

1

3,090,567

SIZE REDUCTION OF METAL PARTICLES

Robert J. Schafer, 150 Meadow Drive, Berea, Ohio, and
Max Quatintetz, 5821 Woodman Court, Parma, Ohio
No Drawing. Filed Sept. 19, 1960, Ser. No. 56,647
4 Claims. (Cl. 241-22)

This invention relates to a novel method of reducing the size of metal particles and, more particularly, it relates to a method for reducing the particle size of metals below about one micron.

The search for methods capable of producing very fine metal powders has become increasingly important as the use of metal powders in powder metallurgy techniques and other applications requiring fine powders has multiplied. While fine metal powders have been produced by nucleation and growth and also mechanical comminution means, the use of nucleation and growth methods is more widespread because of the difficulties in mechanically reducing metal particles to a sufficient degree of fineness. In some instances where comminution means have been employed, there is no reduction in the particle size, but rather the particles tend to increase in size due to agglomeration of the very fine particles. However, although metal powders in the submicron range may be produced, the methods employed have not been considered completely satisfactory because of the high cost and lack of flexibility generally involved in such methods.

In accordance with the present invention, it has been found that the particle size of a wide variety of metals may be successfully reduced below about one micron by mechanical means. Not only does the method of the invention provide for the reduction of metal particles by mechanical means, but also the method employs conventional grinding and milling equipment to achieve the desired particle size reduction. Moreover, the invention provides an economically feasible method for producing commercial quantities of such relatively fine metal powders.

The reduction of metal particles to a size below about one micron is achieved in accordance with the present invention by a method which comprises mixing the metal particles with an inorganic salt and a sufficient quantity of a liquid diluent to form a flowable slurry. The slurry is milled to reduce the size of the particles after which the finely powdered metal may be separated from the salt and diluent. The inorganic salt employed consists essentially of a compound formed from at least one polyvalent ion and is composed of more than two chemical elements. Advantageously, the polyvalent ion is trivalent or tetravalent, and preferably, the anion portion of the compound contains at least two chemical elements.

Among the salts with polyvalent ions containing more than two chemical elements which are suitable for employment in the method of the present invention are the salts of metals such as sodium potassium, aluminum, copper, and salts of non-metals such as ammonia. The salts may be formed from acids such as nitric acid, sulfuric acid, phosphoric acid, chromic acid, and the like. Advantageously, the salts are soluble in a washing liquid to facilitate the separation of the salt from the metal powder after the grinding operation.

While it is essential that the salt employed in the method of the present invention contain a polyvalent ion, it is not necessary that both the cation and anion portions of the compound be polyvalent. For example, the salt may be a sodium salt of pyrophosphoric acid and, thus, contain the monovalent sodium ion with the tetravalent pyrophosphate radical. Likewise, a salt such as aluminum nitrate might be employed in which the aluminum is trivalent while the nitrate radical is mono-

2

valent. However, salts such as aluminum sulfate, in which both ions of the compound are polyvalent, also may be employed.

The salts employed in the method of the present invention may be anhydrous or hydrated salts although if hydrated salts are employed, the quantity thereof may be increased to provide a concentration substantially the same as if an anhydrous salt were employed.

The liquid diluent employed in combination with the inorganic salt may be a conventional solvent or diluent. Although the liquid may be water or an aqueous solution, organic diluents are preferred. Advantageously, the diluent may be a hydrocarbon such as heptane, octane, etc.; an alcohol such as methyl or ethyl alcohol, etc.; a cyclic compound such as cyclohexane, etc.; or a chlorinated hydrocarbon such as methylene chloride, etc.

The proportions of the inorganic salt and the diluent may vary over a wide range. While the specific proportions will depend in part upon the particular materials employed, the minimum proportion of the diluent should be sufficient to maintain the slurry in a flowable state during comminution while the salt will generally comprise at least about 5 or 10% by weight of the metal particles. The maximum proportions are not critical since the employment of large quantities of the salt or diluent will generally only result in a lowering of the grinding efficiency, i.e., a reduction in the quantity of metal powder produced in a given period of time or with a given amount of power. Thus, the proportion of the salt may vary from about one-tenth up to two or three or more times the weight of the metal particles. Generally, the diluent will comprise somewhere in the range of about 50% to 300% by weight of the total solids incorporated in the slurry and preferably between about 70% and 200% of such solids.

The method of the present invention may be employed to reduce the size of a wide variety of ductile, brittle and refractory metals. For example, the method of the invention may be employed to reduce the particle size of metals such as copper, silver, nickel, chromium, iron, tungsten, molybdenum, and columbium as well as a great many other metals and alloys.

The following examples describe in greater detail the production of powdered metals in accordance with the method of the present invention. All of the experiments except Example VIII were conducted in the same apparatus employing the following general procedure. A powdered metal slurry containing the inorganic salt and the organic liquid diluent was milled by placing the slurry in a ball mill jar having an inside diameter of about 4¾ inches and an inside height of about 5 inches. The capacity of the jar was approximately three pints. The jar was constructed of an austenitic stainless steel and had three internal ribs running the length of the jar. These ribs were ¼ inch square in cross-section and were spaced equidistantly around the inside circumference of the jar.

The balls used were ½ inch diameter type 410 stainless steel balls. A sufficient number of balls to fill the jar approximately half full and weighing approximately 3000 grams was employed. The jar containing the slurry and the balls was placed on a rolling mill having a triple set of rolls four feet in length which could accommodate 21 jars simultaneously. The jar was rotated at 48 r.p.m. for several days as set forth below, after which the slurry was removed from the jar. Arbitrarily in the examples, the maximum time that the jars were rotated in the ball mill was 15 days, but this is not to be considered a limitation of the invention as to the time of grinding.

The slurries obtained in each of the examples were allowed to stand to settle the metal powder and the salt. The liquid diluent was then decanted off and the solids

3

washed with hot water to dissolve the inorganic salts. The washing operation was repeated ten times. Each time, the metal powder was placed in a beaker filled with water, the mixture was stirred thoroughly after which the powder was allowed to settle and the liquid was then decanted off. After ten washing cycles, the metal powder was mixed with 190 proof ethyl alcohol and stirred. The resulting suspension was then filtered through a Buchner funnel and the filter cake dried in air at room temperature. The dried filter cake was crushed and then stirred for approximately one minute in an Osterizer. After this step, samples of each powder were tested to determine the particle size using known methods.

Example I

In this example, a number of different inorganic salts were employed with the same metal and diluent and following the procedure described above.

The metal employed was a nickel powder having an average particle size of 2.55 microns sold by the International Nickel Company as Inco carbonyl grade B nickel powder. 210 grams of the nickel powder were combined with 300 milliliters of 200 proof ethyl alcohol and 70 grams of salt. When hydrated salts were employed, the amount of salt used was based on the amount calculated to provide 70 grams of anhydrous material.

The following table lists for each salt the particle size obtained after the specified number of days.

Compound	Formula	Grinding time (days)	Average particle size (microns)
Cerium nitrate	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	8	0.13
Potassium ferricyanide	$\text{K}_3\text{Fe}(\text{CN})_6$	15	0.20
Potassium ferrocyanide	$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	15	0.27
Ammonium molybdate	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{23} \cdot 4\text{H}_2\text{O}$	8	0.37
Sodium dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	5	0.40
Potassium dihydrogen phosphate	KH_2PO_4	15	0.50
Aluminum sulfate	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	4	0.62
Copper sulfate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	15	0.87

Example II

The procedure of this example was the same as Example I except that methylene chloride was substituted for the alcohol diluent with the inorganic salts listed below:

Compounds	Formula	Grinding time (days)	Average particle size (microns)
Sodium pyrophosphate	$\text{Na}_4\text{P}_2\text{O}_7$	15	0.23
Aluminum nitrate	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	2	0.35

Example III

The procedure employed in this example was the same as Example I except for the following: 600 milliliters of ethyl alcohol were employed in each mixture. The total weight of the metal powder and salt combined was 400 grams with the proportions being varied in each run. Ammonium sulfite was employed as the salt in each run and the metal powder was the nickel powder of Example I. The quantity of stainless steel balls was increased to 3120 grams from the 3000 grams employed in Example I. The following table gives the results for each of the runs:

Run	Metal powder (grams)	Salt (grams)	Grinding time (days)	Average particle size (microns)
A	350	50	14	0.35
B	260	200	6	0.30
C	133	267	3	0.40

4

Example IV

The procedure of this example was the same as Example I except that potassium ferricyanide was employed as the salt in each of the runs and the proportions of the salt and the nickel metal powder were carried in each run.

Run	Metal powder (grams)	Salt (grams)	Grinding time (days)	Average particle size (microns)
A	250	25	15	0.77
B	140	140	2	0.45

Example V

The procedure employed in this example was the same as that of Example I except that different size nickel powders were employed as the starting materials. The salt used was potassium ferricyanide. The following table gives the results of experiments employing powders having different original particle sizes:

Source of nickel powders	Original average particle size (microns)	Grinding time (days)	Final average particle size (microns)
National Radiator Co., F 89A-A2	23	8	0.23
Sherritt Gordon Co., F 325	17	15	0.26
C. A. Hardy Co., -300 mesh	9.3	15	0.25
Sherritt Gordon Co., FF 325	4.8	8	0.42
Sherritt Gordon Co., FF 100	2.1	8	0.31

Example VI

The procedures employed in this example were the same as Example V except that powders of various metals other than nickel were employed. The following table gives the results with the listed powders:

Metal powder	Original average particle size (microns)	Grinding Time (days)	Final average particle size (microns)
Copper—Metals Disintegrating Co., Lot 61A	30	2	0.44
Silver—Metals Disintegrating Co. (spherical) Lot 61A	24	8	0.40
Chromium—C. A. Hardy (electrolytic), -325 mesh	8.5	15	0.57
Iron—City Chemical Co. (carbonyl reduced)	7.3	15	0.10
Iron—A. D. MacKay Co. (carbonyl)	3.2	15	0.39

Example VII

The procedure of this example was the same as Example I except for the following:

1750 grams of the nickel powder, 250 grams of ammonium sulfite, and 3000 grams of ethyl alcohol were employed. The mill jar was of a somewhat larger capacity than those employed in the foregoing examples having a capacity of approximately one gallon each. 15.6 kilograms of stainless steel balls were employed in the mill jar. After grinding for ten days, the average particle size was reduced to 0.45 micron.

Example VIII

150 grams of the nickel powder employed in Example I were mixed with 50 grams of ammonium sulfite and 200 milliliters of 200 proof ethyl alcohol. This mixture was then combined with 2000 grams of $\frac{1}{8}$ inch diameter type 410 stainless steel balls in a Research Model No. 01 Szegvari Attritor mill manufactured by Union Process Company of Akron, Ohio. The grinding tank capacity of the mill was approximately 750 milliliters. The agitator was operated at a speed of about 125 r.p.m. After one day, the average particle size was reduced to 0.22 micron. Continuing the operation for an additional 16 hours reduced the average particle size to 0.15 micron.

As shown by the foregoing description and specific examples, the employment of certain inorganic salts and liquid diluents in the grinding of metal powders results in the production of especially fine metal powders having average particle sizes of less than about 1 micron and in many cases less than 0.5 micron. Particularly advantageous results are achieved when the inorganic salt is a water-soluble salt and the diluent is an organic liquid.

The method of the invention not only provides for a reduction in the particle size of metals but achieves this reduction more economically than was possible with methods heretofore employed. Since the particle size reduction may be carried out in conventional grinding and milling apparatus, the method of the invention permits the production of such fine metal powders in commercial quantities.

It is apparent from the above description that various modifications in the specific materials and procedures described may be made within the scope of the invention. Therefore, the invention is not intended to be limited to the particular materials and procedures described in detail herein except as may be required by the appended claims.

What is claimed is:

1. A method of reducing metal particles to a size below about one micron which comprises mixing said metal particles, an inorganic salt and a sufficient quantity of a liquid diluent to form a flowable slurry, and milling said slurry to reduce the size of said metal particles, said salt consisting essentially of a compound formed from at least one polyvalent ion and being composed of more than two chemical elements and said salt comprising between about 5% and 300% by weight of said metal particles, and said diluent being chemically inert to said metal particles and said salt and comprising between about 50% and 300% by weight of the total metal particles and salt.

2. A method of reducing metal particles to a size below about one micron which comprises mixing said metal particles, an inorganic salt and a sufficient quantity of a liquid diluent to form a flowable slurry, and milling said slurry to reduce the size of said metal particles, said salt consisting essentially of a water-soluble compound formed from at least one polyvalent ion and being composed of more than two chemical elements and said salt comprising between about 5% and 300% by weight of said metal particles, and said diluent being chemically inert to said metal particles and said salt and comprising

between about 50% and 300% by weight of the total metal particles and salt.

3. A method of reducing metal particles to a size below about one micron which comprises mixing said metal particles, an inorganic salt and a sufficient quantity of a liquid diluent to form a flowable slurry, and milling said slurry to reduce the size of said metal particles, said salt consisting essentially of a compound formed from at least one polyvalent ion and being composed of more than two chemical elements and said salt comprising between about 10% and 300% by weight of said metal particles, and said diluent being chemically inert to said metal particles and said salt and comprising between about 50% and 300% by weight of the total metal particles and salt.

4. A method of reducing metal particles to a size below about one micron which comprises mixing said metal particles, an inorganic salt and a sufficient quantity of an organic liquid diluent to form a flowable slurry, milling said slurry to reduce the size of said metal particles, and separating said reduced size metal particles from said salt and said diluent, said salt consisting essentially of a water-soluble compound formed from at least one polyvalent ion and an anion composed of at least two chemical elements and said salt comprising between about 10% and 300% by weight of said metal particles, and said diluent being chemically inert to said metal particles and said salt and comprising between about 70% and 200% by weight of the total metal particles and salt.

References Cited in the file of this patent

UNITED STATES PATENTS

1,257,943	Howard	Feb. 26, 1918
1,699,694	Ellis	Jan. 22, 1929
2,259,457	Croll	Oct. 21, 1941

FOREIGN PATENTS

376,242	Great Britain	Jan. 1, 1931
569,402	Great Britain	May 22, 1945
1,001,061	France	Dec. 7, 1949
1,071,455	Germany	Dec. 17, 1959

OTHER REFERENCES

- Progress Report, Ohio State University, Report Number 24, Project Number 252 (pages 1, 2), June 4, 1947.
 Taggart: Pages 22-67, Handbook of Mineral Dressing, Wiley and Sons, New York, copyright 1945.