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METHOD FOR THE FORMATION OF MALLEABLE METAL POWDERS

Erik Tornqvist, Roselle, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware
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The present invention relates to the formation of highly active metallic powders. More particularly, the invention relates to the formation of metallic powders of malleable metals.

Many ductile or malleable metals that are theoretically quite reactive have a tendency to be coated by a layer of oxides or other compounds when exposed to atmospheric conditions and thus lose their reactivity under moderate reaction conditions. Metals such as aluminum, magnesium, copper, zinc, etc., have many potential industrial applications but a decrease in reactivity due to coatings with oxides or other compounds formed as the result of environmental exposure seriously restricts their use especially in organic synthesis where only mild reaction conditions can be tolerated. It is therefore important to remove or at least penetrate the layer coating on these metals.

Treatment of malleable metals with halogens, hydrogen halides, alkyl halides, etc., has been suggested for this purpose and is well known to the art. However, these methods are often not effective and frequently cause undesirable contamination of the metals as well as consumption of the metal. Contamination problems are obviated when the oxide or similar coating is removed or broken up by grinding or ball milling under inert conditions. However, ball milling in particular has not in the past been suitable for malleable metals of low or intermediate hardness, as they form very fine, thin platelets during the ball milling which tends to interlock or weld and form large clusters that are not suitable for chemical reactions.

Now, in accordance with this invention, it has been found that highly active metallic powders of malleable metals that tend to undergo welding during milling can be prepared by attriting the same in the presence of suitable metal halide salts. Following the attriting operation, the metal halide salt grinding aid is separated from the metallic powder by employing conventional extraction, reaction-extraction, sublimation, or mechanical separation techniques, the latter making use of the difference in physical properties between the metal and the halide. The solvents and/or reactants that are employed in the separation operation should be inert to the metals under the conditions used for the separation. The metal halide grinding aids employed in the process of the present invention prevent agglomeration of the metal powder and also serve as reactive abrasives, thus aiding the removal of the coating on the metal surface. As a result, the metals treated in this manner show a much higher reactivity than those treated according to previously known methods and can be used for carrying out reactions which have hitherto been considered impossible.

The malleable metals that can be treated according to the process of the present invention are those which normally weld together or interlock when subjected to a milling or grinding treatment without the presence of the grinding aids of the present invention. The metals that are especially suited to the process of the present invention have a Brinell hardness in the range of from about 1 to 75 and include metals such as: zinc, indium, lead, tin, aluminum, cadmium, gold, silver, magnesium, platinum, copper, palladium, iron, as well as malleable alloys such as magnesium and aluminum, zinc and aluminum, copper and magnesium, and tin and lead. A compila-

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tion of malleable metals with Brinell hardness information can be found in "The Metallurgists' and Chemists' Handbook," 2nd Edition, compiled by D. M. Liddell, McGraw-Hill Co., Inc., New York, 1918, p. 193. Metals having a Brinell hardness greater than 75, such as, for example, nickel, zirconium, beryllium, and cobalt can be ball milled without the presence of the grinding aids of the present invention to form finely divided powders.

The grinding aids employed in the process of the present invention preferably have metal moieties that are at least as electropositive as the metal being milled, i.e., they are either metal halides corresponding to the metals being ground or metal halides, the metal moieties of which are more electropositive than the metals being milled. For example, $AlCl_3$ could be used in the formation of aluminum powders as well as in the production of powders of zinc, cadmium, tin, etc. However, under certain conditions it is also possible to use as the grinding aid a metal halide of a metal which is slightly less electropositive than the metal to be activated. Some contamination of the original metal by the metal of the halide will then generally occur, but this contamination may not always be harmful, especially if it is rather minute as will be the case when the two metals differ only slightly in electropositive character. Thus $AlCl_3$, which is a particularly suitable grinding aid, may be useful for activating magnesium if a slight contamination of the final reaction products with aluminum can be readily tolerated. In general, the most reproducible results are obtained when anhydrous, solid, metal chlorides and bromides of Groups II-A, II-B, III-B, IV-A, IV-B, V-A, V-B, VI-A, VII-A and VIII of the Mendeleev Periodic Table in which the metal is in its lowest valence state are employed. Salts of metals of Groups I-A and I-B can be used as grinding aids; however, these salts are not readily separated from a mixture of the salt and the metal being ground. Salts such as aluminum chloride, aluminum bromide, zinc chloride, zinc bromide, magnesium chloride, magnesium bromide, stannous chloride, stannous bromide, lead chloride, lead bromide, and ferrous chloride are particularly preferred as grinding aids in the process of the present invention.

The attriting operation involving the metal being activated and the grinding aid is preferably conducted in the absence of a diluent; however, diluents can be used. The presence of a diluent during grinding operations generally serves to diminish grinding efficiency, thus making a longer period of grinding necessary for obtaining a desired degree of activation and, additionally, the diluent usually has to be removed from the metal powder product after the grinding operations have been completed and thus presents separation problems. Furthermore, it has been found that powders dry ball milled according to this invention are more reactive than those obtained after milling in the presence of a diluent.

After the grinding operation has been completed, the grinding aid can be separated from the metallic powder by employing any one or a combination of a wide variety of techniques. For example, the metal halide grinding aid can be removed from the mixture of grinding aid and metal powder by sublimation. In a similar manner, the metal halide grinding aid can be reacted with an alkyl metal compound to form a more volatile product which is then removed from the activated metal powder by evaporation, e.g., distillation or sublimation. Additionally, the metal halide grinding aids can be removed from a mixture of grinding aid and metal powder by contacting the mixture with an extractant having an affinity for the grinding aid. Representative examples of such extractant are aromatic hydrocarbons, diphenyl ether, dioxane, and certain tertiary amines. Particularly useful amines are triphenylamine and trialkylamines wherein each alkyl

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group has from 2 to 7 carbon atoms. Following contacting with the inert solvent the metal powder is removed from the total mixture by filtration, decantation or centrifugation.

Another effective method for the separation of the grinding aid from the metal powder because it can be used for the separation of a wide variety of metal halide compounds involves contacting the mixture of grinding aid and metal powder with an alkyl metal compound that will react with or complex with the metal halide of the system to form products soluble in suitable inert solvents. With this method the total mixture is then contacted with a diluent that will solubilize the reaction product or complex, whereupon the mixture is filtered, decanted or centrifuged, possibly with additional diluent washing, and a highly reactive metal powder substantially free of grinding aid is obtained. Particularly valuable alkyl metal compounds are the alkyl aluminum compounds having 2 to 8 carbon atoms per alkyl group. Representative examples of useful alkyl aluminum compounds are trialkyl aluminum compounds such as triethyl aluminum, tripropyl aluminum, triisobutyl aluminum, and the like, and also dialkyl aluminum compounds such as the diethyl aluminum halides, e.g. diethyl aluminum chloride, diisopropyl aluminum chloride, diisobutyl aluminum chloride, and the like. The inert diluent suitable as wash liquids include C_5 to C_{12} straight or branched chain hydrocarbons such as n-hexane, n-heptane, isooctane, and n-decane, cycloparaffins such as cyclohexane and methyl cyclohexane, aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene, etc.

The dry milling process is carried out by placing the malleable metal to be activated and the metal halide grinding aid in a ball mill, a pebble mill or another suitable grinding device and then milling the metal halide and malleable metal in the absence of diluents in an inert atmosphere, such as a nitrogen or argon atmosphere which is substantially free of oxygen and water vapor, for a period of time sufficient to substantially attrite the malleable metal. Effective grinding can normally be secured when the molar ratio of malleable metal to metal halide grinding aid present in the grinding zone lies in the range of from about 1:1 to 20:1. However, the most efficient activation is usually obtained when the molar ratio of malleable metal to metal halide grinding aid present in the grinding zone lies within the range of from about 3:1 to 12:1.

The optimum time period for the dry milling operation depends in general upon the efficiency of the equipment used, the malleable metal being ground, the grinding aid used, the ratio between metal and metal halide, and the degree of attrition (activation) desired. To obtain a powder of a malleable metal in which the major portion of the particles is within the size range of from about 0.1 to 20 microns, ball milling times of from about 0.2 hour to 30 days can be used. However, times ranging from 0.2 to 10 days will be more common. The time period most suitable for any given attriting equipment can, of course, be easily determined by routine experimentation.

The pressure at which the milling operation is conducted is not critical; however, the temperature used should be well below the melting points of the malleable metal and the grinding aid so as to prevent fusion of the two components. Temperatures in the range of from about 0 to 100° C. are commonly used. The temperatures at which the grinding aid is removed from the mixture of grinding aid and metal powder will in general depend upon the method of separation used, the diluents used, and the nature of the grinding aid. Preferably, temperatures in the range of from about -10° C. to 400° C. can be used; however, temperatures in the range of from about 10° to 250° C. are preferred.

The grinding operation of the present invention can be conducted either as a batch or as a continuous process.

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While the desired attrition of the malleable metal may be obtained by use of tight steel rolls or jet impact, attrition, the use of heavy ball milling is preferred as the amount of attrition desired is usually very severe. In ball milling operations utilizing either conventional ball mills or swinging mills, it is advantageous to use steel balls or some other suitable high density grinding media having a specific gravity of at least 7. However, less dense grinding media such as flint pebbles can also be used for obtaining highly activated metal powders if longer milling periods are utilized. Generally, the balls used should be large enough in diameter to give high shearing intensity; however, the size of the balls is not too critical since smaller balls give more collisions and this partly makes up for the difference in ball diameter. Thus, in laboratory ball mills having a volume of from about 1 to 10 liters, one may advantageously use steel balls of ¼ to 1" in diameter, while in commercial operations larger sizes, such as up to 2" in diameter, are usually preferred.

The activated powders of malleable metals having Brinell hardnesses in the range of from about 1 to 75 as produced by the process of the present invention have many varied uses. For example, aluminum powder that has been activated by ball milling in the presence of aluminum chloride is so active that it readily reacts with chlorobenzene to make phenyl aluminum chloride, whereas aluminum that has not been subjected to the process of the present invention will show little or no reaction. Additionally, magnesium ground in the presence of magnesium chloride or aluminum chloride will readily react with alkyl halides in the absence of ether to make ether free Grignard reagents, whereas the non-activated magnesium will not react in the absence of ether. Furthermore, aluminum and copper powders as prepared by the process of the present invention readily react with titanium tetrachloride in a substantially aromatic diluent under very mild conditions to form nearly quantitative yields of titanium trichloride cocrystallized with either aluminum chloride or copper chloride. These materials are excellent catalyst components for the formation of solid polymers of alpha olefins.

This invention and its advantages will be better understood by reference to the following examples:

Example 1

Seven activated $nAl-1AlCl_3$ mixtures were prepared by milling the components together in stainless steel jars with chrome alloy steel balls as the grinding medium. The composition of the charges and the milling conditions are shown in Table I. Finely divided powders were obtained in most cases but as indicated in the table, while four days of ball milling a $12Al-1AlCl_3$ mixture (Run 1) resulted in the formation of a finely divided aluminum colored product, 14 days of milling the same mixture (Run 2) resulted in severe caking and in the formation of a considerably darker product. Fourteen days of ball milling an $8Al-1AlCl_3$ mixture in a 2.5 l. jar also resulted in appreciable caking (Run 3) while milling of the same mixture for the same time in a 7.7 l. jar resulted in only slight caking (Run 4). Very dark products having a color approaching that of finely divided iron powder were obtained in both cases. The finely divided products from milling $6Al-1AlCl_3$ (Run 5), $5Al-1AlCl_3$ (Run 6) and $3Al-1AlCl_3$ (Run 7) were also considerably darker than the starting materials.

The pronounced deepening in color indicated the changes happening during the grinding, since milling of aluminum powders according to previously known techniques has always yielded powders of a color typical for aluminum. Particularly surprising was the dark color of the $5Al-1AlCl_3$ and $3Al-1AlCl_3$ preparations, since these contained 50 and 62% of colorless $AlCl_3$, respectively. However, this observation became less surprising once it had been established that the grinding had a unique effect, since these preparations were milled under

unusually favorable conditions, i.e., in a 7.7 l. jar instead of a 2.5 l. jar and with no caking taking place.

metal particles without any apparent attrition taking place. Runs Nos. 6 and 7 illustrate the necessity of the

TABLE I.—ACTIVATION OF ALUMINUM BY BALL MILLING WITH AlCl_3

Run	1	2	3	4	5	6	7
Charge:							
Aluminum Powder, g. ^a	324	324	324	1,296	324	810	486
AlCl_3 , g.	133.4	133.4	200	800	266.7	800	800
Al/AlCl_3 Molar Ratio	12	12	8	8	6	5	8
Milling Conditions:							
Grinding Medium				Chrome Alloy Steel Balls			
Jar Size, l.	2.5	2.5	2.5	7.7	2.5	7.7	7.7
Time, days	4	14	14	14	14	14	14
Color of Product	Aluminum	Dark metallic.	Very dark, slightly lighter than 4.	Very dark, like iron powder.	Dark bluish, metallic.	Very dark, almost like iron powder.	Lighter than 6.
Remarks		Caked ^b	Caked ^c	Slight caking			

^a Alcoa #123, average particle diameter, 16 microns.

^b After the cake had been broken up, 66.7 g. AlCl_3 was added to the jar to bring the Al/AlCl_3 ratio to 8 and the milling continued. No caking took place during the first 4½ hours of grinding, but it had occurred after 7 hours.

^c 200 g. of the caked material were broken up and charged to a 1.02 l. steel jar and milled for 2 hours. This yielded a finely divided powder containing only a few small lumps.

After the grinding operation, substantially pure, activated, finely divided aluminum powders were prepared from the $n\text{Al}-\text{AlCl}_3$ mixtures by removing the AlCl_3 through washing with an n-heptane solution of triethyl aluminum. A typical illustrative procedure used for the $12\text{Al}-1\text{AlCl}_3$ preparation from Run 1 was as follows.

A 152.4 gram aliquot of the activated aluminum-aluminum chloride mixture was slurried in 350 ml. of n-heptane in a dry, nitrogen-blanketed, 4-necked, 1 liter reaction flask which was equipped with stirrer, addition funnel, thermometer well, and reflux condenser. To the mixture contained in the reaction flask was added with stirring over a period of 8 minutes 400 ml. of dry n-heptane containing 76.1 grams of dissolved triethyl aluminum. During the period when the triethyl aluminum was added to the reaction flask the temperature of the flask rose from 26° to 36° C. due to the reaction between the aluminum chloride and triethyl aluminum. The reaction mixture was then stirred for 1 hour whereupon it was filtered in a dry box. After washing with several portions of dry n-heptane and drying in vacuo on a steam bath, a quantitative yield of substantially pure activated aluminum powder was obtained.

Example 2

To illustrate the general effectiveness of the grinding method of the present invention for preparing a wide variety of activated metal powders of malleable metals, six different metals were ground with varying amounts of aluminum chloride. The results of the tests and the conditions at which they were effected are set forth in Table II below.

TABLE II

Run	1	2	3	4	5	6	7
Metal	Cu	Ag	Mg	Zn	Cd	Sn	Sn
Charge:							
Metal (gr.)	381.2	323.7	291.6	784.6	337.2	256.1	256.1
AlCl_3 (gr.)	66.7	33.4	133.3	133.3	66.7	66.7	33.4
Metal/ AlCl_3 (mol/mol)	12	12	12	12	6	6	12
Ball Mill Size (gal.)	¼	¼	¼	¼	¼	¼	¼
Milling Time (days)	3	3	4	4	3	3	3
Product State	(*)	(*)	(*)	(*)	(*)	(*)	(*)

(*) Finely divided powder. (b) Cake.

As is indicated by the data in Table II above, excellent milling was obtained in all cases where a sufficient amount of aluminum chloride grinding aid was present. The presence of the grinding aid served both to reduce the metal particle size and to form clean, oxide-free metal surfaces. The above results contrast sharply with the poorer results obtained in milling experiments wherein pure metals were ground without the presence of a grinding aid and either caking (cluster formation) occurred or rather large platelets were formed from the original

presence of a grinding aid when powders of malleable metals are desired. In Run No. 6 wherein the mole ratio of metal to aluminum chloride was 6, a finely divided powder was obtained, whereas in Run No. 7 wherein the metal to aluminum chloride mole ratio was 12, a cake of tin and aluminum chloride was obtained.

Example 3

To further demonstrate the general effectiveness of the metal grinding method of this invention, 339 grams of zinc powder and 35.2 grams of anhydrous zinc chloride were placed in a ¼ gallon stainless steel jar and milled with chrome alloy steel balls under inert conditions for five days. After completion of the milling, a very finely divided powder was obtained from which the zinc chloride could be removed by AlEt_3 -n-heptane washing analogous to the method described in Example 1.

Example 4

The following experiment was conducted to demonstrate the extremely high reactivity of metal powders prepared in accordance with the method of the present invention. A 4-necked, 2-liter reaction flask equipped with stirrer, reflux condenser and thermowell was charged inside a nitrogen-containing dry box with the following reagents: 189.7 g. (1 mole) TiCl_4 , 9 g. (½ atom) aluminum powder prepared according to Example 1, Run 1, and 750 ml. of dry benzene. A strongly exothermic reaction started immediately and the flask had to be cooled with ice in order to avoid boiling of the benzene diluent before the flask and its auxiliary equipment

could be set up in a hood. In spite of the ice cooling the temperature rose to 64° C. in 7 minutes. The stirred and nitrogen-blanketed flask was heated to 81.5° C. within 20 minutes and the mixture was refluxed for 1 hour. The contents of the flask were then filtered in a dry box, thoroughly washed with n-heptane and dried in vacuo. A yield of 184.2 g. of a cocrystalline material having the composition $\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$ and the structure of beta- TiCl_3 was obtained. The yield obtained was essentially quantitative considering that the theo-

retical yield is 198.7 g. and that minor losses took place during the recovery procedure.

By contrast, the use of commercial aluminum powder (Alcoa #101 or 123) did not result in more than a 10 to 20% yield even when refluxing periods as long as 12 to 15 hours were used.

Example 5

An activated 12A1—1A1C₁₃ mixture was prepared by milling 927 grams of aluminum powder and 400 grams of aluminum chloride with flint pebbles in a 1-gallon porcelain jar for 17 days. Substantially pure activated aluminum powder was then obtained from this finely-divided mixture by washing the mixture with triethyl aluminum and n-heptane according to the method described in Example 1.

Example 6

A 50-gram aliquot of the ball milled 6A1—1A1C₁₃ mixture prepared as described in Example 1, Run 5 was charged to a 25 mm. O.D. Pyrex tube. The tube was inserted into a heavy duty combustion tube furnace. Vacuum was then applied and the tube and its contents were heated to 170° C. The contents of the tube were maintained at a temperature of 170° C. and under a vacuum varying from 4–5 mm. of mercury for a period of 1 hour to sublime the A1C₁₃ from the A1—A1C₁₃ mixture. Following the heating period the tube was permitted to cool to room temperature and 26.8 grams of substantially pure highly reactive aluminum powder were recovered.

The advantages of this invention will be apparent to those skilled in the art. Highly active powders of malleable metals can be directly prepared by the process of the present invention. It is to be understood that this invention is not limited to the specific examples set forth herein, which have been offered merely as illustrations, and that modifications may be made without departing from the spirit and scope of the appended claims.

What is claimed is:

1. A method for producing powders of malleable metals which comprises severely grinding in the absence of a diluent, a non-fused mixture consisting essentially of at least one malleable metal having a Brinell hardness ranging from about 1 to 75 and at least one solid metal halide grinding aid selected from the group consisting of chlorides and bromides of metals of Groups II-A, II-B, III-B, IV-A, IV-B, V-A, V-B, VI-A, VII-A, and VIII of the Mendeleev Periodic Table, the metal moiety of said metal halide grinding aid being at least as electropositive as the malleable metal being ground, and recovering a powder of said malleable metal substantially free of said grinding aid.

2. The method of claim 1, wherein the metal halide grinding aid is a metal chloride.

3. A method for producing powders of malleable metals which comprises severely grinding in the absence of a diluent a non-fused mixture consisting essentially of at least one malleable metal having a Brinell hardness ranging from about 1 to 75 and at least one solid metal halide grinding aid selected from the group con-

sisting of chlorides and bromides of metals of Groups II-A, II-B, III-B, IV-A, IV-B, V-A, V-B, VI-A, VII-A, and VIII of the Mendeleev Periodic Table, the metal moiety of said metal halide grinding aid being at least as electropositive as the malleable metal being ground, contacting the mixture with an extractant having an affinity for said grinding aid, and recovering a powder of said malleable metal substantially free of said grinding aid.

4. The method of claim 3, wherein the extractant is a trialkylamine, each alkyl group of said amine having from 2 to 7 carbon atoms.

5. The method of claim 3, wherein the extractant is a triphenylamine.

6. A method for producing powders of malleable metals which comprises severely grinding a mixture comprising at least one malleable metal having a Brinell hardness ranging from about 1 to 75 and at least one solid metal halide grinding aid, contacting said mixture with an alkyl metal compound having at least two alkyl groups per molecule to react said grinding aid with said alkyl metal compound, washing said mixture with a diluent having a solvent affinity for said reaction product of said grinding aid and said alkyl metal compound, and recovering a powder of said malleable metal substantially free of said grinding aid.

7. The method of claim 6, wherein said alkyl metal compound is an alkyl aluminum compound.

8. The method of claim 6, wherein said alkyl metal compound is an alkyl aluminum compound, said compound having from 2 to 8 carbon atoms per alkyl group and said alkyl aluminum compound is present in amounts sufficient to react and completely solubilize substantially all of said grinding aid.

9. The method of claim 6, wherein said washing diluent is an aliphatic hydrocarbon liquid having from 5 to 12 carbon atoms per molecule.

10. A method for producing aluminum powder which comprises ball milling a mixture comprising aluminum and aluminum chloride for a period of from about 0.2 hour to 30 days, contacting said mixture with triethyl aluminum in amounts sufficient to react and substantially completely solubilize the aluminum chloride of said mixture, washing said mixture with n-heptane, and recovering aluminum powder substantially free of aluminum chloride.

11. A method for producing aluminum powder which comprises ball milling a mixture comprising aluminum and aluminum chloride for a period of from about 0.2 hour to 30 days, heating said mixture for a time sufficient to sublime at least a major portion of said aluminum chloride, and recovering aluminum powder substantially free of aluminum chloride.

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ANDREW R. JUHASZ, *Primary Examiner*.

H. F. PEPPER, *Assistant Examiner*.