United States Patent Office 2,965,474
Patented Dec. 20, 1960

2,965,474

REDUCTION OF METAL OXIDES

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No Drawing. Filed July 18, 1958, Ser. No. 749,313

7 Claims. (Cl. 75—34)

This invention relates to the reduction of metal oxide powders utilizing a detonation reaction.

According to this invention there is provided a process for reducing metal oxides to finely divided free metal which comprises introducing the metal oxide preferably in comminuted form into a detonation apparatus, introducing a detonable charge of an oxidant and fuel gas into the detonation apparatus the reaction products of which result in an atmosphere which is substantially reducing to the metal oxide, suspending the metal oxide in the detonable charge and igniting such charge. Ignition of the detonable mixture results in a detonation wave which rapidly passes through the detonation apparatus. This detonation wave and associated hot gases heat the metal oxide to reaction temperature, reduce the oxide to free metal and propel the resulting finely divided metal toward a collecting means. This finely divided free metal is collected either as a very fine powder or as a coating on an object or other collector utilized for such purpose.

By the term "detonation" is meant a very rapid burning or other exothermic reaction in which the flame front moves through the unburned material at velocities higher than the velocity of sound in the unburned material, and therefore characterized as supersonic velocities. (Typical calculated velocities of sound at normal pressure are 1085 ft./sec. at 18° C. in a 50% oxygen–50% acetylene mixture, 1384 ft./sec. in the same mixture at 200° C. and 1122 ft./sec. at 18° C. in a 9.5% acetylene–90.5% air mixture.) The rate of flame propagation is far greater in a detonation than in a deflagration, which is a burning or other exothermic reaction in which the velocity of flame propagation does not exceed the velocity of sound in the unburned material. According to Wilhelm Jost's "Explosion and Combustion Processes in Gases," McGraw-Hill Book Company, Inc., New York (1946), pages 160 to 210 of which are devoted to detonations in gases, the velocity of the flame front in gas detonations thus far investigated is from 1 to 4 kilometers per second (about 3280 to 13,120 ft. per second), as compared to, for instance, 50 ft. per second for a typical deflagration.

There are many laboratory and industrial uses for finely divided metal powders. They can be used, for example, as catalysts for chemical reactions, as adsorbents and as raw materials for powder metallurgy techniques. Previously finely divided metals in substantially pure form could only be obtained by grinding operations on the massive metal or by chemical reduction of metal compounds often at high pressures.

It is accordingly an object of the present invention to provide a novel process for the direct reduction of metal oxide to free metal.

It is still another object to provide such a process which will produce the free metal in a finely divided state.

Other objects and advantages will be apparent from the following description and examples.

In order to reduce most metal oxides to the free metal it is necessary to elevate their temperature greatly and provide a reducing agent which will combine with the oxygen in the oxide, then the metal must either be cooled rapidly or remain shielded from the atmosphere while it cools slowly.

It has been found that the detonation phenomenon provides an ideal energy source for the reduction of metal oxides, even those of the refractory metals.

Heretofore, apparatus has been proposed for utilizing detonation waves and associated phenomena to impart energy to powders provided in a detonable fluid body to propel said powders at high temperatures and velocities against the surface of a body to be coated. Such apparatus, disclosed and claimed in application Serial No. 275,332, filed March 7, 1952, by R. M. Poorman et al., issued on August 2, 1955, as U.S. Patent No. 2,714,563, is termed a "detonation gun" and comprises an elongated barrel having an open end, means for introducing a detonable body of detonable fluid into said barrel, means for providing powder material in said detonable body of detonable fluid in said barrel, means for controlling the supply of fluid fuel and oxidant of said detonable fluid, and a mixing and ignition zone at the rear of the barrel including ignition means for igniting said detonable fluid in said barrel. The powdered material is carried into the barrel either through the fuel gas stream or oxidant stream, or by a separate stream which introduces the powdered material into the barrel of the detonation gun.

When metal oxide powders are introduced into the downstream or barrel portion of a detonation gun, such as is disclosed in the above-mentioned U.S. patent, finely divided free metal is produced when the oxidant and fuel gases used for the detonable mixture result in a reducing atmosphere during the detonation. The free metal resulting from the detonation may be either collected as a finely divided powder near the open end of the gun barrel or may be impinged on an object placed near said barrel as a dense adherent coating.

The high temperature and brief duration of the detonation reaction is thought to be responsible for the surprising results achieved with this method. The finely divided nature of the metal oxides used apparently allows them to be normally raised to a sufficiently high temperature by the detonation reaction so as to be reduced by the controlled reducing atmosphere of the reaction. The reducing atmosphere within the detonation gun also apparently shields the finely divided free metal product long enough to allow it to cool down to a point where it does not readily recombine with the atmosphere as it leaves the gun.

The following examples illustrate specific metal oxides that have been reduced to the finely divided free metal state by means of a detonation reaction.

EXAMPLE I

Reduction of tungsten oxide

Oxygen at 2.05 c.f.m. and acetylene at 1.95 c.f.m. were fed into a detonation chamber of a detonation gun so as to form a detonable mixture having an oxygen/carbon atomic ratio of 1.05. Downstream of the ignition zone of the detonation chamber WO_3 powder at 20 grams per minute was introduced to the detonable gas mixture by means of an argon carrier gas stream of 0.4 c.f.m. The detonable mixture was ignited about 4 times per second by means of a spark plug with attendant nitrogen purge of the detonation gun between detonations. A fine powder was collected at the outlet of the detonation gun which had a surface area of 35.70 sq. meters/gm. and contained 92.4 wt. percent tungsten.

EXAMPLE II

Reduction of iron oxide

Oxygen gas at 2.75 c.f.m. and 1.0 c.f.m. propane were

fed into a detonation chamber so as to form a detonable mixture. Fe_2O_3 powder at a rate of about 10 grams/min. was introduced to the detonatable gas mixture downstream of the ignition zone of the detonation chamber by means of a 0.61 c.f.m. propane stream. The detonable mixture was ignited about 4 times per second with a nitrogen purge of the detonation chamber between detonations. A fine powder was collected at the outlet of the equipment which contained 74.3 wt. percent iron.

EXAMPLE III

Reduction of iron oxide

Oxygen at 3.3 c.f.m. and propane at 1.25 c.f.m. were fed into a detonation chamber. Fe_3O_4 powder at about 10 grams/min. was introduced to the detonable gas mixture downstream of the ignition zone of the detonation chamber in a propane carrier gas stream of 0.61 c.f.m. The detonation mixture was ignited about 4 times per second and the detonation chamber was purged with nitrogen between detonations. A fine powder product was collected at the outlet of the equipment which contained 77.6 wt. percent iron.

EXAMPLE IV

Reduction of molybdenum oxide

Oxygen at 2.83 c.f.m. and acetylene at 2.17 c.f.m. were fed into a detonation chamber to form a detonable mixture having an oxygen/carbon atomic ratio of 1.3. MoO_3 powder at about 20 grams/min. was introduced to the detonable gas mixture downstream of the ignition zone of the detonation chamber in a nitrogen carrier stream of 0.5 c.f.m. The detonation mixture was ignited about 4 times per second and the detonation chamber was purged with nitrogen between detonations. A fine powder product was collected at the equipment outlet which had a surface area of 19.2 sq. meters/gm. and contained free molybdenum metal as indicated by X-ray diffraction means.

EXAMPLE V

Reduction of cobalt oxide

Acetylene at 3.25 c.f.m. and oxygen at 3.25 c.f.m. were fed into the detonation equipment. Cobalt oxide powder at a rate of 5 lb. per hour entrained in a nitrogen carrier gas stream of 0.5 c.f.m. was introduced into the detonation chamber downstream of the detonation ignition zone. The detonable mixture was ignited with nitrogen after each detonation. A powder product was collected at the equipment outlet and it was found by analysis to be cobalt metal substantially free of oxides.

From the above examples the surprising efficiency of this novel reaction can readily be seen. The process thus disclosed should have great utility and use where extremely fine particle size metal powders are desired.

What is claimed is:

1. A process for reducing metal oxides to finely divided free metal which comprises introducing the metal oxide into a detonable mixture of oxidant and fuel contained within an elongated chamber having such length to diameter ratio as to support a detonation, said detonable mixture having detonation characteristics such that the metal oxide is reduced to free metal, igniting the detonable mixture to produce a detonation wave and associated hot gases within said chamber which react with said metal oxide to produce finely divided free metal and which propel the finely divided metal toward a collecting means maintaining the metal powder within the reducing atmosphere which originated within the elongated chamber until it cools to a temperature below which substantial atmospheric oxidation occurs, and recovering the so-reduced product.

2. A process for reducing metal oxides to finely divided free metal which comprises providing within a detonation gun having a barrel of such length to diameter ratio as to support a detonation with a mixing and ignition chamber at one end and a powder collecting means at the other end, a detonable charge of oxidant and fuel, suspending in said detonable charge a comminuted metal oxide reducible under the detonation conditions produced by said detonable charge, igniting the detonable charge to produce a detonation wave and associated hot gases which react with said comminuted metal oxide to produce finely divided free metal and which propel the finely divided metal toward the collecting means, maintaining the metal powder within the reducing atmosphere which originated within the elongated chamber until it cools to a temperature below which substantial atmospheric oxidation occurs, and recovering the so reduced product.

3. A process in accordance with claim 2, wherein said fuel and oxidant mixture is an acetylene-oxygen mixture and said comminuted metal oxide is tungsten oxide, and said finely divided product contains free tungsten metal.

4. A process in accordance with claim 2 wherein said fuel and oxidant mixture consists of propane and oxygen, said comminuted metal oxide is ferric oxide, and said finely divided product contains free iron metal.

5. A process in accordance with claim 2, wherein said fuel and oxidant mixture consists of propane and oxygen, said comminuted metal oxide is ferrous oxide, and said finely divided product contains free iron metal.

6. A process in accordance with claim 2, wherein said fuel and oxidant mixture consists of acetylene and oxygen, said comminuted metal oxide is molybdenum oxide, and said finely divided product contains free molybdenum metal.

7. A process in accordance with claim 2, wherein said fuel and oxidant mixture consists of acetylene and oxygen, said comminuted metal oxide is cobalt oxide, and said finely divided product contains free cobalt metal.

References Cited in the file of this patent

UNITED STATES PATENTS

1,291,965	McCourt	Jan. 21, 1919
2,125,909	Gahl	Aug. 9, 1938