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FLUIDIZED REDUCTION OF OXIDES ON FINE METAL POWDERS WITHOUT SINTERING

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16. Abstract

In the process of reducing extremely fine metal particles (av. particle size $\leq$ 1000 A) covered with an oxide layer, the metal particles are fluidized by a gas flow contg. H, heated, and reduced. The method uniformly and easily reduces surface oxide layers of the extremely fine metal particles without causing sintering. The metal particles are useful for magnetic recording materials, conductive paste, powder metallurgy materials, chem. reagents, and catalysts.

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(54) Method of deoxidizing ultrafine metal particles

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DETAILS

1. Name of Invention.

Method of deoxidizing ultrafine metal particles.

2. Area covered by the present patent application.

The present method is for deoxidization of ultrafine metal primary particles of diameter less than 1000 Å and whose surfaces are covered with oxide layers. The method is characterized by fluidizing ultrafine metal particles by a gas flow containing hydrogen and heating at elevated temperatures.

3. Detailed explanation of the present method.

The present invention is a method of deoxidizing ultrafine metal primary particles of the average diameter less than 1000 Å.

It is well known that ultrafine metal particles of the average diameter less than 1000 Å have excellent properties for materials for electronics and magnetic recording, conductive paste, powder metallurgy, reagents for chemical reaction and catalysts.

In the conventional methods, fine metal powder (for example, more than 1 micron) is manufactured by mechanically pulverizing metal or processing metal containing chemical reagents in solution by appropriate deoxidizers. For manufacturing extremely fine metal particles (usually the diameter less than 1 μ), the vacuum vaporization method in which metal is heated and evaporated in vacuum (less than 10^{-3} torr) or the method of vaporizing metal in an environmental (buffer) gas such as argon, nitrogen and hydrogen, of pressure less than several hundred torrs is used.

In these methods, if the diameter of manufactured metal particles becomes less than the order of microns, the particles tend to spontaneously ignite in air because of the high specific surface area and the strong affinity to oxygen. Therefore, in the manufacturing process, oxygen is removed from the surface of fine metal particles and then the particles are stored or transported. It is, of course, possible to prevent spontaneous ignition by sealing metals in gases or liquids which do not react with metals in the manufacturing process. However, it will make manufacturing, storage and transportation of the particles very complex and increase potential dangers. This situation has been restricting application of ultrafine metal particles. A method for deoxidizing ultrafine metal particles covered with oxide layers without spoiling the characteristics (for example, increasing the grain diameter by sintering) will be of great value in industry.

The present invention aims at solving these problems. In other words, the purpose of the present invention is to offer a method of deoxidizing ultrafine metal particles covered with oxide layers without changing the characteristic features.

The present inventor examined many reduction methods in order to achieve the above mentioned goal. He found a successful method in which ultrafine metal particles are dispersed in solvents such as water and alcohol, and deoxidizing reagents such as sodium boride hydride, hydrazine and hormarine. However, this approach has several difficulties. For example, reduction reagents may be too strong or too weak for a particular metal. Also, solvents may spoil the deoxided surface, and setting the optimal conditions for reduction temperature and processing time, etc., is rather cumbersome.

Further, it was found that if ultrafine metal particles were formed into a fixed bed and the temperature was raised in the buffer gas, localized sintering or insufficiently deoxidized domains appeared because of imperfect heat removal and uneven gas flows.

Further study proved that if ultrafine metal particles were fluidized by a hydrogen containing gas flow and heated, uniform deoxidization without sintering could be easily accomplished. The present invention is based on this discovery.

The essence of the present invention is concerned with a method of deoxidizing ultrafine metal primary particles (the average diameter less than 1000 Å) by fluidizing the particles by a gas flow containing hydrogen and heating.

In the present invention, the primary particles of the average diameter less than 1000 Å include the secondary particle forms which are assemblies of particles of the average diameter less than 1000 Å and the particles are combined by physical and chemical forces to form, for example, fibers.

The method can be applied to all kinds of metal including noble metals such as silver and others such as copper, nickel and cobalt.

In the method of the present invention, ultrafine particles of these metals are sent into a fluidization reactor, and fluidized by a pure hydrogen gas in normal cases and by a hydrogen gas diluted by inert gases if the reaction speed is to be slowed.

The space speed (the empty tower standard) of the gas flow is 500-1000 l/hr in GHSV. However, for increasing the gain, the speed of 1000-5000 l/hr is preferred. The reduction temperature of 100-300 is recommended. If the temperature is lower than this range, the reaction is too slow and if higher, sintering may occur. The time duration for the metal particles to stay in the flow is 0.1-10 minutes and 0.1-1 minute is recommended. These conditions depend on metals and desired reduction speeds.

Example 1

We sent 0.1 g of ultrafine primary nickel particles of the average diameter 300 Å and covered with oxide layers in the fluidization reactor of the outer diameter 10 mm ϕ. The air in the reactor was first replaced by nitrogen gas and then the particles were fluidized by using a hydrogen gas flow. The hydrogen gas was supplied at the rate of 120 ml/minutes at the normal temperature and pressure. The height of the layer was 18 mm. The temperature was increased from the normal to 175°C, and maintained at the temperature for 0.25 minutes. Then the outer wall of the reactor was rapidly cooled. The specific surface area of the obtained deoxidized ultrafine nickel particles was 27.0 m^2/g. Comparison with the specific surface area of 27.3 m^2/g before deoxidization showed that sintering had been prevented. Because of the loss of oxygen accompanying the reduction which generated vapor, the weight loss was 0.005 g.

Example 2

We deoxidized ultrafine nickel particles of the average diameter of 500 Å and covered with oxide layers by the same method as in example 1. The specific surface areas before and after deoxidization were 2.2 m^2/g and 2.1 m^2/g, respectively. The weight loss was 0.006 g.

Example 3

We deoxidized ultrafine nickel particles of the average primary particle diameter 1000 Å and covered with oxide layers by the same method as in previous examples. The specific surface areas before and after reduction were 2.2 m^2/g and 2.1 m^2/g, respectively. The weight loss was 0.003 g.

Example 4

We deoxidized ultrafine copper particles of the average primary particle diameter 500 Å and covered with oxide layers by the same method as in example 1. The specific surface areas before and after reduction were 7.6 m^2/g and 7.3 m^3/g, respectively. The weight loss was 0.003 g.

As described above, the present method makes it possible to deoxidize the oxide layers on the surfaces of ultrafine metal particles uniformly and easily without causing sintering.

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(1) [2.2 m^2/g] in the 6th line of page 6 in the detailed explanation should be corrected to [20.3 m^2/g].

(2) [2.1 m^2/g] in the 7th line of the same page should be [19.7 m^2/g].

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   Part of the detailed explanations in the detail of the invention.

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