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METHODS FOR PASSIVATING METAL POWDERS
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1 Claim. (Cl. 117-100)

This invention relates to processes for treating finely divided metal powders and more particularly to a process for passivating sub-micron size particles of metals which are normally pyrophoric in the presence of oxygen.

The use of iron, nickel and cobalt powders comprised of particles under one micron in size has, in the past, been limited by the fact that such powders are extremely reactive with oxygen and must therefore be isolated from air during handling and processing to prevent spontaneous combustion. Obviously, when the powders must be isolated from any oxygen containing environments, such as air, any processes, such as sintering, become more difficult and expensive. Thus, although it is apparent that metal powders of sub-micron particle size would be of value as binders in producing high density sintered bodies, such use has not generally been possible due to the required, special, time consuming, and expensive processing steps.

It is therefore a principal object of this invention to provide a process for passivating submicron size, normally pyrophoric powders of iron, nickel and cobalt to render them substantially inert to oxygen.

Other objects and advantages of this invention will be in part obvious and in part explained by reference to the accompanying specification.

Since normally pyrophoric sub-micron size metal powders would be of great value, as previously discussed, if they were not so difficult and dangerous to handle, it was attempted to reduce the pyrophoric tendencies by cooling the powders in liquid and gaseous mediums. During the course of this work it was noted that when the powders were treated with certain specified mediums they became permanently passivated and that temperature had no apparent effect on the particle reactivity. That is, cooling of the powders was of no particular value in assisting passivation, the effect occurring by some other mechanism. The results and observations obtained from the work resulted in the present invention.

Generally, this invention relates to a process for passivating sub-micron sized particles of iron, nickel, cobalt and combinations thereof by contacting the particles with a gas or liquid passivating medium selected from the group consisting of nitrogen [N₂], titanium tetrachloride [TiCl₄], silicon tetrachloride [SiCl₄], and carbon tetrachloride [CCl₄], to render the particles substantially inert to oxygen and the invention also relates to a process for producing sintered bodies from the passivated particles.

It has been recognized that high density sintered bodies of improved physical characteristics could be produced if metal powders having sub-micron particle size could be used as filler or binder materials. Such sub-micron size particles are also of value as catalysts, under selected conditions. However, the highly reactive state of the powders has prevented their general use in normal engineering and technical situations.

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The process by which the sub-micron size particles of iron, nickel, cobalt or combinations thereof are passivated or rendered inert to oxygen comprises contacting the powder with passivating medium selected from the group consisting of nitrogen, titanium tetrachloride, silicon tetrachloride and carbon tetrachloride. The powders are kept in contact with the passivating medium for a time sufficient to render the powders substantially inert to oxygen, the precise time depending on the passivating medium used. For example, if gaseous nitrogen rather than liquid nitrogen is used, a longer period of time is required before the powders become inert to oxygen. By comparison, if liquid nitrogen is used, the passivating effect occurs practically instantaneously.

As an example, a quantity of iron powder having an average particle size of 0.10 micron was placed in a suitable receptacle and liquid nitrogen poured into contact with it. Although the time of contact between the nitrogen and the iron powder was extremely brief, only a few seconds, the iron had been completely passivated. This passivated powder was observed at varying time intervals following treatment and even after several weeks there was no evidence that the passivation was other than permanent.

Treatment similar to that just described was also carried out on a second sample of iron particles having average particle size, this time the powder being contacted with gaseous rather than liquid nitrogen. In this case a contact time on the order of 14 to 16 hours, was required to insure that complete passivation had been effected. In both cases the metal particles had become permanently inert to oxygen.

When one of the tetrachlorides is used the process is preferably varied somewhat. Specifically, a quantity of metal powder, either iron, nickel, cobalt or some combination thereof is located in a suitable receptacle and a stream of pure dry hydrogen is bubbled through the tetrachloride so that it becomes saturated with tetrachloride vapor. The vapor laden hydrogen is then passed over the metal powder so that the powder is intimately contacted with the chloride held in vapor suspension in the hydrogen. As an example, a quantity of iron having a particle size averaging about 0.10 micron was subjected to a stream of hydrogen gas which had been bubbled through titanium tetrachloride. The powder was inactivated and evidenced no sign of affinity for oxygen upon exposure to air, so that it could be used in the presence of oxygen without any special precautionary steps being taken. If desired, although this step is not felt to be necessary, the iron powder may be heated to about 500° C. so that any halides such as FeCl₂, which might be formed during the passivating would be removed.

Although the exact reason for the passivating effect is not clearly understood, it is felt that the probable explanation is the presence of a protective layer on the outside of the particles. In the case of nitrogen, the layer would be an adsorbed layer of nitrogen, whereas in the tetrachlorides, the layer would be an alloy of iron with the metal part of the tetrachloride compound. For example, if iron were the metal powder being used and nitrogen the passivating medium, a layer of adsorbed gas would be present over the entire outer periphery of the particle. On the other hand, if titanium tetrachloride were the passivating medium a layer of an iron-titanium alloy would probably be on the particle surfaces. Simi-

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lar protective coatings would be formed on cobalt or nickel and where silicon or carbon tetrachloride were used for passivation, the protective layer on the outer surface of the particles would vary accordingly.

Thus the present invention provides a process for producing passivated normally oxygen reactive metal powders of less than 1 micron particle size which are resistant to combination with oxygen. Since these powders are inert to oxygen, they can be easily handled and processed according to existing powder metallurgy techniques to produce higher density bodies than has heretofore been producible by these methods.

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

A process for passivating submicron sized particles of

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a metal selected from the group consisting of iron, nickel, cobalt and combinations thereof, comprising contacting the particles with liquid nitrogen to render the particles substantially inert to oxygen.

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