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POWDER METALLURGY PROCESS

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FIG. 1

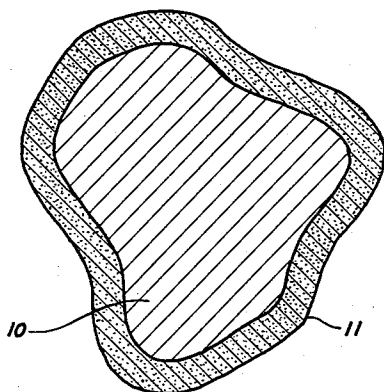


FIG. 2

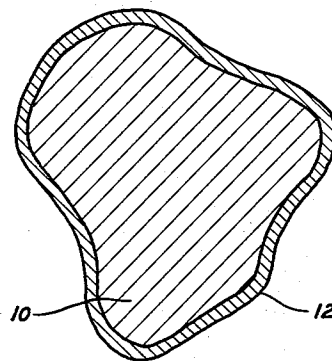
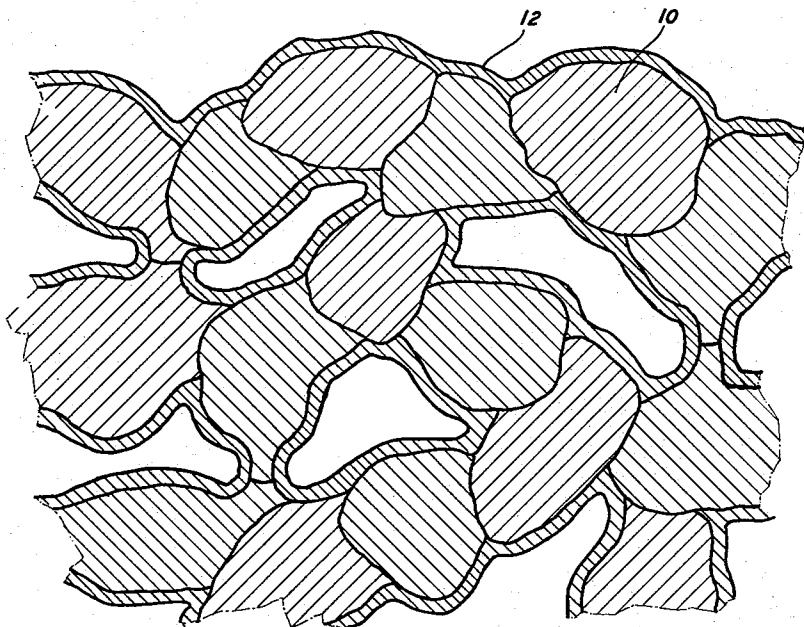


FIG. 3



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POWDER METALLURGY PROCESS

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9 Claims. (Cl. 29—182.5)

This invention relates to a method for the production of solid structures from metal particles. Porous structures of a film-forming metal fabricated in accordance with this invention find special application as anodes in electrolytic capacitors.

The science of powder metallurgy has enabled complex metal structures to be produced by methods which are economically advantageous in comparison with other metal-shaping techniques. The production of a structure by powder metallurgy techniques generally involves the steps of pressing a mass of metal particles into a desired shape and then sintering the pressed compact to cause the metal particles to coalesce.

The uses to which structures fabricated by powder metallurgy are applied are varied, and consequently a range of densities and porosities is required. High density bodies are employed in those situations where the physical properties of the metal in its elemental form are to be duplicated as closely as possible. On the other hand, certain applications require structures of high porosity and low density. Such items as self-lubricated bearings, filters, and diaphragms fall into the latter class.

In general, the density of a structure may be controlled over a wide range by judicious choice of the conditions under which it is produced. However, for a certain group of metals, there existed a limitation in the prior art powder metallurgy processes which precluded the fabrication of structures of less than a certain density. This limitation results from certain requirements of the pressing step. The pressing step must necessarily result in the formation of metal-to-metal contacts among the particles so that the grain growth necessary to produce a unified mass may occur during the sintering operation. If the particles have a refractory coating, such as an oxide layer, such coating must be partially cracked or broken during the pressing step to permit the formation of the necessary metal-to-metal contacts. If the particles from which the porous body is to be fabricated consist of a relatively soft metal coated with a relatively hard oxide, the high pressures required to crack or break the oxide also result in increased compactness of the pressed mass. Accordingly, a high-density, low-porosity structure results. Metals in this category include aluminum, magnesium, titanium, and zirconium.

The present invention permits the production of porous structures of the above-described class of metals, the relative densities of which are lower than heretofore attainable. An important application of this invention is the fabrication of porous aluminum bodies for use as anodes in electrolytic capacitors. (See copending application Serial No. 346,416, filed April 2, 1953, which discloses solid electrolytic capacitors employing porous structures as anodes.) The high effective surface area to volume ratio of the low-density bodies of this invention permits the fabrication of capacitors whose capacitance to volume ratio equals that of aluminum foil wet electrolytic capacitors of commercial quality.

The present invention is described below in terms of aluminum, the metal of special interest. It is, however, to be appreciated that the procedures apply equally well to all members of the above-identified class of soft metals covered with a hard oxide coating.

In accordance with the present invention the aluminum particles are pretreated prior to the operations of press-

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ing and sintering. By means of this pretreatment, described in detail below, a thin, soft hydrated oxide coating is substituted for the hard, refractory, thermal oxide normally present on aluminum particles. The presence of this soft, thin coating permits realization of metal-to-metal contacts at lower pressures, and, accordingly, structures of lower densities may be produced.

An important inherent advantage of the present invention resides in the fact that scoring and galling of the internal die surfaces are minimized during the pressing step. In prior art processes, lubricants such as paraffin and stearic acid were necessary to reduce the abrasive effects of the hard aluminum oxide. The introduction of these lubricants made the sintering operation more complicated since these lubricants had to be evaporated slowly at low temperatures to prevent the compact from disintegrating.

In accordance with the present invention, the removal of the hard oxide layer and the formation of the soft hydrated coating may be accomplished in the same processing step. For example, the aluminum particles are contacted with a solution of aqueous sodium hydroxide which removes the thermal oxide by undercutting and attacking the aluminum substrate. By agitating the particles during this step, the thermal oxide shell surrounding each particle is effectively removed. The soft hydrated oxide coating which forms upon exposure of the aluminum substrate is the result of the reaction between aluminum and water. Following this step, the particles are washed in cold water, dried at low temperatures, and then pressed and sintered.

Alternatively, the hard thermal oxide film may be removed by exposing the aluminum particles to solutions which attack the oxide directly. An example of such a solution is an aqueous solution of chromic and phosphoric acids. The formation of the soft hydrated oxide coating occurs upon exposure of the aluminum substrate.

Porous aluminum bodies with relative densities as low as .5 have been fabricated by the present invention. Solid electrolytic capacitors constructed with such low-density bodies as anodes have capacitance-to-volume ratios comparable to those of commercial grade aluminum foil, wet electrolytic capacitors.

The invention will be better understood from the following more detailed description taken in conjunction with the accompanying drawings in which:

FIG. 1 is a sectional view of an aluminum particle having a thermal oxide coating;

FIG. 2 is a sectional view of the aluminum particle of FIG. 1 in which a thin hydrated oxide film has been substituted for the thermal oxide in accordance with the present invention; and

FIG. 3 is a sectional view of a portion of a porous structure produced by compacting particles of the type shown in FIG. 2.

With further reference to the drawings, FIG. 1 shows aluminum particle 10 which is covered with a refractory oxide coating 11. The usual method of manufacturing aluminum particles consists of blowing the molten aluminum in a stream of air. Accordingly, at such elevated temperatures, a hard, brittle, thermal oxide is formed almost instantaneously on the surface of each of the particles.

In accordance with one aspect of this invention, such particles are treated with aqueous sodium hydroxide to remove the thermal oxide 11 and substitute a thin, hydrated oxide film. Aluminum particle 10 with soft hydrated oxide film 12 is shown in FIG. 2.

A mass of particles of the type shown in FIG. 2 is then pressed into a compact, and the compact is then sintered. FIG. 3 is a cross-sectional view of a body so produced.

Although the detailed description which follows is directed to a method for producing porous structures from particles of aluminum, it is to be understood that the present invention is equally applicable to other soft metals which are covered with a relatively hard, refractory oxide in their usual state. Examples of such metals, in addition to aluminum, are magnesium, titanium and zirconium.

The first step of the present invention is the treatment of the aluminum particles to remove the thermal oxide coating. The removal of the hard, thermal oxide coating may be accomplished by either of two general methods. The first method involves contacting the particles with a reagent which attacks the thermal oxide and dissolves it. There are a number of such reagents known in the art. Of these reagents, those which do not substantially affect the underlying aluminum metal are preferred. Exemplary of this preferred type of reagent is an aqueous solution of chromic and phosphoric acids. The use of this solution is disclosed in an article in the procedure of the American Society of Testing Materials, volume 40, pages 959-966. Other common reagents which attack the thermal oxide directly are hydrazine sulfate (see *Z. Elektrochem.*, volume 56, pages 373-379), and aqueous hydrofluoric acid (see *Materials and Methods*, volume 27, No. 4, page 82).

One of the most convenient of these reagents is an aqueous solution containing 4 percent by weight of phosphoric acid (H_3PO_4) and 2 percent by weight of chromium trioxide (CrO_3). The advantage of this solution is that it does not attack aluminum metal. The particles are contacted with this solution, maintained at a temperature conveniently in the range of from 70° C. to 90° C., for a period of time in the range of from 5 to 20 minutes. The minimum time of 5 minutes is required to assure substantially complete removal of the oxide from the aluminum particles being treated in the temperature range above. The upper limit is occasioned solely by economic considerations, no disadvantage resulting from longer exposure time.

As an alternative to dissolving the thermal oxide film by attacking it directly, the film may be removed by using a reagent which undercuts the oxide by attacking the aluminum substrate. By agitating the particles during this step, the oxide shell is removed from the core of aluminum. Upon exposure of the entire aluminum surface to the reagent, the aluminum dissolves rapidly. Accordingly, it is necessary to carefully monitor the time during which the particles are in contact with the reagent. This may be done visually as described below.

Reagents which react with aluminum and cause it to dissolve are well known in the art. Exemplary of such reagents are the strong alkali hydroxides and carbonates, and the strong acids. Included in the former group are sodium hydroxide, potassium hydroxide, lithium hydroxide, and the carbonates of these alkali metals. Hydrochloric and sulfuric acids are members of the latter group.

The alkali hydroxides have been found to be especially suited for use in the present invention. These strong hydroxides may be used singly or in combination, or may be buffered with bicarbonates to decrease the rate of reaction of the reagent with aluminum and thereby permit a higher degree of control.

It has been found that an aqueous solution of sodium hydroxide of a strength in the range of from .08 percent to 3 percent by weight is advantageous for the removal of the thermal oxide coating. This solution is preferably used at a temperature of approximately 50° C. The particles are immersed for a period of time in the range of from 30 seconds to 60 seconds for the higher concentrations of the above range, this time being increased to approximately 180 seconds for the lower concentrations. The particles, which are agitated throughout this treatment, undergo a color change during the process—from a dark gray to a silvery or light gray.

It is to be appreciated that the removal of the oxide is essentially a chemical reaction, and the times and temperatures suggested above may be varied in accordance with thermodynamic principles.

Following either of the above-described alternative methods for the removal of the thermal oxide, the particles are washed in cold water.

To reduce the hazard of fire or explosion occurring due to the contact of dry unoxidized aluminum particles with the oxygen in the atmosphere, it may be desirable to treat the aluminum particles with cold concentrated nitric acid following the cold water wash to insure the formation of a protective, soft, hydrated oxide over the entire surface area of the particles. Following this treatment in nitric acid, the particles are again washed in cold water.

The next step in the inventive processes is the drying of the aluminum particles. This is conveniently accomplished by washing the particles with a high-volatility, water-miscible solvent, such as methyl alcohol or acetone, and subsequently evaporating the solvent. Alternatively, the water-wet particles may be vacuum- or air-dried. In any event, care should be taken not to expose the aluminum particles to elevated temperatures, since this would tend to convert the soft, hydrated oxide into the refractory, brittle form.

After drying, the particles are pressed into a compact of the desired shape. The pressing operation is conducted in the conventional manner in that the loose powder is placed in a die cavity and pressure thereafter applied to produce a shape with the desired density. A press of the conventional double-acting type which can be preset to give a pressed body of predetermined dimensions is preferred, although any type of press used in the art is suitable. (See "Treatise of Powder Metallurgy," C. G. Goetzl, Interscience Publishers, New York (1949-1952).) Using such a press, the procedure involves calculating the volume of the shape to be pressed, calculating the weight of the body from this volume and the relative density desired, weighing such quantity of treated aluminum particles and placing them into the die cavity, and applying pressure to the press to compact the particles to the desired dimensions.

In the fabrication of porous structures in accordance with this invention from aluminum particles of purity of 99.85 percent and greater (exclusive of oxide coating), there is slight galling of the die cavity during the pressing step. It has been determined that wetting the aluminum particles with a high volatility hydrocarbon solvent, such as for example benzene, xylene or toluene, eliminates this problem. The reason for the difference in pressing characteristics of the powders of varying purity is not presently understood. The mechanism by which the high volatility solvent overcomes this difficulty is also unknown. It does not appear that the action of these solvents can be considered analogous to that of the conventional lubricants heretofore used in the pressing of aluminum. The conventional lubricants are generally high molecular weight materials and their beneficial properties have been considered to stem from the physical properties associated with their lubricating characteristics.

The effect of particle size, shape and structure of the resultant pressed compact are well known in the art. (See "Treatise on Powder Metallurgy," supra.) The effect of the apparent density of the particles to be molded is also known in the prior art, as are the effects of the speed of the press and the magnitude of the pressure applied.

If the structure is destined for use as an anode in an electrolytic capacitor, it is convenient to insert into the mass of particles to be pressed a metal wire which will serve as one electrode of the capacitor. Alternatively, this electrode may be welded to the structure after sintering.

Following the pressing step, the so-called "green" com-

part is sintered. This sintering operation, which is conducted at temperatures in the vicinity of the melting point of aluminum, causes the particles to coalesce into one continuous mass. The actual mechanism of the sintering technique is as yet not fully understood. The factors affecting this type of operation are discussed in detail in chapter XIV of the Goetzel Treatise, referred to above.

It has been determined that a temperature in the range of from 580° C. to 650° C. is preferred for the sintering of green compacts produced in accordance with this invention. The body is sintered at a temperature in the preferred range for a period of from two to three hours. The maximum temperature at which sintering may be conducted is 658° C., the melting point of aluminum. At temperatures substantially below the lower limit of approximately 580° C., the sintering must be conducted for extremely long periods of time to produce the necessary welding between grains and the grain growth required for a mechanically sound structure. An increase in the temperature of sintering permits the sintering time to be decreased in accordance with well-known principles. Times as low as one hour and as high as four hours have been successfully used with temperatures in the preferred range.

If the porous aluminum body is being fabricated for use as an anode in an electrolytic capacitor, it is desirable that the sintering operation be conducted either in vacuo or in a reducing or inert atmosphere. This is occasioned by the fact that the sintered structure must be treated to remove any thermal oxide prior to the anodizing step in the fabrication of the electrolytic capacitor. Accordingly, sintering, in an oxidizing atmosphere such as air, increases the thickness of the oxide film on the sintered body and complicates its removal.

Another illustrative example set forth below outlines the fabrication of a porous body from magnesium particles. Magnesium, like aluminum and the other metals mentioned above, is a soft metal which forms a hard, brittle oxide coating. However, magnesium is more reactive than aluminum and consequently the oxide coating found on magnesium particles is much thicker. Accordingly, it has been considered difficult, if not impossible, to fabricate porous structures of magnesium employing powder metallurgy techniques.

In accordance with this invention, magnesium particles are treated in the manner set forth above for aluminum. The preferred method of removing the hard oxide coating is the use of diluted strong acids, such as chromic, hydrochloric or sulfuric acids, which readily react with the oxide.

The particles are pressed and sintered in the manner described above to produce the desired shape.

The low density aluminum structures produced in accordance with this invention are suitable for use as anodes in electrolytic capacitors of either the solid or liquid type.

A brief description of the method of producing such capacitors follows.

The sintered structure is first cleaned to remove any thermal oxide which may have formed during the sintering process. This is conveniently accomplished by utilizing any one of the reagents disclosed herein or any others known in the art. The porous structure is then washed in cold water to remove all traces of the reagent.

The aluminum body is now ready to be incorporated in a liquid electrolytic capacitor. The capacitor is constructed in the conventional manner using a buffered boric acid solution, for example, as the electrolyte. Capacitors of this type, made in accordance with the procedure herein, have been found to have volume efficiencies in excess of 250 volt-microfarads/cubic centimeter.

If a solid electrolytic capacitor is desired, the aluminum body is boiled for approximately five minutes following the above cleaning procedure. This boiling treatment has been found to have a beneficial effect on the over-all characteristics of the capacitor, the details of

which are discussed in copending application Serial No. 758,977, filed September 4, 1958.

The aluminum body is then anodized in the conventional manner using, for example, buffered boric acid, as the electrolyte.

The next step involves coating the electrode of the capacitor with a quartz cement for approximately an inch of length from the point at which it enters the porous body. This procedure is necessary to prevent shorting of the capacitor due to the electrically conductive coatings applied to the body during subsequent operational steps. Methods of fabricating a solid electrolytic capacitor are well known in the art. One of these is outlined below.

The anodized aluminum body is coated with a layer of manganese dioxide by immersing it in a solution of manganous nitrate and then heating to a temperature in the range of 250°–400° C. for approximately 60 seconds. Following two such applications of manganese dioxide, the body is then reanodized at a voltage approximately equal to 90 percent of the voltage employed in the anodizing step. The current density is maintained at a low level during the reanodizing. The pyrolysis and reanodizing steps are repeated to assure complete coverage of the surface area with manganese dioxide.

After the last reanodizing step, an aqueous slurry of graphite is applied over the manganese dioxide, and the body is then dried. A protective shell, consisting for example of a Schooped metal film is then applied to the graphite. The last step in the fabrication of the capacitor is the soldering of an electrode wire lead to the metal shell.

Solid electrolytic capacitors of this type have been found to have volume efficiencies in excess of 250 volt-microfarads/cubic centimeter and, in general, compare favorably with aluminum foil electrolytic capacitors of commercial quality.

The following examples are illustrative of the present invention.

Example No. 1

A porous aluminum body of .5 relative density was fabricated in the following manner:

Granular aluminum particles of —80 +120 mesh and of 99.85 percent purity were covered with an aqueous solution containing 4 percent by weight of phosphoric acid and 2 percent by weight of chromic acid. The solution was maintained at a temperature of approximately 80° C. and the particles were agitated intermittently throughout the 15-minute treating period.

The particles were washed in cold water following the above treatment. The particles were dried by agitating them in contact with acetone followed by evaporation of the acetone.

The shape which was to be produced was a cylinder $\frac{3}{16}$ inch in diameter and $\frac{1}{4}$ inch in length. Such a shape has a volume of .0069 cubic inch. Since the relative density of the finished body was to be .5, the weight of aluminum particles required to produce such a structure was calculated to be .153 gram. This weight of aluminum particles was introduced into a conventional die. The press which was used, a conventional double-action type, was preset to produce a pressed compact of the desired dimensions. The press was equipped with a safety valve which prevented attainment of pressures in excess of 10 tons per square inch.

The aluminum particles were compacted under pressure to the desired cylindrical shape.

The compact was then sintered at a temperature of approximately 650° C. for a period of approximately 2 hours, resulting in a porous body of .5 relative density.

Example No. 2

A porous body of .6 relative density was constructed in accordance with the procedure of Example No. 1 except that the aluminum particles used were of 99.99

percent purity and were wet with benzene prior to pressing.

Example No. 3

The identical procedure was used as in Example No. 1 above with the exception that the die and press were adjusted to produce a body of .7 relative density.

Example No. 4

Aluminum particles of the type described in Example No. 1 were treated in an aqueous solution containing .3 percent sodium hydroxide by weight. The sodium hydroxide solution was maintained at a temperature of approximately 50° C. and the particles were agitated continuously throughout the 2-minute treating period. The particles were rinsed successively in cold water and cold concentrated nitric acid.

The drying, pressing and sintering procedure described in Example 1 was used to produce a porous aluminum body of relative density .6.

Example No. 5

Particles of magnesium of +35 mesh and of greater than 95 percent purity were contacted with an aqueous solution of chromic acid of 20 percent strength by weight. The acid solution was maintained at a temperature of approximately 50° C., and the particles were agitated intermittently throughout the 3-5 minute treating period.

A drying, pressing and sintering procedure, identical with that described in Example 1 was then followed, producing a porous magnesium body of relative density .75.

Example No. 6

A solid electrolytic capacitor was fabricated utilizing a porous aluminum body of relative density .6 fabricated in accordance with the procedure outlined in Example 1, but using a smaller die which required only 0.112 gram of aluminum.

The sintered aluminum body was treated successively with an aqueous solution of phosphoric and chromic acids, a concentrated sulfuric acid solution saturated with chromium trioxide and concentrated nitric acid.

Each of the above treatments was preceded and succeeded by a rinse in cold water.

The aluminum body was then immersed in three separate containers of boiling water for a total immersion time of approximately five minutes.

The porous aluminum body was anodized to a voltage of 100 volts using a buffered boric acid solution as the electrolyte.

After the rinsing in cold water and drying, the anodized aluminum body was immersed in a 50 percent aqueous solution of manganous nitrate and then heated in air at a temperature of 400° C. for approximately 60 seconds. This procedure was repeated and the body then reanodized at a low current density to 90 volts in the electrolyte used in the anodizing step. The pyrolysis and reanodization were repeated once.

An aqueous slurry of graphite was applied to the manganese dioxide coated aluminum body. The body was then dried and covered with a metal shell by spraying with soft molten solder. A wire lead was soldered to the metal covering.

The capacitor so fabricated had a capacitance of more than 1 microfarad and a leakage current of 15 microamperes at a voltage of 35 volts.

Example No. 7

A wet electrolytic capacitor was constructed utilizing a porous aluminum body fabricated in accordance with the procedure outlined in Example 1.

The aluminum body was cleaned and anodized in accordance with the procedure described in Example 6. The capacitor employed the anodized body as the anode and a buffered boric acid solution as the electrolyte.

The capacitor so constructed had a capacitance of more than 1 microfarad and a leakage current of 20 microamperes at 35 volts.

It is to be appreciated that the present invention resides primarily in the fabrication of porous metal structures. Although the description is chiefly in terms of the properties of such structures which permit their use as anodes in electrolytic capacitors, it is to be understood that the characteristics of the structures of this invention may be altered to meet the requirements of other applications. Variations and substitutions in the described processes may be made by one skilled in the art without departing from the spirit and scope of this invention.

What is claimed is:

1. The process of fabricating a porous structure from oxide-coated metal particles by powder metallurgy techniques comprising the steps pretreating particles of a metal selected from the group consisting of aluminum, magnesium, zirconium and titanium in an aqueous solution selected from the group consisting of hydrazine sulfate, hydrofluoric acid, solutions of chromic and phosphoric acids, hydrochloric acid, sulfuric acid, to effect a substitution of a soft hydrated oxide film for the oxide coating originally present on the particles, and pressing the particles to form a compact.
2. The process of claim 1 in which said metal particles are aluminum and said reagent is an aqueous solution of chromic and phosphoric acids.
3. A porous structure of aluminum produced in accordance with claim 1.
4. A porous structure of magnesium produced in accordance with claim 1.
5. The process in accordance with claim 1 in which the compact is sintered following the pressing step.
6. The process of fabricating a porous aluminum structure comprising the steps of treating particles of aluminum having an oxide coating in an aqueous solution selected from the group consisting of hydrazine sulfate, hydrofluoric acid, solutions of chromic and phosphoric acids, hydrochloric acid, sulfuric acid, said particles having a purity of at least 99.85 percent exclusive of the oxide coating, to effect a substitution of a soft hydrated oxide film for the oxide coating present on the particles, wetting the treated particles with a high volatility hydrocarbon solvent, pressing the solvent-wetted particles into a desired shape, and sintering the pressed shape.
7. The process of fabricating a porous structure from oxide-coated metal particles by powder metallurgy techniques comprising the steps of pretreating particles of a metal selected from the group consisting of aluminum, magnesium, zirconium, and titanium in an aqueous solution selected from the group consisting of strong alkali hydroxides and strong alkali carbonates to effect a substitution of a soft hydrated oxide film for the oxide coating originally present on the particles and pressing the particles to form a compact.
8. A porous structure of aluminum produced in accordance with claim 7.
9. The process of claim 7 in which the said metal particles are aluminum and the said reagent is an aqueous solution of sodium hydroxide.

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