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 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 microstructure. 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 re-

moves 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 and may be car-
rried out as separate steps, in which case, the coated metal powder is first consolidated by cold pressing, re-

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 have very satisfactory characteristics required of the metal particle coating. Gadolinium, for example, is entirely satisfactory. However, for economic reasons 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—5 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. Coated 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, re-
quiring about 75,000 to 125,000 p.s.i., followed by sintering in the temperature range aforesaid. 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 then used with accompanying continuous agitation, and the residual salt of the precipitating agent is removed 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. 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. Similarly, it is equally difficult to specify weight ratios of particles of a metal of the group consisting of titanium, zirconium and base alloys of said metals, with particles of an oxide of a metal of the group consisting of calcium, magnesium, beryllium, thorium, gadolinium and mixtures thereof, said oxide particles having a maximum dimension less than one-tenth that of said metal particles, whereby said metal particles are individually coated with said metal oxide, separating said coated metal particles from non-adhering metal oxide, and thereupon consolidating the so-coated particles by application of pressure and heat at sintering temperatures. The process which comprises: thoroughly admixing finely divided particles of a metal of the group consisting of titanium, zirconium and base alloys of said metals with particles of an oxide of a metal of the group consisting of calcium, magnesium, beryllium, thorium, gadolinium and mixtures thereof, said oxide particles having a maximum dimension less than one-tenth that of said metal particles, whereby said metal particles are individually coated with said metal oxide, separating said coated metal particles from non-adhering metal oxide, and thereupon consolidating the so-coated particles by application of pressure and heat at sintering temperatures, whereby said so-coated particles are consolidated. The process which comprises: thoroughly admixing finely divided particles of a metal of the group consisting of titanium, zirconium and base alloys of said metals with particles of an oxide of a metal of the group consisting of calcium, magnesium, beryllium, thorium, gadolinium and mixtures thereof, said oxide particles having a maximum dimension less than one-tenth that of said metal particles, whereby said metal particles are individually coated with said metal oxide, separating said coated metal particles from non-adhering metal oxide, and thereupon consolidating the so-coated particles by application of pressure and heat at sintering temperatures, whereby said so-coated particles are consolidated. The process which comprises: thoroughly admixing finely divided particles of a metal of the group consisting of titanium, zirconium and base alloys of said metals with particles of an oxide of a metal of the group consisting of calcium, magnesium, beryllium, thorium, gadolinium and mixtures thereof, said oxide particles having a maximum dimension less than one-tenth that of said metal particles, whereby said metal particles are individually coated with said metal oxide, separating said coated metal particles from non-adhering metal oxide, and thereupon consolidating the so-coated particles by application of pressure and heat at sintering temperatures, whereby said so-coated particles are consolidated.
a mean maximum dimension substantially smaller than that of said metal particles, whereby said metal particles are individually coated with said oxide, and thereupon consolidating the so-coated particles by application of pressure and heat at the sintering temperature in an atmosphere which is inert with respect to said metal.

7. A process for the production of a sintered compact which comprises: thoroughly admixing particles of a metal selected from the group consisting of titanium, zirconium and base alloys of each having a mean dimension not greater than about two microns with particles of a metal oxide characterized by substantial insolubility in said metal and thermal stability in the presence of said metal at the sintering temperature, said oxide particles having a mean maximum dimension substantially smaller than that of said metal particles, whereby said metal particles are individually coated with said oxide, thereupon consolidating the so-coated particles by application of pressure and heat at the sintering temperature in an atmosphere which is inert with respect to said metal, and mechanically working the pressed, sintered compact to develop maximum properties therein.

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