

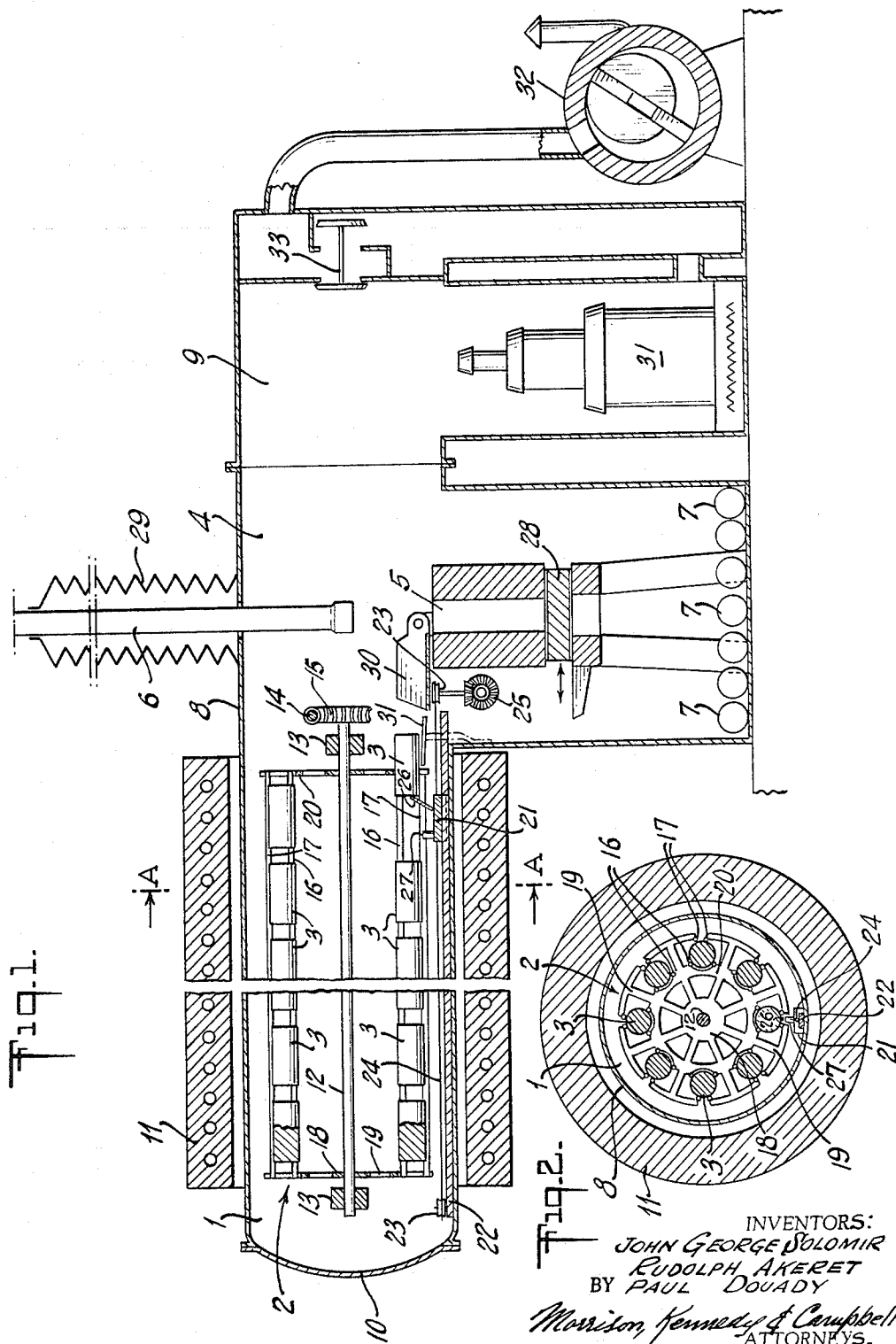
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METHOD FOR THE MANUFACTURE OF DENSE SINTERED ARTICLES

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METHOD FOR THE MANUFACTURE OF DENSE SINTERED ARTICLES

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6 Claims. (Cl. 75—214)

This invention relates to the manufacture of dense articles made from metal powder and sintered in a vacuum, particularly of objects pressed from aluminum powder or aluminum alloy powder, having, when heated up to several hundred degrees centigrade or after this heating, a higher tensile strength and a higher temperature than objects made from the same material but not by powder metallurgy. Such sintered aluminum objects of a considerable high-temperature stability have become known about 15 years ago by the investigations of Swiss Aluminium Ltd.

The aluminum powder utilized for the purpose is usually manufactured from comminuted aluminum by several hours dry grinding in a ball mill with addition of a small amount of stearic acid, in an atmosphere with a measured content of oxygen. Several phenomena hereby occur: The metallic surface is coated with a layer of brittle oxide which is broken again during the further milling or deformation of the metal particles; at the same time the particles are welded to each other wherever the metallic surface is laid bare by the oxide layer being shorn off. By alternate comminution and welding particles are thus formed which contain oxide as a fine dispersion and which are further coated with an oxide skin to which in turn a layer of grease adheres. Such a powder therefore contains, according to the type, 6 to 15% of oxide which is not pure Al_2O_3 but is in a more or less hydrated state, and some tenths of percent of grease consisting of stearic acid as well as aluminum stearate.

For the manufacture of semiproducts this powder is usually first cold-compacted into cylindrical shape in a vertical press with a compacting pressure of 1–2 t./cm.², these cold-compacts having a porosity of about 25 to 35%. Subsequently several compacts are, for the sintering process, packed together in a sheet of pure aluminum, heated up to 550 to 600° C. in the course of several hours and kept at this temperature for a further several hours. This heat-treatment starts certain processes which cause the generation of gases: The air enclosed in the pores is partially expelled due to dilation, the greasy remnants are volatilized; the water chemically bonded in the hydrated oxide is liberated at this temperature forming steam, parts of which react exothermically with the metallic aluminum, forming further oxide and hydrogen, the latter either escaping as a gas or being dissolved in the aluminum. As the latter two phenomena are exothermic the heating of the still porous cold-compacts has to be done slowly in order to avoid their destruction through overheating. Apart from this danger, the transformation of the hydrate of aluminum oxide requires a relatively long period to be completed.

The exothermic reactions also take place if wet milled powder is utilized.

In the course of the heat treatment of the compact a sintering process takes place, which however, differs from the sintering usually known in powder metallurgy in that there is no shrinkage and the pores do not disappear.

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The physical properties characteristic for sintered aluminum are fully obtained only through the subsequent hot forming. First the compacts are e.g. upset in the container of an extrusion press against a blank die at a pressure of 4 to 10 t./cm.². Finally the material is thoroughly kneaded by extrusion whereby a metallic, technically useful, ductile, sintered material is obtained.

The sintered aluminum manufactured in the described way at normal atmospheric pressure necessarily still contains a certain amount of gas or of material generating gas at high temperature.

If in the course of certain applications the sintered aluminum is exposed to high temperatures for days or even for months, the gases diffuse out of the sintered material and thus may cause the formation of minute pores or fissures. This phenomenon may cause serious trouble, particularly in the case of nuclear reactors where absolute density and undisturbed heat transfer are of necessity and only material of the highest possible structural stability may be incorporated.

Moreover, in many cases it would be of high usefulness to be able to weld sintered aluminum, like the classic aluminum alloys, either to itself or to one of the usual aluminum alloys, by a fusion welding operation. It has however been found that this proceeding is not feasible with normal, gas containing sintered aluminum, the gases contained in the metal being expelled therefrom by the fusion process and the welding area therefore getting porous.

These two examples, chosen among a great number, already show where disadvantages can be avoided if sintered aluminum with a very low gas content is available.

It has already been mentioned that a sintered aluminum manufactured by the normal process can be degassed by a subsequently performed vacuum heat-treatment. Thus a report of the Atomic Energy Commission of Denmark, published 1961, mentions that slabs annealed at 600° C. for 96 hours in a high vacuum, after a subsequent annealing operation at 635° C. for 2 hours in normal atmosphere, do not show any surface blistering. Reference samples annealed without the application of vacuum in air at 600° C. for 96 hours are, after a second annealing operation in normal atmosphere at 635° C. for 2 hours, considerably blistered. The determination of the gas content in samples treated in a vacuum or without a vacuum has confirmed the possibility of such a subsequent degasification of rolled or extruded products made from sintered aluminum.

In practice however such as degasification of semiproducts or finished bodies is hardly practical. The treatment of bodies of a certain thickness requires too much time. For bulky articles, e.g. tubes, the furnaces would have to be too large.

Much more efficient and more economical is the degasification during the manufacture of the sintered aluminum, be it the powder or the porous compacts. Such a manner of proceeding, which is, according to today's requirements, more and more of importance, was taken in view by the fundamental patents of the Swiss Aluminium Ltd. when they say that the manufacture of the sintered aluminum compacts may be performed entirely or partially under low pressure, which means: in a more or less advanced vacuum.

Since that time, the application of vacuum has been mentioned on several occasions in the technical literature describing the manufacture of sintered aluminum products.

The heat-treatment, subsequently called vacuum-sintering, of a cold-pressed, porous compact of aluminum powder in a vacuum, aiming at its degasification and

sintering, may be performed in several ways. As already mentioned, the porosity of the cold-compact made of aluminum powder is substantially retained and therefore the compact is extremely sensitive to subsequent oxidation when exposed to air at elevated temperatures. Consequently it is very useful if the compact sintered in a vacuum and still porous undergoes a hot-upsetting operation, called sinter-pressing, while still under vacuum.

This could be done by carrying out the vacuum sintering step in the container used for the subsequent hot-upsetting or sinterpressing of the compact. This manner of proceeding is used in special cases in the powder-metallurgical manufacture of small bodies of other materials. For the production of sinter-aluminum products this method is not practical since due to aforementioned processes the sintering time of necessity is very long, which would mean the blocking of a press for many hours to produce one single compact.

To avoid this disadvantage it is possible to use a method for vacuum-sintering, which is known from the usual manufacture of sintered aluminum: The cold-compacts are wrapped, before the sintering process, in pure aluminum foil or thin aluminum sheet and then set into the chamber of the vacuum-sintering furnace. The gases liberated during heating however can only escape through the folded joints of the wrapper, which fact diminishes considerably the efficiency of the vacuum-treatment with regard to the degasification.

Experiments in Swiss Aluminium Ltd. have revealed that an appreciably lower gas content may be attained by treating the cold-compacts without a wrapper in a vacuum-sintering furnace. The results of these experiments are shown in the following table, whereby sintering time is called the time during which the compacts are kept at the given sintering temperature:

Vacuum in Torr	Sintering temperature, ° C.	Sintering time, h.	Gas contents, cm. ³ /100 g.	
			Sintered with wrapper	Sintered without wrapper
5.10 ⁻³ -10 ⁻¹	610	7	2.6	1.5
10 ⁻⁴ -10 ⁻³	610	7	3.1	1.8
5.10 ⁻³ -10 ⁻¹	610	24	2.4	1.5
10 ⁻⁴ -10 ⁻³	610	24	2.2	1.7
5.10 ⁻³ -10 ⁻¹	630	7	3.2	1.5
10 ⁻⁴ -10 ⁻³	630	7	2.4	1.6
10 ⁻⁴ -10 ⁻³	630	24	2.4	1.5

As already mentioned the compacts must not be exposed to air when transported in hot state to the press because of the intolerable subsequent oxidation.

The purpose of the present invention, based on these statements of Swiss Aluminium Ltd. and taking into account the special conditions of the manufacture of sintered aluminum compacts, is to eliminate the drawbacks of the known methods of vacuum-treatment and to allow an economical industrial production of vacuum sintered compacts.

In the sintered aluminum compacts as described the particles of aluminum oxide have a hardening effect even at elevated temperature, being insoluble in the matrix.

In the course of the last years this method of dispersion hardening has been applied also to further material, i.e. it has been suggested to effect a dispersion hardening in aluminum by means of other dispersions than oxides or to utilize different material as a matrix, e.g. iron, nickel, magnesium, copper and the like. It may be desired to manufacture dense sintered compacts with a low content or completely free of gas from all these combinations.

The present invention, relating first of all to the manufacture of sintered aluminum compacts, may also

be applied to metallic as well as nonmetallic, e.g. ceramic, material.

The method of manufacturing in a vacuum dense sintered bodies with a low content of gas according to this invention is characterized by the facts that cold-compacts are made from powder, that a number of these compacts, without being wrapped, are heated and sintered in a vacuum inside the heated portion of a gastight chamber, that the compacts are then, one after the other, while still under vacuum, transported to another portion of the chamber and, one at a time, submitted to a hot-upsetting operation inside the container of a compacting press.

For the manufacture of sintered aluminum compacts in vacuo from an oxide containing aluminum powder, there are made from this powder cold-compacts a number of which, without being wrapped, are heated for some hours to a temperature somewhat below the melting point of aluminum and sintered inside the heated section of a gastight chamber, the compacts thus degasified being then, still in vacuo moved, one at a time, into another section of the chamber and are there submitted to a hot-upsetting operation inside the container of a compacting press.

When working by this method it is advisable to keep the cold-compacts after 1 to 10 hours, preferably 2 to 5 hours heating at a temperature of 550 to 650° C., preferably 600 to 630° C. for 2 to 100 hours, preferably 12 to 25 hours. Towards the end of this heat-treatment in the heated portion of the vacuum chamber there is to be kept a vacuum of less than 10 mm. Hg, preferably of less than 10⁻² mm. Hg for at least the last one hour.

The vacuum may be applied from the beginning of the heat-treatment; it is however advisable to start with an average vacuum and to apply the high vacuum only after the sintering temperature (above 550° C.) has been attained.

The apparatus for the manufacture of dense sintered compacts in a vacuum, according to this invention may consist substantially of a gastight chamber connected to a vacuum-pump unit, a portion of which chamber, being developed into a sintering chamber, is provided with a heating device as well as a device to receive a number of cold-compacts, in which sintering chamber these compacts are submitted to heating and vacuum-sintering; and a further portion of which gastight chamber is developed into a pressing room, wherein at least the tooling of a compacting press is accommodated and where the sintered compacts are subsequently hot-upset, one at a time, the vacuum chamber being equipped with a transport device for the moving of the individual compacts from the heated portion of the chamber to the container of the press.

The device inside the sintering furnace receiving the compacts to be sintered may have the form of, e.g. a conveyer belt or a drumshaped receptacle. In order to keep the surface of the compacts as free as possible for degasification, the supporting members of the receiving device are preferably formed of slats or grids.

The accompanying drawing presents schematically and as an example one version of the apparatus for carrying out the invention,

FIG. 1 presenting a longitudinal section and

FIG. 2 presenting a cross section following the line A—A of FIG. 1.

The apparatus chiefly comprises a heatable sintering chamber 1 containing a device 2 for simultaneously receiving a number of cold-compacts 3 to be degasified and sintered, a pressing room 4 wherein the compacting tools, i.e. the container 5 and the plunger of the press 6, are situated respectively are reaching in to leave sufficient room for the reception of the hot-upset compacts 7 of one charge, whereby these members are enclosed in a vacuumtight metal casing 8 connected to a vacuum-pump unit 9. The heatable sintering chamber 1 has cylindrical shape and is closed at one end by a cover 10

which may be removed e.g. for the charging of the cold-compacts 3 into the receiving device 2. The sintering chamber 1 is heated from outside by an electrical furnace 11 open at both ends, which advantageously can be displaced longitudinally and may be removed for control or repair purposes. It is however possible as well to provide for a complementary heating inside the sintering chamber or even to accommodate the complete heating device inside this sintering chamber.

The receiving device 2 consists of a drum-shaped cage rotatable round its axle 12. Both ends of this axle are embedded in the bearings 13 fixed to the casing of the sintering chamber 1 by supporting members not shown in this drawing.

The rotation of the receiving device 2 is performed through a worm gear drive 14-15 the spindle 14 of which is reaching out through the casing of the vacuum chamber and is operated from the outside. Instead of a worm gear drive a bevel gear or any other form may be adopted.

In order to keep the surfaces of the individual cold-compacts 3 placed inside the receiving device 2 as free as possible for the degasification, the actual supporting members are made of slats arranged in the longitudinal direction of the cage in a way to form two concentric circles, whereby the slats of the inner circle are designated by the number 16 and those of the outer circle by the number 17. These slats 16 and 17 may be fixed at both of their ends to discs fixed for their part to the axle 12 and forming the front ends of the cage 2. For the feeding and removing of the cold-compacts respectively into and out of the cage the discs have perforations in the extension of the rows of cold-compacts. For reasons of vacuum technique however, the front end discs of the cage preferably do not have massive center portions but are developed into wheels with spokes 18 in order to facilitate the degasification through these front ends. For reasons of stability it is advisable to connect the spokes 19 by a ring 20, arranged between the rows of cold-compacts 3 and the axle 12 of the cage 2, to which ring the inner slats 16 of the cage are fixed. When the cage has a certain length it may be necessary to support the slats 16 and 17 by further wheels with spokes arranged between the ends of the cage.

Inside this receiving device the cold-compacts are set within the single rows at short distances in order not to obstruct the degasification in any direction.

In FIG. 1 only the top and the bottom row of cold-compacts with their corresponding supporting slats are shown, in order not to overcharge the drawing. There are however arranged in the cage such rows of cold-compacts and such supporting slats round about, as is to be seen in the cross section FIG. 2.

In the apparatus as described the removing of the sintered compacts from the cage is done by means of a sliding carriage 21. This carriage travels on a rail 22 fixed in longitudinal direction to the inside, preferably the bottom, of the sintering chamber 1 and reaching out into the adjacent pressing room, which sliding carriage is displaced by an endless wire rope 24, arranged between two return pulleys 23 and being moved to and fro from outside the vacuum chamber by a suitable gear 25.

The sliding carriage has a hinged tappet 26 held in upright position, e.g. by a spring not shown in this drawing. This tappet 26 is able to stretch in between two of the outer slats 17 supporting the compacts of one file.

Besides this the sliding carriage 21 has a fixed security pin 27 which too stretches in between the outer slats 17 of the cage and protects the hinged tappet 26 from being damaged through unintended turning of the cage 2 during the removing of the compacts 3.

In order to give way to the sliding carriage to pass with upright tappet by the wheels with spokes, the outer rings of the latter are broken between the spokes, as shown in FIG. 2. Therefore the end portions of these spokes have

the shape of an anchor to the flukes of which the outer slats 17 of the cage are fixed.

During the degassing treatment the sliding carriage has its place outside the range of the cage in the unheated pressing room of the vacuum chamber.

To remove the first compact the drum cage is first brought into a position which places one row of compacts exactly above the sliding carriage and in which position the discharging can proceed. Then the sliding carriage is moved into the sintering chamber so far that the hinged tappet 26, being pressed down when passing by the first compact, gets back in its upright position behind this first compact and into the interstice between the latter and the second compact. Then the sliding carriage is pulled out of the sintering chamber whereby the first compact is removed out of the cage.

To remove the second compact out of the cage, the sliding carriage is drawn back into the sintering chamber so far that the hinged tappet is set up again into the interstice between the second and the third compact and then pulled out again from the sintering chamber. This proceeding is repeated until all the compacts of one file are removed from the cage.

Subsequently the sliding carriage is removed out of the range of the cage, and the cage turned so far as to place a further file of compacts into removing position. The compacts of this file are then removed in the way already described.

Obviously it is possible too to remove several compacts together at the same time from the cage and to submit them to the hot-upsetting in the container of the press one at a time. At any rate the capacity of the receiving device of the sintering chamber is, in the case of the invention as described, a multiple of the capacity of the container of the press, which means that the number of compacts being heated at one time requires a plurality of hot-upsetting operations. But even when it is said in the present description of this invention that the compacts are hot-upset one at a time, this invention nevertheless comprises the possibility to manufacture compacts of a small size, allowing to feed several of these compacts simultaneously to the container of the press and to submit them to the hot-upsetting operation at once.

Inside the pressing room 4 there is placed the heated container 5 of a compacting press, propped and fixed in any suitable manner to the bottom of the vacuum chamber. The bottom of this container is formed by a blind die 28 laterally movable from the outside. It is however possible too to provide for another hydraulic punch entering through the bottom of the pressing chamber, instead of a blind die. Through the casing of the vacuum chamber passes in from the outside the punch 6 of the press, a pair of bellows securing the vacuum tight closure between the casing of the chamber and the punch. For practical reasons the driving means for the press are situated outside the vacuum chamber.

On the rim of the container there is arranged a tipping trough 30 taking over the compacts removed from the cage and setting them into the container of the press. In order to bridge the gap between the cage 2 and the tipping trough 20 two juxtaposed and permanent sliding bars are fixed, between which the tappet 26 of the sliding carriage 21 may travel to push the compacts into the tipping trough 30.

After the hot-upsetting of the single compacts in the container 5 the bottom of the latter is opened and the hot-upset compact removed. These compacts are stored in the lower portion of the pressing room 4 until the last compact of the charge has been hot-upset. Then the vacuum may be abandoned and the compacts removed from the pressing room through an aperture not shown in the drawing.

The vacuum chamber is connected, whenever possible without reduction of the cross-sectional area, to the dif-

fusion pump 31 of the pumpstand 9. As a pre-vacuum pump there serves e.g. the rotary oil pump 32.

In order not to have to pass the whole of the gases through the diffusion pump 31 when degasification starts, the pre-vacuum pump 32 may be connected directly to the vacuum chamber through the by-pass valve 33.

The accompanying drawing shows the vacuum-pumpstand 9 following the pressing room 4. It would however be possible to place the pumpstand at the other end of the entire apparatus, i.e. in front of the sintering chamber, instead of the cover 10, which latter would then have to close the pressing room. The feeding of the cage would in this case have to be done across the pressing room.

For the hot-upsetting of the degassed compacts, taking place in the pressing room of the described apparatus, the punch is pressed upon the compact set in the container in such a way that the specific pressure is 2 to 20 t./cm.², preferably 6 to 12 t./cm.². When the punch has borne upon the compact during a certain time, preferably 5 to 30 seconds with this pressure, the blank die 28 at the bottom of the container is removed and the compact pushed down by the punch into the lower portion of the pressing room which has such a capacity as to receive all the compacts of one charge of the cage after the hot-upsetting.

When such an apparatus has a size e.g. allowing compacts of 50 mm. diameter, a press of a power of 200 t. is sufficient to apply a specific pressure of 10 t./cm.² over the cross-section of the container 5. The length of the cold-compact may be about 120 mm., that of the hot-upset compact about 80 mm. corresponding to a weight of about 400 grams. In a cage of an external diameter of 300 to 350 mm. and a length of 2300 mm. 120 compacts may be heated and sintered at once. According to experience a good degasification requires a vacuum-treatment of 12 to 20 hours at 600 to 630° C. An apparatus of the size as mentioned will therefore allow in 24 working hours an output of 120 sintered compacts with a low gas content, each of 50 mm. diameter, 80 mm. length and an average total weight of 50 kgs. Sintered aluminum compacts produced by this method are a useful starting material for the manufacture of small thin walled smooth or finned tubes to be manufactured by extrusion. Such tubes are used as canning tubes for nuclear fuel elements, e.g. in organically cooled reactors.

The utilization of small sintered compacts, manufactured according to this invention, as a primary material for extruding respectively impact extruding of small, thin-walled tubes has the further advantage over the traditional manufacture of such tubes from extruded billets that the loss incurred in the extrusion of these billets is greatly diminished.

It is to be understood that the present invention is not to be limited to the exact details of the method as shown and described. Obvious modifications may occur and be realized without departing from the spirit of this invention and the scope of the appended claims. Certain subject matter not claimed herein is claimed in our copending application Serial No. 527,434 filed February 15, 1966, as a continuation-in-part hereof.

The invention being thus described, what is claimed as new and desired to be secured by Letters Patent, is as follows:

1. Method for the manufacture of dense sintered compacts having a low gas content, made from metal powder, in which aluminum powder covered with aluminum oxide is cold-pressed to give cold-compacts, without being wrapped, being heated and sintered for several hours in the heated portion of a gastight chamber at a temperature slightly below the melting point of aluminum, said compacts being thereby degassed, and then, still in said vacuum, moved to another portion of said gastight chamber and in said portion of said chamber hot-upset in the container of a press, said cold-compacts being heated up for degasification and sintering in the course of 1 to 10 hours, and kept for a further 2 to 100 hours at a temperature of 500 to 650° C., towards the end of said heat-treatment a vacuum of less than 10 mm. Hg being achieved and kept for at least one hour.
2. Method according to claim 1 in which the cold compacts are heated up for degasification and sintering in the course of 2 to 5 hours and kept for a further 12 to 25 hours at a temperature of 500 to 650° C.
3. Method according to claim 2 wherein the heating for said 12 to 25 hours is at a temperature of 600 to 630° C.
4. Method according to claim 3 wherein said vacuum is less than 10⁻² mm. Hg.
5. Method according to claim 1 wherein said vacuum is less than 10⁻² mm. Hg.
6. Method according to claim 1 wherein said temperature is from 600 to 630° C.

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