of the quantities of azodicarbonamide (decomposition gas volume 270 ml./g.) and sulfonhydrazide (decomposition gas volume 110 ml./g.) used to obtain about the same grain size distribution is approximately 1:3.

(c) Compression pressure

If the pressure is low and the density of the compressed piece is too low, there will be a large proportion of fine powder after pulverization. In the case of UO_2, 800 kg./cm.^{2} or more is preferable. The upper limit of this pressure is determined by the following consideration. This granulated powder is made into a shaped piece and then sintered. If the density of granulated powder in this sintered piece is too high, the shaped piece may have cracks in it and have a poor appearance, and grain borders in the sintered piece may become distinct and the surface may lose its smoothness. In consequence, it is preferable that the molding density at the time of granulation does not exceed 80% of the molding density for sintering.

I claim:

1. The method of granulating compacted fine powder materials into a selected coarser grain size comprising the steps of mixing a volatile foaming agent with the fine powder materials, compressing the mixture to form a molded piece, heating the molded piece to volatize the foaming agent from within the molded piece thereby causing the latter to fissure and break up into coarse grains.

2. The method of granulating of claim **1** characterized by the step of selectively controlling the coarse grain size by varying the ratio of the foaming agent mixed with the fine powder materials.

3. The method of granulating of claim **1** characterized by the step of selectively controlling the coarse grain size by varying the grain size of the foaming agent mixed with the fine powder materials.

4. The method of granulating of claim **1** characterized by the step of selectively controlling the coarse grain size by varying the amount of the compression used in compressing the mixture to form a molded piece.

5. The method of granulating of claim **1** characterized by the step of adding a foaming auxiliary agent to the mixture to lower the volatizing temperature of the foaming agent.

6. The method of granulating of claim **1** characterized by the step of providing an inert atmosphere during the step of heating to volatize the foaming agent.

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23—313; 264—54, 65, 117, 140

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,739,048 Dated June 12, 1973

Inventor(s) Kazutoshi Morita

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, after line 7, insert the following:

"Claims priority, application Japan Serial No. 82,523/1968 filed November 13, 1968."

Signed and sealed this 16th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR. Attesting Officer	C. MARSHALL DANN Commissioner of Patents

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