CELLULAR METAL AND METHOD OF MAKING

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No Drawing. Filed Dec. 30, 1963, Ser. No. 334,564

6 Claims. (Cl. 29—183)

This invention relates to cellular metal and to a method for making the same and, more particularly, is concerned with a novel process for preparing void-containing structures of aluminum.

It is an object of the instant invention to provide a novel process for preparing light weight, strong, cellular metals.

An additional object is to provide an aluminum base, open-void, cellular structure of relatively uniform cell size whose cells may be conveniently controlled by feed stock selection.

A further object is to provide a novel process for preparing an aluminum oxide-coated aluminum cellular structure.

Still another object is to provide an aluminum nitride-coated aluminum cellular structure and a method for its preparation.

Other objects and advantages will become apparent from reading the detailed description of the invention disclosed hereinafter.

In general, the present invention comprises coating a metal particle with a material which has a substantially higher melting point than the metal particle itself by heating the metal and a second material to a temperature below the melting point of the metal particle thereby to provide a coating of the reaction product of said metal and said second material on said metal. The so-coated metal particle is subsequently heated to a temperature above the melting point of the metal. The pressure on the coating of said particle is reduced while maintaining the metal at a temperature where it is molten thereby rupturing the surface coating on the particle and allowing at least a portion of the molten metal therein to flow out from the interior of the coated particle thus creating a void space within the coating, i.e., forming a hollow cell.

Cell size of the cellular structure so formed by the process of the present invention is dependent on the size of metal particles employed. With extremely small particles of metal, e.g., powders, the surface tension of the molten metal may prevent its escape from the coating. With large particles, as the metal core melts, the coating itself may collapse and no voids or cells are formed. For optimum performance, particles in the size range of from about 4 to about 50 mesh, U.S. Standard Sieve, ordinarily are used. However, particles somewhat larger and smaller than from 4 to 50 mesh, U.S. Standard Sieve can satisfactorily be employed.

Although the resulting product ordinarily consists of a cellular structure having open, interconnected cells and a metal matrix coated with the high melting surface coating, this void-containing product can be prepared as free flowing individual cells by substantial elimination of all the interstitial aluminum, which provides the cementing action joining the cells in the unitized cellular structure, from the external surfaces of the particle. Removal of a large portion of molten metal from the exterior of the ruptured cells can be readily achieved if agitation is applied during the cell-forming stage to "shake" the molten metal down. In addition, centrifugal force may be used to help separate the molten metal from the coated surface.

In practicing one variation of the invention, an aluminum nitride-coated aluminum cellular structure is obtained by placing particulate aluminum having a particle size within the range of from about 50 to about 4 mesh, U.S. Standard Sieve, in a vessel or rector which permits gas flow around and between the particles. This metal is controllably heated to a temperature above about 660° C. and below the melting point of aluminum nitride (about 2000° C.), with a preferred temperature being about 800° C., in a nitrogen atmosphere at about atmospheric pressure, employing a rate of heating such that a coating of aluminum nitride forms on the particulate metal aluminum prior to the metal reaching its melting point, i.e., about 660° C. When the temperature of the coated pellets reaches the predetermined operating temperature range, the pressure on the entire charge in the furnace is reduced to an absolute pressure of from about 730 millimeters mercury to about 0.001 millimeter mercury. As the pressure is reduced, the aluminum nitride coating on the particles ruptures and molten aluminum flows out of the ruptured aluminum nitride coating. A part of this molten aluminum is retained in the interstices between the aluminum nitride-coated aluminum particles; the remainder flows to the bottom of the reactor vessel. The temperature of the charge is reduced below the melting point of aluminum thereby providing an aluminum nitride-coated aluminum cellular metal structure. Total shell thickness of the aluminum nitride-coated cells ordinarily ranges from 0.01 inch to 0.014 inch. This cellular structure readily can be separated from the substantially solid mass of aluminum in the bottom of the reactor.

Aluminum nitride is not stable in air or water and forms aluminum oxide and ammonia when exposed thereto. Therefore, as the so-formed cellular product is contacted with the normal atmosphere, reaction with aluminum nitride occurs thus giving a cellular product in the form of an aluminum oxide-coated aluminum cellular metal.

The rate of heating is controlled such that the reaction of aluminum and nitrogen ordinarily occurs within about 4 to about 20 minutes from the time the heat is first applied and in any event, is such that formation of the aluminum nitride coating substantially is complete before the temperature reaches the melting point of the aluminum metal.

Nitrogen need be present only in amounts stoichiometrically needed to react with aluminum to form aluminum nitride occurs thus giving a cellular product in the form of an aluminum oxide-coated aluminum cellular metal.

The term "metal," as used hereinafter, is meant to include both the metallic element itself as well as alloys thereof.

The other materials which can be used to react with the metal particles of aluminum or magnesium to form a coating on said metal particle include, for example, ammonium to form a nitride coating; oxygen or water vapor to form an oxide coating; carbon dioxide to form an oxide coating on magnesium; sulfur-containing compounds to form sulfide coatings; and borax and other boron oxide source materials to form an oxide coating. Additional silicate-forming, sulfate-forming and sulfate-forming materials can be used. With gaseous materials, the reactant can be passed between the particulate coating-inducing metal as described hereinbefore. With solid reactants, conveniently these can be blended with the particulate metal prior to heating to provide a mixture wherein the metal and coating material are in close contact. With such material, the total amount of coating
material is to be less than that which reacts, on a stoichiometric basis, with all of the metal present.

The cellular structure of the instant invention finds utility as a sandwich core material wherein strength and lightness are desired, for example, for use in automobiles, aircraft, ships and the like. In addition, this cellular structure may be used as a metallic filter which would have great particle retention power due to the large void volumes in such a filter.

The following examples are merely illustrative of the invention and are in no way meant to limit it thereto.

**Example I**

About 10 grams of particulated \((-6/-8+8\) mesh, U.S. Standard Sieve) aluminum was placed in a crucible which was, in turn, placed in a vacuum furnace (3 kw. unit). The furnace was filled with nitrogen. The aluminum charge was heated within a 20 minute period to about 1100° C. range and held at that temperature for about 50 minutes. During this period, no molten metal was observed in the crucible, thereby indicating formation of an enveloping nitride coating on the surface of each of the particles. The furnace was de-energized and the pressure reduced to about 30 millimeters mercury absolute for about a 90 second period. The weight of the molten aluminum metal inside the sphere along with the decrease in external pressure burst holes in the shell wall of the particles. This molten metal flowed to the bottom of the crucible. The pressure was raised to about atmospheric and the temperature reduced to below the melting point of aluminum. This produced a unitized cellular structure having interconnected cells which weighed only about 4 grams. About 6 grams of residual metal in the form of an apparently solid mass remained in the bottom of the crucible. The aluminum nitride-coated structure was separated from the residual solid residue. When contacted with water or air, this structure gave off ammonia indicating reaction with the aluminum nitride and formation of an oxide surface coating. The cell wall did not disintegrate which indicated that a substantial percent of the shell is aluminum metal.

**Example II**

In order to show that reactants other than nitrogen alone may be used in the method of this invention, a thoroughly mixed combination of about 10 grams of aluminum powder of \(-6/-8+8\) mesh size and about 5 grams of a mixture containing about 67 percent by weight H₂BO₃, about 18 percent by weight B₂O₃ and about 15 percent by weight Na₂B₂O₄ were placed in a crucible which was, in turn, placed in a vacuum furnace and heated at about atmospheric pressure from ambient temperature to about 850° C. over a period of 25 minutes in a nitrogen atmosphere. Following this heating, a reduced pressure of about 75 millimeters mercury absolute was pulled on the vessel during a 50 second period. At these conditions, the molten aluminum broke through the nitride shell of the particles and flowed downward to the bottom of the crucible. The residual void containing particles were substantially free-flowing and not cemented together.

About 90 percent of the resulting particles were hollow and had about a 0.013 inch wall thickness. The material was not as reactive when brought into contact with water which indicated that the aforementioned boron oxide-containing materials had reacted with the aluminum to form aluminum oxide which became a part of the shell.

**Example III**

About 10 grams of particulated aluminum \((-8/-20+20\) mesh) and 5 grams of borax were placed in a crucible and thoroughly mixed. The crucible was then placed in a vacuum furnace. The furnace was filled with argon. The charge was then heated within a 30 minute period to about 800° C. The temperature in the furnace was then allowed to drop to 750° C. over a period of 15 minutes. The furnace pressure was reduced to about 50 mm. Hg whereupon the particles burst and molten aluminum gravity flowed to the bottom of the vessel.

When the material was cooled below the melting point of aluminum, a cellular structure composed of hollow spheres of aluminum coated with said silicon dioxide was obtained.

In a manner similar to the foregoing examples, cellular structures of magnesium, tin, zinc, lead, copper and iron coated with various second materials having a higher melting point than the base itself can be obtained. Various modifications may be made in the present invention without departing from the spirit or scope thereof, and it is to be understood that we limit ourselves only as defined in the appended claims.

What is claimed is:

1. The method of making a cellular metal structure which comprises:
   (a) reacting a particulate metal with a second material at a temperature below the melting point of the metal particle to provide a coating of the reaction product of said metal and said second material on said metal, said coating having a substantially higher melting point than the metal particle;
   (b) heating the so-coated particulate metal to a temperature above the melting point of said metal but below the melting point of said coating;
   (c) reducing the external pressure on the coated surface of said metal thereby rupturing the coating;
   (d) allowing a portion of molten metal to flow out of the coating through the ruptures of said coating thus creating a void space within the coating; and
   (e) cooling the residual void-containing structure of said metal and said coating material below the melting point of said metal.

2. The method in accordance with claim 1 wherein the particulate metal is aluminum and has a particle size within the range of from about 50 to about 4 mesh, U.S. Standard Sieve, and the second material is nitrogen.

3. The method of making an aluminum nitride-coated aluminum cellular structure which comprises:
   (a) heating aluminum particles having a particle size within the range of from about 50 to about 4 mesh, U.S. Standard Sieve, to a temperature below about 660° C. in a nitrogen atmosphere thereby coating the aluminum particles with aluminum nitride;
   (b) heating said coated aluminum particles to a temperature above about 660° C. and below about 2000° C. thereby melting the aluminum within said coating;
   (c) reducing the external pressure on said coated aluminum particles and rupturing the coating;
   (d) allowing a portion of the molten aluminum from the interior of said coated particles to flow through the ruptures in said coating, thereby creating a voided space within said coating; and
   (e) cooling the residual void containing aluminum nitride-coated aluminum cellular structure below 660° C.

4. The method in accordance with claim 3 and including the step of exposing the aluminum nitride-coated aluminum cellular structure to the atmosphere.

5. The method of making an aluminum oxide-coated aluminum cellular structure which comprises:
   (a) admixing aluminum particles having a particle size within the range of from about 50 to about 4 mesh, U.S. Standard Sieve, with a quantity of a boron oxide-containing material which is less than
that stoichiometrically needed to react with said aluminum;
(b) heating the above admixture to a temperature below about 660° C. thereby coating the alumi-
nium particles with aluminum oxide;
(c) heating said coated aluminum particles to a tem-
perature above about 660° C. and below about 2000° C. thereby melting the aluminum within said coating;
(d) reducing the pressure on said oxide coating there-
by rupturing the coating;
(e) allowing a portion of the molten aluminum to
flow through said oxide coating through the rup-
ture in said coating thereby creating a void space
within said coating; and
(f) cooling the residual void containing aluminum
oxide-coated aluminum structure below 660° C.
6. An article of manufacture comprising a cellular
metal structure composed of cells of aluminum nitride-
coated aluminum.

References Cited by the Examiner
UNITED STATES PATENTS
2,434,775 1/1948 Sosnick --------------- 29—192
3,135,044 6/1964 Mote --------------- 75—20

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