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METHOD OF PRODUCING FINELY DIVIDED METALS

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The present invention relates to the production of fine metal powders by the thermal decomposition of a metal carbonyl or mixtures of different metal carbonyls.

The decomposition of a metal carbonyl such as the carbonyl of iron or nickel or mixtures thereof is described, for example, in U. S. Patents Nos. 1,759,659 and 1,759,661 and is usually effected by introducing the carbonyl in its vaporized form into a heated vessel in such a manner that the decomposition takes place substantially in the free space of the vessel instead of by contact with the heated walls of the vessel. The metal carbonyl decomposes with the formation of carbon monoxide gas and finely divided metal which is conducted out of the decomposer space by the gas stream and is separated by mechanical, magnetic, or other means.

Metal powders, such as those of iron, nickel and cobalt, produced in this manner have a wide particle size distribution of say from 2 to 20 microns, and contain usually chemically combined carbon and oxygen, the amount of which is dependent primarily upon the temperature at which the decomposition of the carbonyl is carried out. For example, at a decomposition temperature of from 250° to 300° C., the carbon content of the iron powder produced may amount to 9% to 1.2% and above.

One of the most promising applications of finely divided metal powders lies in the electronic field as magnetic materials. Recent developments in the use of such magnetic materials have shown that besides a suitable carbon content, the size of the individual metal particles as well as the particle size distribution of a mixture of such particles are of the greatest importance for the performance in electric devices, particularly in the high frequency and ultra-high frequency field. For applications in the range of say 10 to 50 meg. and above, iron particles having a diameter of 3 to 4 microns or less perform satisfactory, whereas the performance of particles with an average diameter of 6 to 8 microns is inferior. Particles with even larger diameters are of little utility for high frequency work.

As the metal carbonyl decomposition process has been heretofore operated, it invariably led to mixtures having a large percentage of oversized particles, i. e., particle sizes having a diameter of 12 microns or above. Considerable effort has been made in the past to separate such mixtures of particles of widely different sizes into suitable fractions to remove the undesirable particles above a certain maximum size. However, no improvements have been devised for the decomposition process itself which would automatically eliminate the formation of oversized particles or result in powders of a definite, desired particle size. As a matter of fact, the art had about concluded that the only way to obtain uniform particles of the desired size was by the fractionation method.

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I have now found very surprisingly indeed that the thermal decomposition of metal carbonyl can be effected to yield metal powders with a closely controlled particle size distribution and substantially free from particles above a specified, desired maximum size. In general, the new process is capable of producing metal powders particularly suited for application in the high frequency electronic field where contamination of the powder with oversized fractions must be avoided.

The improvement which enables me to thermally decompose metal carbonyls to yield metal powders with a controlled particle size distribution and substantially free from undesired oversized fractions consists in the step of limiting, in the decomposition space and under decomposition conditions, the contact of undecomposed metal carbonyl with the metal particles formed in the reaction to a predetermined time which is specific for the desired maximum particle size of the powder produced and for the conditions of temperature, pressure and throughout under which the decomposition reaction is carried out. The growth of the initially formed metal nuclei to particles of, say, 3 to 5 microns in diameter is assumed to be due to the decomposition of the metal carbonyl on the metal surface of the individual particles, resulting in the well known spherical form and shell structure of carbonyl metal powder. By working as above, i. e., by limiting, under decomposition conditions, the contact time of the metal carbonyl with already formed metal particles to a definite maximum value, I have found that the growth of the individual particles can be arrested at practically any desired particle size.

It should be noted that in the process of decomposing metal carbonyls, the use of diluent gases as well as of reduced pressure have been described, which steps may lead to a decrease in the chances of collision between undecomposed metal carbonyl and already formed metal particles. However, no attempts were made previously to control the particle size distribution of the metal powder formed, or to avoid the formation of oversized fractions by limiting the time of

contact between metal carbonyl and metal powder, which I have recognized for the first time to be the controlling factor in obtaining particle size control. Consequently, by previous operations only inferior powders unsuitable for the requirements of the electronic ultra-high frequency technique were produced. My new process may make use of diluents or reduced pressures for the decomposition reaction, but the adjustment of the proper residence time is the governing factor in avoiding oversized particles.

Thus, if at a certain time of contact, temperature, pressure and diluent concentration, the decomposition leads to oversized particles and an undesired particle size distribution, effective control of the particle size and particle size distribution cannot be attained by any variation in the temperature, pressure or gas concentration so long as the contact time is maintained constant. However, by an appropriate adjustment in the contact time, the control over particle size and their distribution can be effectively realized. It will, of course, be understood that when an appropriate contact time giving the desired control has been established for any particular temperature, pressure and concentration of gas, the contact time may be varied by variations in the temperature, pressure or concentration of the gas although these alone do not establish the contact time. It is obvious that the limiting, in the decomposition space, of the contact time of metal carbonyl with already formed metal particles can be achieved by several means. One of my preferred methods is by maintaining a definite rate of decomposition by proper temperature control in the decomposition space, and by adjusting the throughput of metal carbonyl through the said decomposition space, both conditions depending to some extent on the pressure maintained in the reaction space. Generally the temperature of decomposition will range from 150 to 350° C., the pressure from 2 mm. to 1 atm., the pressure being lower the higher the temperature, and the throughput will be such under such temperature and pressure conditions and depending upon the size of the reactor that the time of contact between the first formed metal particles and the metal carbonyl shall range from a fraction of a second to not more than 20 seconds. The contact time is measured by the time the metal carbonyl or its decomposition products are in the reactor under decomposition conditions, i. e., at the temperature at which decomposition occurs.

The metal carbonyl may be diluted with inert gases, such as ammonia, nitrogen, hydrogen and carbon monoxide to facilitate the control, the range of the dilution being such that there is present from about 10 to 75% of metal carbonyl.

It will be understood that my new process for obtaining metal powders of definite desired particle size as above involves the complete decomposition, in one pass, of the metal carbonyl entering the reaction space. However, the process may be carried out in such a way that undecomposed carbonyl is left in the reaction mixture leaving the decomposition space. In the latter operation, provisions are made at the end of the time allowed for the contact between metal carbonyl and already formed metal particles to arrest the decomposition reaction, for example, by quenching of the hot reaction mixture with cold liquids or cold gases. The liquids or gases employed are inert to the reactants and may be silicon oils such as are described in U. S. Patents Nos. 2,258,218, 2,258,220 and 2,258,222, or hydrocarbon oils, such as kerosene or gasoline, ammonia, nitrogen, hydrogen or carbon monoxide. The liquids and gases will be cooled below the reaction temperature, say, from about 120° C. to room temperature.

The reaction may also be arrested by removal of the metal particles grown to the desired size from the reaction mixture by means of magnets surrounding the wall of the reactor at a point along the path of travel of the gases, such that the desired time of contact between initially formed carbonyl metal and metal carbonyl will have elapsed when the magnets are reached.

Examples of metal carbonyls to which my process is applicable are iron, nickel, cobalt and molybdenum. The metal carbonyls may be used along or in admixture with each other, such as a mixture of nickel and iron carbonyl, a mixture of cobalt and molybdenum carbonyl, and the like.

An illustration of the results which may be achieved by following my procedure is afforded by the following. When decomposing iron carbonyl vapor in the free space of a heated cylindrical vessel at a temperature of 280° C., under an absolute pressure of 1 atm., and at such a throughput that a contact time in the heated reactor space of iron carbonyl vapor with metal particles of approximately 240 seconds is achieved, a metal powder is obtained with a weight average particle diameter of 7 to 8 microns, containing oversized particles amounting to approximately 15% by weight of the powder and having a diameter of 12 microns and above.

However, when according to the present invention the reaction conditions of temperature, pressure and throughout are adjusted in such a manner that a rapid decomposition of the metal carbonyl is achieved and the contact of the metal carbonyl with already formed iron particles is limited to a maximum time of 10 seconds, a metal powder is obtained with a weight average particle diameter of 4 to 5 microns. This powder is substantially free from particles having a diameter of 9 microns or more.

It can be clearly seen that by performing the decomposition reaction at a very rapid rate and limiting, under suitable conditions of temperature, pressure and throughput, the time of contact between metal carbonyl and already formed metal particles, i. e., to one second or less, particles having a weight average diameter of 2 microns, 1 micron, or less than 1 micron can be produced. An essentially instantaneous decomposition which can be achieved under properly adjusted conditions, i. e., a temperature of 300° C. and a vacuum of 20 mm. mercury, results in the formation of an extremely fine metal powder consisting of particles of less than $\frac{1}{10}$ of a micron in diameter and substantially free from any oversized material.

The following example will further illustrate the nature of this invention, but the invention is not restricted to this example.

Example

Iron penta carbonyl is evaporated in a steam heated evaporator and the vapor led at the rate of 1 cu. ft. per minute at atmospheric pressure into the free space of a cylindrical vessel 16 ft. high and having a diameter of 3 ft. and maintained by means of a vacuum pump at an absolute pressure of 30 mm. mercury. The vessel is heated by means of a hot gas circulating through a jacket surrounding the decomposition chamber.

The temperature inside the decomposition vessel is thus held at 250° C. The carbonyl vapor entering the reaction zone continuously from the top is decomposed, by radiant heat, within 2 to 3 seconds, into finely divided iron particles and carbon monoxide gas. The reaction mixture is continuously withdrawn from the bottom of the decomposition chamber and separated by means of a separating tank and filter, yielding iron particles with an average diameter of 2–3 microns, and substantially free from particles above 6 microns in diameter.

If in the above reaction the decomposition time, i. e., the time of contact between iron carbonyl and already formed metal particles is increased to 8–9 seconds, for example, by decreasing the temperature in the reactor to 220° C. and increasing the pressure to 100 mm. mercury, a metal powder is obtained with an average particle diameter of 5–6 microns.

I claim:

1. In the production of fine metal powders by thermally decomposing a metal carbonyl, the step of controlling substantially all of the distribution of the average particle size within a range of about 2 microns and the maximum particle size to a small amount above the average, said maximum size being no more than about 3 to 4 microns larger than the average, which particles are produced by limiting the contact in the decomposition space of undecomposed metal carbonyl with the metal particles formed in the reaction to a definite length of time not exceeding 20 seconds specifically for the desired average and maximum particle size of the powder produced at a reaction temperature of 150–350° C. and a pressure from 20 mm. to 100 mm. absolute.

2. The process as defined in claim 1 in which the decomposition of the metal carbonyl is carried out under such operating conditions that undecomposed metal carbonyl is withdrawn from the reaction space, together with the decomposition products, and the separation of the metal powder produced is subsequently effected.

3. The process as defined in claim 1 wherein the metal carbonyl is iron carbonyl and wherein the temperature, pressure and throughput are adjusted within the stated range so that decomposition is substantially complete in less than 10 seconds.

4. The process as defined in claim 1 wherein the metal carbonyl is iron carbonyl and wherein the temperature, pressure and throughput are adjusted within the stated range so that the decomposition is substantially complete in less than five seconds.

5. The process as defined in claim 1 wherein the metal carbonyl is iron carbonyl and wherein the temperature, pressure and throughput are adjusted within the stated range so that decomposition is essentially instantaneous.

HANS BELLER.

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