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PRODUCTION OF MOLDED METALLIC ARTICLES

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My invention relates to the production of molded metallic articles.

While my invention may be employed for various purposes, it is particularly advantageous for the production of so-called permanent molds for metal casting and the like and will be explained by reference to the foundry art. Many different types of molds have been suggested for use instead of sand molds in the foundry, such as so-called permanent molds, semi-permanent molds, and plaster molds which, like sand molds, provide for only one pouring. Suggestions for molds to take the place of sand molds stem from real or fancied limitations in the use of sand molds and important among the limitations in the use of sand molds is the fact that they provide for only one pouring while the so-called permanent mold or semi-permanent mold provides for a number of pourings. No mold heretofore suggested is fully satisfactory as a substitute for sand molds principally because, notwithstanding venting procedures and the like resorted to in the case of permanent iron or steel molds, they do not provide adequately for the release of air trapped in the mold and for the release of gas given off by the molten metal. The permeability of the sand mold is very important in permitting the escape of such air and gases. Among the real objections to the use of some types of novel molds, however, is the fact that they are not readily made by the use of foundry skill but introduce into an already highly specialized and technical field, namely, the foundry field, a requirement for other types of skills, techniques and specialized equipment heretofore generally foreign to such field. Those skilled in the art are well aware of the problems thereby introduced not only from the personnel standpoint but, more important, from the economic standpoint.

The principal object of my invention is the provision of an improved technique and improved material particularly adapted for the production of molded articles such as permanent or semi-permanent foundry molds.

Another object is the provision of a technique and article, the utilization of which involves skills, common to the foundry and like establishments, in which my invention is adapted to be practiced.

Other objects and features of the invention will be brought out in the detailed description which follows:

In accordance with the general features of the invention, I produce a molded article comprising a matrix of sintered metallic particles substantially free of extraneous matter and with the metallic particles interconnected by a bond of metallic material, the molded article being porous and having a density of only about 25 to 50% of that of a similar article formed of a solid metallic mass having an identical or substantially identical composition. While the molded metal article preferably has a density of only about 25 to 50% of that of a corresponding solid metal article, and preferably between 30 and 40% thereof, the process used can be employed in such a way as to modify the density of the molded metal article at the will of the operator.

The process comprises forming a powdered metallic mixture having approximately the consistency of damp molding sand, the powdered mixture comprising a desired mixture of metal particles of suitable mesh size and a reducible metallic compound, preferably a metallic hydroxide, which will form with water a paste having a binding action but which may be reduced to a metal without leaving a deleterious residue within the structure of the molded article. The moldable mixture is molded like ordinary foundry sand, preliminarily dried and heated in a reducing atmosphere at a high enough temperature and for a sufficient length of time to reduce the reducible metallic compound and partially sinter the metallic particles to produce a strong self-sustaining article, shaped by molding, and adapted for use as a porous metallic mold into which molten metal can be cast for the production of metal castings. The porosity or density of the final article can be controlled in various ways, such as by controlling the mesh of the metallic particles and also by the use of supplementary binding materials which, on heating of the molded mass, will be volatilized or otherwise removed to leave interstitial voids and thus increase the gas permeability and decrease the density of the molded article.

My invention is particularly adapted for the production of ferrous articles in which a paste of ferric hydroxide is employed as a binder and in which powdered ammonium chloride, and other volatile substances, is employed as a supplementary bonding material. The ferrous powder may comprise only substantially pure iron or the article, as produced, may comprise a ferrous alloy formed either by mixing iron powder and a powdered alloying constituent, or by directly employing a powder of the ferrous alloy desired. I prefer to employ the alloy powder directly, first, because the method which I employ does not lend itself to the actual production of alloys by powder metallurgy as does the usual technique involving

high pressures and high sintering temperatures, and, secondly, because many types of alloys are commonly produced in powdered form as a by-product of industry and can readily be utilized in the practice of my invention. I have found, for example, that saw filings, some hammer mill scale, and many other types of finely divided metallic wastes heretofore considered of little value industrially can be employed directly in the practice of my invention.

In accordance with one manner of carrying out my invention, I first classified saw filings to produce a powdered product 100% of which would pass a 40 mesh screen and 90% of which was retained on a 100 mesh screen. A ferric hydroxide paste was formed by producing a solution of ferric chloride and adding ammonium hydroxide thereto. A reaction is produced resulting in the precipitation of ferric hydroxide which was filtered from the solution without washing and was found, on analysis, to contain 30% ferric hydroxide, the balance being water and ammonium chloride solution. 80 parts of the iron powder described, 4 parts of granulated ammonium chloride and 16 parts of the ferric hydroxide paste produced in the manner described were then thoroughly mixed with a composition produced having approximately the consistency of damp molding sand. The composition was then tamped into a relatively small mold using about the same pressure and following about the same technique used in the production of sand molds in the ordinary foundry. The resulting shaped article was immediately placed in a non-oxidizing atmosphere and allowed to dry. When it was dry, it was heated in an atmosphere containing a substantial amount of hydrogen at a temperature of 2100 degrees F. for two hours and forty-five minutes. The article had a wall thickness not substantially greater than one inch and after cooling was found to be a strong self-sustaining article, the individual particles of which were sintered together, and the ferric hydroxide substantially entirely reduced to metallic iron. The product had approximately ⅓ the density of the ferrous material from which the saw filings were produced and had about 66% porosity.

In accordance with another example, I selected powdered material comprising essentially pure iron, the said powdered material passing a 50 mesh screen but being retained on a 200 mesh screen. 78% of this powdered material, 15% by weight of a ferric hydroxide paste (containing 30% ferric hydroxide), and 7% by weight of dry ammonium chloride were thoroughly mixed to form a molding composition having about the consistency of damp molding sand. This material was then molded to form discs four inches in diameter and ½ inch in thickness, using only enough molding pressure to form a semi-adherent body but not enough pressure to closely compact the metallic particles. These molded discs were first dried and then heated at 2000 degrees F. for two and one-half hours in a reducing atmosphere comprising essentially hydrogen. The sintered discs produced had a uniform structure from 28 to 30% the density of solid iron and formed excellent filters for the removal of water and other impurities from gasoline. By passing high temperature steam through the pores of such filters, the exposed surface was partially converted to magnetic oxide which resisted further oxidation and rendered the material very suitable for various types of filtering operations.

Those skilled in the art will understand that various modifications in procedure and composition are possible within the scope of the invention as herein disclosed and hereinafter claimed. The particle size of the metallic particles or metallic powder may be varied extensively and the uniformity or lack of uniformity of particle size has a bearing upon the density and characteristic of the final product. The firmness with which the particles are compacted together when molded and the manner of compacting also have a bearing upon the density and uniformity of the product. Generally speaking, the technique employed in foundry practice, when producing green sand or dry sand molds, cores and the like, may be followed. The sintering time and temperature may also vary considerably depending upon the specific character of the molding composition and the cross sectional area thereof. I have found, for example, that if the wall of a product to be sintered comprising essentially powdered iron is approximately one inch in thickness and the heating temperature is 2100 degrees F., a well sintered product is produced in from two and one-half to three hours. If the temperature is raised, the sintering time may be reduced and vice versa. Generally speaking, I prefer to employ a sintering temperature at least of the order of 2000 degrees F. when operating with ferrous powders but I have found that temperatures considerably below 2000 degrees F. may be employed with, of course, considerably increased time allotted to the sintering operation.

The permanent binder employed, preferably a metallic hydroxide, may be modified considerably both in composition and amount. The binder must comprise a material which can be reduced to a metal which is not deleterious in the environment in which it is employed as a binder. Since the binder comprises a relatively small amount of the mass of the completed article, considerable latitude is permitted in the selection of a binder. If a product is to be produced comprising essentally chromium, for example, ferric hydroxide may sometimes be employed as a binder without deleterious results on the final product desired. Many other metallic oxides any hyhroxides, such as copper hydroxides, and particularly those which form colloidal or colloidal like suspensions are preferred. It is to be noted, however, that the metallic hydroxide comprises an essential part of the permanent binder upon its reduction and while it is desirable that it also have some function as a temporary binder during the initial molding operation, a separate temporary binder can be depended upon in many instances, particularly when it is desired to form a relatively porous final product. Such materials as ammonium chloride, and other volatile materials providing a bonding action are suitable as temporary binders. I wish to point out also that while the metallic hydroxide employed as a binder is preferably introduced as a paste, I have had some success in producing a binder in situ as, for example, by treating iron powder with a relatively small amount of acid to form a surface comprising a metallic salt and neutralizing the metallic salt with a base such as ammonium hydroxide to produce a thin coating of ferric hydroxide about the residual metallic granules in sufficient amount to produce a bonding action.

Such particles may be molded together and reduced in the manner described to produce a final sintered product.

It must not be assumed that my invention is limited to the production of ferrous molded sintered products, since may different types of molded products may be produced in like manner. I have mentioned chromium which may be employed as such or mixed with other metal powders such as nickel, iron, cobalt, copper, manganese, aluminum, cadmium, magnesium, tin, zinc, and the like, all of which may be used alone or in admixture with each other. While, preferably, the particles employed are metallic, the presence of some oxide is not deleterious in many instances because of a reducing action which takes place in the furnace. I have found, for example, that magnetic iron oxide, hammer mill scale and like materials may comprise at least a part of the metallic powder employed and a suitable final molded product produced for many purposes.

I have referred in the early parts of this specification to production of permanent molds and molded articles produced in accordance with my invention, particularly when fabricated of ferrous particles, and very suitable for the production of certain types of molds which can be used repeatedly without appreciable impairment. Various types of mold washes may be employed on such molds depending upon the type of metal being cast. The very great advantage of such molds is that they can be produced in an ordinary foundry employing ordinary foundry equipment and by men skilled in foundry practice. The metals of my invention may have other utility where a light, strong, porous, metallic body is desired. Illustrations of such use are filters of various kinds. There may be other uses which those skilled in the art will readily understand where a combination of metallic properties, lightness and controlled porosity are important.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. The method of producing a molded article which comprises mixing metallic particles with a hydrated metal hydroxide forming colloidal-like suspensions and capable of being reduced in a reducing atmosphere, forming the mixture to a desired shape and heating the shaped mixture in a reducing atmosphere to reduce the said metal hydroxide to metal.

2. The method of producing a molded article which comprises mixing metallic particles with a vaporizable temporary binder and a hydrated metal hydroxide forming colloidal-like suspensions and capable of being reduced in a reducing atmosphere, forming the mixture to a desired shape and heating the shaped mixture in a reducing atmosphere to reduce the said metal hydroxide to metal.

3. The method of producing a molded article which comprises mixing metallic particles with a metal hydroxide paste to form a mixture having the general consistency of damp molding sand, said metal hydroxide being of a type forming colloidal-like suspensions and reducible in a reducing atmosphere, molding an article therefrom, and heating the article in a reducing atmosphere.

4. The method of producing a molded article which comprises mixing metallic particles with a metal hydroxide paste and a temporary vaporizable binder to form a mixture having the general consistency of damp molding sand, said metal hydroxide being of a type forming colloidal-like suspensions and reducible in a reducing atmosphere, molding an article therefrom, and heating the article in a reducing atmosphere.

5. The method of producing a molded article which comprises mixing together a powdered metal consisting essentially of iron and a ferric hydroxide paste to form a damp moldable material, molding an article therefrom and heating the article in a reducing atmosphere.

6. The method of producing a molded article which comprises mixing together a powdered metal consisting essentially of iron, a temporary vaporizable binder and a ferric hydroxide paste to form a damp moldable material, molding an article therefrom and heating the article in a reducing atmosphere.

7. The method of producing a molded article which comprises mixing together a powdered metal consisting essentially of iron, ammonium chloride, and a ferric hydroxide paste to form a damp moldable material, molding an article therefrom and heating the article in a reducing atmosphere.

8. The method of forming a permanent mold, which comprises mixing together powdered iron and a ferric hydroxide paste to form a mixture having the general consistency of damp foundry sand, forming a mold therefrom, and heating the resulting mold in a reducing atmosphere.

9. The method of producing a sintered metal product which comprises mixing together particles, comprising essentially iron, with a gelatinous paste comprising approximately 30% iron hydroxide in a water solution of ammonium chloride to form a mixture having approximately the consistency of damp molding sand, molding an article from said mixture, drying the article and finally sintering the dried article in a reducing atmosphere, the reduced iron hydroxide thereby forming a ferrous bond between the said iron particles.

10. The method of producing a sintered metal product which comprises mixing together metal particles and a water paste of iron hydroxide to form a damp moldable mixture, molding an article from said mixture, and then heating the article in a reducing atmosphere.

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