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POWDER METALLURGY PROCESSES AND PRODUCTS

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This invention pertains to the art of powder metallurgy, more especially as applied to metals which are highly reactive chemically, such as titanium, zirconium and base alloys of each, and to new materials of superior characteristics formed thereof and processes for producing the same by novel powder metallurgy techniques.

A primary object of the invention is to provide materials of such chemically reactive metals in the manner above referred to which possess superior hot strength properties as compared to those of these same metals as produced in massive form directly from an initially molten state.

In accordance with the basic procedure of the invention this is accomplished by reducing the metal to an extremely fine particle size, ordinarily on the order of 1 to 2 microns, more or less, in mean minimum dimension, applying to each particle a thin, protective coating of a stable metal oxide, and thereupon consolidating by pressing and sintering.

As is now well known, finely powdered aluminum upon air heating to develop an oxide coating on each particle followed by pressing, sintering and working, results in a material of greatly enhanced strength, creep and fatigue resistance at elevated temperatures as compared to the aluminum metal itself as obtained, for example, by casting from the molten state. The useful service temperature of aluminum is thus raised from 200–400° F. to about 600–800° F. Sintered oxidized aluminum powder thus has much higher elevated temperature strength than does aluminum itself or any of its wrought and cast alloys. Worked shapes of the material have some residual ductility—enough to be definitely useful.

The reason for this is not too well understood. One explanation is that by starting with aluminum in fine particle size of the order aforesaid and applying to each particle a thin oxide coating, as by heating in air, and thereupon consolidating by pressing, sintering and working, the oxide coating in each particle breaks up into small, discrete platelets which distribute themselves like fence pickets about the particles, leaving the intervening portions of the aluminum particles exposed to each other to be welded together and coalesced by the pressing, sintering and subsequent hot and/or cold working operations. The oxide platelets, however, prevent recrystallization of the small aluminum particles, thus preventing grain growth from particle-to-particle, thereby retaining the original micro-structure. The slip shear strength is thus increased as compared to that of massive aluminum as produced from the molten state. This latter on cooling produces relatively large crystals, which reduce the slip shear strength, for this reason and presumably also for the reason that the recrystallization probably removes some voids between crystals thus further reducing the slip shear strength.

It has been attempted to produce analogous results with titanium powder, using controlled oxidation, nitriding or carburizing, to produce a skin or adherent coating on each powder particle. Since, however, extremely fine powders must be used, if at sintering temperatures any diffusion occurs, a homogeneous alloy will result and the purpose defeated. Unfortunately, the oxide, nitride and carbide of titanium are readily soluble in titanium and diffuse rapidly into the metal at minimum sintering temperatures of about 1300–1400° F. Instead of sintering to an adherent mixture with properties governed by the duplex structure, the composite homogenizes at least in part and a normal alloy results. The methods applicable to finely divided aluminum are thus not satisfactory when applied to powdered metals such as titanium, zirconium and base alloys of those metals.

In accordance with the present invention, it is proposed to coat the titanium or zirconium particles with a metal oxide other than an oxide of the base metal particle, which oxide is insoluble in the metal at sintering temperatures. Furthermore, the metal oxide with which the titanium particles, for example, are coated must be one which is stable in contact with titanium at the elevated temperature. That is to say, the metal oxide must not decompose thus providing oxygen for combination with titanium at the elevated temperature.

The oxides of calcium, magnesium, beryllium and thorium fulfill both stability and insolubility requirements for use with titanium and zirconium and base alloys of these metals, and may be employed individually or in admixture in the present invention. Certain of the rare earth oxides also exhibit the necessary characteristics required of the metal particle coating. Gadolinium, for example, is entirely satisfactory. However, for economic reason the alkaline earth metal oxides mentioned and thorium oxide will generally be employed.

The particles of the base metal are very finely divided, preferably having a mean minimum dimension of the order of about 1–2 microns or less. In order to assure the requisite coating of the finely divided metal, the particles of metal oxide must have a mean maximum diameter substantially less than the mean diameter of the metal particles. To produce a substantially continuous coating on the metal particles, the metal oxide particles should be of the order of about ten times smaller than the metal powder. Colloidal suspensions of the coating materials provide an excellent source of the metal oxide in a sufficiently fine state of subdivision.

Coating may be effected by agitating the base metal powder in a colloidal suspension. When coating has been effected, the suspending liquid is drawn off and the thus coated metal powder dried, after which it is consolidated by pressing and sintering. The so-coated particles are consolidated into an integral composition by concurrent pressing at about 5000 to 10,000 p.s.i. at sintering temperatures of about 1300–2000° F., and preferably at about 1400–1700° F. over a period of about 5 to 25 hours. Alternatively, pressing and sintering may be carried out as separate steps, in which case, the coated metal powder is first consolidated by cold pressing, requiring about 75,000 to 125,000 p.s.i., followed by sintering in the temperature range aforesaid.

Because of the ready solubility of nitrogen and oxygen in the base metal, sintering is effected in an atmosphere not containing appreciable quantities of these elements, in order to obtain maximum uniformity of properties in the sintered product. Preferably, the atmosphere is inert with respect to titanium, for example, as argon. The method of the present invention thus departs from the teachings of the sintered aluminum powder metallurgy art wherein the aluminum particles with a surface coating of aluminum oxide are sintered in an oxidizing atmosphere. The problem of solubility of surface metal oxide coating is not encountered in the aluminum powder metallurgy art.

Alternatively, coating may be effected as follows: A colloidal gel may be produced as, for example, by precipitating a metal oxide in hydrated form by the addition of a precipitating agent to an aqueous solution of a salt of the metal, the resulting reaction mixture being allowed to stand until the hydrated oxide precipitate

formed has settled, whereupon the supernatant liquid is poured off. The resulting gel is then mixed with the base metal powder, for example, titanium or a titanium base alloy. The mixture is thereupon dried with accompanying continuous agitation, and the residual salt of the precipitating agent leached out with a non-aqueous solvent. The bound water in the particle coating is then drawn off by heating in a vacuum, and the coated metal powder thus obtained is ready for use in the production of pressed and sintered powder metallurgy products in accordance with the invention.

In accordance with another modification, the metal oxide in an extremely fine state of subdivision in the form of a dry powder may be thoroughly admixed with the base metal powder as by ball milling or tumbling, and the resulting mixture pressed and sintered as aforesaid. This thorough admixing coats the base metal particles with the finely divided metal oxide in a loosely adherent manner, which, however functions in the same manner as the colloidally applied coating to provide powder metallurgy products of improved high temperature properties on subsequent pressing, sintering and working.

Thus, for example, magnesia or one or more of the other metal oxides above referred to may be ball milled, either dry or in admixture with a liquid such as alcohol, a liquid hydrocarbon, or even water, provided steps are taken to rid the hydrate formed of its water which would be strongly bound. With any of these modifications the ball milling is continued until the coating of the finely divided metal oxide is produced upon the metal particles, or until the metal oxide is reduced to a state of subdivision fine enough to coat the metal particles more or less continuously. At this juncture, titanium for example is added and the ball milling continued until microscopic examination reveals that the base metal particles have acquired a more or less continuous coating of the metal oxide. The coating metal oxide when reduced to a sufficiently fine state of subdivision will adhere to the base metal particles sufficiently well to permit removal of the excess metal oxide by screening or blowing. In the event ball milling is carried out in a liquid medium, the excess slurry is drained off following coating of the base metal particles, and the residual mass dried, whereupon excess coating powder is removed by screening or blowing as aforesaid. The material thus obtained is ready for use in the production of pressed and sintered products. If the liquid medium employed is water, a final drying is effected mild heating in a vacuum prior to consolidation.

It is difficult to prescribe the ultimate thickness of the metal oxide coating because of the permissible variation of particle size and the starting metal oxide itself. Similarly, it is equally difficult to specify weight ratios

of metal to metal oxide powder. However, it is sufficient to say that the concentration of metal oxide in the finished sintered product should be such that the product does not contain more than about 20% by weight oxygen, and preferably less than 20% by weight oxygen.

This application is a continuation-in-part of my application for U.S. Letters Patent Serial No. 420,440, filed April, 1, 1954, now abandoned.

What is claimed is:

1. A composition for production of metal-ceramic, sintered compacts, consisting essentially of a powder mixture of a metal selected from the group consisting of titanium, zirconium and base alloys thereof, and a ceramic material selected from the group consisting of oxides of calcium, magnesium, beryllium, thorium, gadolinium and mixtures thereof, said metal being present in said composition in the form of discrete particles having a mean maximum dimension not greater than about 2 microns, said oxide being present in said composition in the form of discrete particles preferably having a mean maximum dimension not greater than about one-tenth that of said metal particles, and said oxide particles forming a substantially continuous coating about said metal particles.

2. A composition for production of sintered compacts, comprising a mixture of solid particulates consisting essentially of a metal selected from the group consisting of titanium, zirconium and base alloys thereof, the particles of said metal having a mean maximum dimension not greater than about two microns, and a metal oxide characterized by substantial insolubility in said metal and thermal stability in the presence of said metal at the sintering temperature, and the particles of the said metal oxide having dimensions so as to provide a substantially continuous coating of metal oxide particles about the individual metal particles.

3. A sintered and consolidated article comprising a composition in accordance with claim 2.

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