United States Patent Office 2,893,859
Patented July 7, 1959

2,893,859

METHOD OF MANUFACTURE OF HOMOGENEOUS COMPOSITIONS

Bernard H. Triffleman, Fairlawn, N.J.

No Drawing. Application February 21, 1956
Serial No. 566,767

9 Claims. (Cl. 75—.5)

The present invention relates to a method for producing homogeneous compositions of several elements, and in particular to methods and techniques for making alloy metal powders, ceramic-metal powders, pure alloys in regulus form, alloys of difficult to reduce materials, minerals, synthetic minerals and ceramics.

The technology of producing alloy metal powders may be broadly classified into two general types of processes, those which are basically mechanical and those which are essentially physicochemical or chemical. Mechanical processes, such as milling, shotting and atomizing of the alloy, require an alloy which has been melted or is in molten state. As a practical matter, this limits mechanical processes to metals which are miscible. Many important combinations of metals, such as silver and nickel and various metal-ceramic mixtures, cannot be prepared by such mechanical processes because the several constituents readily segregate in the molten state. Furthermore, a high order of purity of the ultimate alloy powder is frequently not attainable in that the original starting materials contain impurities, such as carbon and silicon, which end up in the alloy.

Included among the physico-chemical and chemical methods of the preparation of alloy metal powders are processes involving precipitation, electrodeposition and decomposition of particular compounds. Chemical precipitation methods have the advantage of producing alloys which cannot be made by melting but exhibit the disadvantage that the precipitate must be subjected to filtering, very thorough washing and drying. Apart from the serious increases in the ultimate price of the finished product, handling of voluminous precipitates for mass production of alloy powders is at best difficult. Further expense is involved in this type of processing in that many processes do not make provision for recovering the chemicals employed in achieving the precipitation.

Electrodeposition to produce alloy metal powders involves the use of plating techniques; and for each type of alloy powder to be prepared, different baths and operating conditions must be established. These techniques are highly specialized, to such an extent that the production of each alloy powder is a process in itself; and therefore currently only very few alloy powders are made by this method.

Decomposition techniques are exemplified by the carbonyl and hydride methods, which necessarily are limited to those metals which can be made into carbonyls and hydrides. Since comparatively few metal powders can be prepared by these processes and the cost is comparatively high, serious limitations are placed on the application of these techniques.

Broadly, it is an object of the present invention to provide an improved process for the production of alloy metal powders which obviate one or more of the aforesaid difficulties. Advantageously, the present method finds application in making alloy metal powders from alloys of miscible and non-miscible metals; avoids incorporation of impurities from the starting materials in the

final products; facilitates the production of a great variety of powdered materials; and allows for processing in a manner compatible with mass production techniques at cost factors which are favorable in comparison to known processing methods.

Apart from the important advantages realized in the manufacture of alloy metal powders, the present invention makes possible the preparation of synthetic minerals, ceramic-type mixtures of oxides, and the production of alloys of refractory metals. In each instance, the processing involves the same general steps as for the preparation of alloy metal powders. Accordingly, in its generalized application, numerous variants will occur to those skilled in the art of metallurgy.

Still further, for the preparation of difficult reducible alloys, including ferrotitanium, ferroaluminum, and beryllium copper, processing according to the present invention facilitates reduction at lower temperatures as compared to presently known methods. This brings about substantial savings in plant equipment and material simplification of processing.

In accordance with the generalized method aspects of the present invention, a homogeneous composition of several elements may be prepared from a homogeneous solution of the several elements in a volatile solvent. The term "solution" is intended to include true solutions and colloidal suspensions. The solution is dried under conditions appropriate to drive off substantially all of the volatile solvents, without causing segregation of the several elements. The drying action, which may be characterized as "quick-drying," forms a homogeneous molecular mixture of the several elements in solid form, which may be further treated to obtain a molecular mixture in powdered form or a regulus alloy.

Alloy metal powders which can be processed according to this invention includes those alloys which can be reduced from a mixed oxide below the melting temperature of the alloy, and below the temperature at which one or more of the alloy constituents will melt and segregate from the remaining unreduced oxides. Examples of the alloys which can be made, without limitation, include stellites, brass, bronze, nickel-silver, silver-nickel alloys, various steels including stainless and tool steels, Nichrome, Monel, tungsten-molybdenum alloys, tungsten-silver alloys, and a variety of solder materials.

Metal-ceramic powders, frequently referred to as ceramets, may be prepared. These powders are molecular mixtures of metals and ceramics, which have the properties of both the metal and the ceramic, with each particle the same and the metal and ceramic not separable. Examples of metal-ceramic powders, without limitation, are stainless steel containing 5% aluminum oxide, tungsten containing 1% thorium oxide, and nickel containing 50% zirconium dioxide.

Included among the alloys of difficult reducible metals are, without limitation, ferro-titanium, ferro-aluminum, cupro-aluminum, ferro chrome and spiegeleisen.

Included among the minerals which may be processed according to the invention are zircon and spinel; and included among the synthetic minerals and ceramics are various ferrites, cements and refractory materials.

In its specific aspect the present invention includes four main processing steps which are as follows:

(1) A solution is made of the desired elements by dissolving the elements, their oxides or ores, in an appropriate volatile solvent, such as nitric acid, sulfuric acid, ammonia, or water.

(2) The solution prepared according to (1) is subjected to "quick-drying." Most of the volatile solvents are quickly evaporated and no segregation occurs in the non-volatile elements which ultimately make up the end product. The volatile solvent which evaporates off may

be collected in its original form or in a form which can be readily converted to the original state. The ability to collect the volatile solvents makes the process particularly suitable for commercial production.

(3) The homogeneous molecular mixture of the several elements in solid form resulting from (2) is heated to drive off any residue of the volatile solvent. Once again the volatile by-product may be collected in its original state or in a form which can be readily converted to its original state. This step is optional and depends upon the completeness of the volatilization of the solvent in step (2)

The original elements after the further heating step are in a molecular mixture which is comparable to a mineral; and where synthetic minerals or like products are being prepared, no further processing is required. However for many applications, either or both of the following additional steps may be required:

(4) The solid molecular mixture of the several elements derived from step (3) may be comminuted by mechanical means to the desired fineness, and reduced to an alloy-metal powder or ceramet.

(5) To obtain a metal in regulus form, those metals which do not segregate may be melted, or the mixed oxides from step (3) may be reduced directly to a molten metal.

To facilitate a more thorough understanding of the present invention, details of each step of the present process will be set forth:

In accordance with the first step, the preparation of the homogeneous solution of the several elements in the volatile solvent achieve a molecular mixture of the elements. The use of volatile solvents in achieving the molecular mixture allow for the recovery and reuse of the solvent. In many instances, the ability to achieve a substantially continuous process will make the difference between an economically sound process capable of plant production and one finding only laboratory interest. Among the solvents which are suitable for the preparation of the solution, and which are commercially available at comparatively low cost are nitric acid, sulfuric acid, ammonia and water. In that nitrates are most easily decomposed, and since most elements are soluble in nitric acid, most of the illustrative examples detailed hereinafter will deal with nitrate solutions; however it is not to be construed that other solutions, such as those of sulfates and still others, are not equally usable in the present process.

Typical solutions for preparing some illustrative mixtures in accordance with step (1) are as follows:

A. Stainless steel powder—a solution of ferric and nickel nitrates, chromic acid and free nitric acid.

B. Brass powder—a solution of copper and zinc nitrates.

C. Silver-nickel alloys—a solution of silver and nickel nitrates.

D. Tungsten-molybdenum alloys—a solution of tungsten trioxide and molybdenum trioxide in ammonia.

E. Ferrotitanium—a solution containing titanium and iron sulfates, and free sulfuric acid.

F. A ceramet containing stainless steel and aluminum oxide—a solution containing aluminum, nickel and iron nitrates, chromic acid and free nitric acid.

G. Steel—a solution containing ferric nitrate and colloidal graphite.

H. Zirconium silicate—a solution containing zirconium nitrate and colloidal silica.

The solutions prepared in accordance with (G) and (H) are not true solutions; however when these solutions are decomposed in accordance with the teachings of the invention, the products will be a near molecular mixture, which upon heating will become a true molecular mixture. The solution according to (G) and (H) will be recognized as colloidal suspensions.

In accordance with the second step, a homogeneous, easily friable solid mixture of the desired elements is produced; and the rest of the elements are volatilized in a form which can be easily converted to the original solvent. For example, if nitric acid is used to dissolve the desired elements in solution, then conditions should be established to recover as much nitric acid as possible, and not to volatilize the nitrogen of the nitric acid as nitrogen gas. This step is carried out by subjecting the solution to "quick-drying," such as will occur on a rotary drum dryer or flash dryer. In "quick-drying," the elements do not segregate, whereas in "slow-drying" (i.e. pan-evaporation-to-dryness) segregation of the elements occur. This may be because of one compound being more insoluble than the other, or because one compound thermally decomposes at a lower temperature than the other, resulting in a non-homogeneous mixture.

In "quick-drying" the following chemical reactions predominate:

$$M(H_2O)_6(NO_3)_2 \rightarrow 2HNO_3.6H_2O + MO$$

In "slow-drying" the following chemical reactions predominate:

$$M(H_2O)_6(NO_3)_2 \rightarrow M(NO_3)_2 + 6H_2O$$
$$M(NO_3)_2 \rightarrow MO + 2NO_2 + \tfrac{1}{2}O_2$$

Thus in quick-drying, more of the solvent is recovered in its original form; further, quick-drying causes the particles to take on a sponge-like form which is easily friable, whereas in slow-drying produces hard crust-like solids.

Examples of the quick-drying are as follows:

(*a*) A solution containing iron and nickel nitrates, chromic acid, and free nitric acid (designed to yield an end product of an 18–8 stainless steel) was fed dropwise onto a hot metal surface maintained at 300° C. and the resultant particles were removed from the surface after ten seconds. The resulting solid mixture had 5% of the original nitrate content of the input material and the solid was easily friable. The evolved nitrogen was 80% in the form of nitric acid, with the remainder of the nitrogen in the form of lower oxides, as nitrogen dioxide (NO_2) and nitric oxide (NO).

(*b*) A nearly neutral (pH 5) solution of copper and zinc nitrates (designed to yield an end product of a 90% copper and 10% zinc brass) was fed dropwise onto a hot metal surface maintained at 400° C. and the resultant solid product was removed from the surface in ten seconds. The resulting molecular mixture had 4% of the original nitrate content of the input solution and was easily friable. The evolved nitrogen was 85% in the form of nitric acid, with the remainder of the nitrogen in the form of lower oxides, as NO_2 and NO.

(*c*) An ammoniacal solution of molybdic and tungstic oxides (designed to yield an end product of an alloy containing 50% Mo, and 50% W) was fed dropwise onto a hot metal surface maintained at 150° C. and the resulting particles were removed from the surface after ten seconds. The resulting solid mixture contained none of the original ammonia, and the ammonia was quantitatively recovered.

(*d*) A solution containing iron and titanium sulfates and free sulfuric acid (designed to yield an end product of a 50% iron 50% titanium alloy) was fed dropwise onto a hot metal surface maintained at 450° C. and the particles were removed from the surface after thirty seconds. The resulting solid mixture had 50% of the original sulfate content of the input material, and the solid was easily friable. The evolved sulfur was 80% in the form of sulfuric acid, with the remainder of the sulfur in the form of sulfur dioxide (SO_2).

The third step completes the removal of the volatile elements, and homogenization and interaction of the remaining oxides. Again, the volatile elements should be in a form where they can be easily converted to the original solvent. The product from this step is a synthetic

mineral and/or ceramic; and where only these products are wanted, the process is completed. In accordance with step (3), the product from step (2) is heated fairly rapidly at a temperature above the decomposition point of the remaining compounds; and the volatile solvent driven off is quickly removed from the hot zone.

The resulting mixed stainless steel oxides and nitrates from step (2) (Example *a*) were calcined at 800° C. for ten minutes and the volatile elements recovered. The evolved nitrogen was 26% in the form of HNO_3, 60% in the form of NO_2, and 14% in the form of NO. The solid product was free of nitrogen. This solid continued to glow for about five minutes after removal from the furnace, indicating an interaction of the mixed oxides.

It is possible in this step to drive off the volatile solvent and to minimize the interacting of the oxides by rapidly cooling the product. Such a mixture will then have a very reactive surface.

The product from the iron titanium decomposition of step (2) (Example *d*) was heated at 800° C. for forty minutes and the volatile elements recovered. The evolved sulfur was all in the form SO_2. The solid product was substantially free of sulphur.

The product from the ammoniacal solution for tungsten and molybdenum oxides (Example *c*) did not require calcining to drive off the rest of the ammonia because this was all accomplished in step (2).

In accordance with the fourth step, the synthetic minerals from step (3) are converted into metal powders and ceramets. This step is accomplished by heating the oxides from step (3) in a rotary kiln, Hereshoff furnace, tube furnace or like apparatus under a reducing atmosphere, such as hydrogen, methane, cracked methane, or with a solid carbonaceous material.

Examples of the reduction step are as follows:

Stainless steel oxides from step (3) (Example *a*) were heated at 1250° C. for forty-five minutes in a tube furnace under very dry hydrogen. The product had sintered slightly, but this was rectified by adding the powder to a hammer mill where disintegration of the particles to their prereduction size was easily accomplished. The product was an 18–8 stainless steel powder having very good compacting properties and showing excellent corrosion resistance to nitric acid.

Brass oxides from step (3) (Example *b*) were heated at 800° C. under an atmosphere of 50% hydrogen and 50% carbon monoxide for thirty minutes. Reduction was complete as determined by standard tests, such as those described by the Metal Powder Association. The powder had excellent compacting properties, good flow rate, and good apparent density.

Stainless steel oxides from step (3) containing some aluminum oxide was reduced at 1350° C. for thirty minutes under a very dry hydrogen atmosphere. The resulting powder was a stainless steel ceramet having good compacting and other metal powder properties; after pressing, the ceramet exhibited good strength at high temperatures.

Since in many cases only a small percentage of the volatile solvent is left in the product after step (2), it may be commercially sound in accordance with the present invention to eliminate step (3) and reduce the oxides directly, allowing the small amount of volatile solvent to be lost with the spent reduction gases. In view of the greater reactivity of the oxides from step (2), the reduction can be completed in a shorter time; and the resulting metal powder shows a higher apparent density for a given reduction time.

As an example of direct reduction, monel oxide was reduced at 900° C. for thirty minutes. The resulting powder had an apparent specific gravity of 2.5 Monel metal powder prepared by the complete process, and reduced at 900° C. for forty minutes, had an apparent specific gravity of 2.0.

In accordance with the fifth step, the metal powder

or the mixed oxides are converted into a metal of regulus form. For example, a casting made of a stainless steel which consists only of iron, chromium, and nickel and no silicon, carbon and other impurities generally found in ordinary 304 stainless may be required.

Such molten stainless steel can be made by melting down the powder from step (4) in an induction furnace. Loss of metal in this step by oxidation can be avoided by maintaining a hydrogen atmosphere over the top of the crucible. The resulting alloy will have a high order of purity; and may be formulated with precisely calculated percentages of the several constituents.

The preparation of metal powders before the making of metal in regulus form is not essential for the smelting can be direct from the mixed oxides. For example, a melt of brass was made by melting a small amount of brass in an induction furnace; and to this melt a mixture of brass oxides and carbon was added and heated. Reduction of the oxides took place and a large melt of brass resulted. The smelting need not be confined to an induction furnace, for the same could be accomplished in a shaft or other type of ore-smelting furnace.

The following examples will further illustrate how the present invention may be carried out in practice, but the invention is not restricted to these examples.

Example I.—304 stainless stel powder and metal in regulus form

(*a*) 70 parts iron (i.e. Armco iron filings) were dissolved in excess nitric acid according to the following formula:

$$Fe+6HNO_3 \rightarrow Fe(NO_3)_3+3H_2O+3NO_2$$

(*b*) 10 parts nickel (i.e. turnings) were dissolved in excess nitric acid according to the following formula:

$$Ni+4HNO_3 \rightarrow Ni(NO_3)_2+2H_2O+2NO_2$$

(It is understood that in each reaction the NO_2 would be recovered for reoxidation and reuse in actual plant operation.)

(*c*) 40 parts CrO_3 were dissolved in water.

(*d*) All three solutions prepared by steps (*a*), (*b*) and (*c*) were mixed, filtered to remove any insoluble impurities, and concentrated to a temperature of 120° C.

(*e*) The resulting solution was "quick-dried" by being subjected dropwise to a metal surface maintained at 300° C. where rapid evaporation of the water and decomposition took place according to the following possible reactions:

$$2Fe(H_2O)_6(NO_3)_3 \rightarrow Fe_2O_3+6HNO_3+9H_2O$$

$$Fe(H_2O)_6(NO_3)_3 \rightarrow Fe(OH)_2NO_3+2HNO_3+5H_2O$$

The dried product was removed from the metal in ten seconds. The evolved gases were condensed and recovered as strong nitric acid. The evolved nitrogen was in the form of 80% HNO_3, with the remainder in the form of NO_2 and NO.

(*f*) The solid material was ground in a hammer mill until the particles all passed a screen of 100 mesh. This material had 5% of the nitrates when figures as $Fe(NO_3)_3$.

(*g*) The mixed oxides from step (*f*) were then heated for ten minutes at 800° C. to remove most of the volatiles. Practically all the nitrogen was evolved as HNO_3 or NO_2 according to the following possible reactions:

$$2Fe(OH)_2NO_3 \rightarrow Fe_2O_3+2HNO_3+H_2O$$

$$2Fe(OH)_2NO_3 \rightarrow Fe_2O_3+2NO_2+2H_2O+O_2$$

(*h*) The stainless steel oxides from step (*g*) were reduced at 1250° C. under a very dry hydrogen atmosphere for forty five minutes. A slightly sintered mass resulted from this reduction.

(*i*) The product from step (*h*) was fed to a hammer mill where the particles disintegrated to their prereduction size. The final product, 304 stainless steel powder,

showed good strength when compacted under normal pressure. The stainless steel powder also showed very good corrosion resistance to nitric acid.

(*j*) Part of the stainless steel powder from step (*i*) was placed in a zirconia crucible of an induction furnace and melted down under a hydrogen atmosphere to a regulus form, forming a stainles steel alloy free of carbon and silicon.

Example II.—304 stainless steel—5% Al_2O_3 ceramet

$Al(OH)_3$ was dissolved in excess nitric acid according to the following formula:

$$Al(OH)_3+3HNO_3\rightarrow Al(NO_3)_3+3H_2O$$

The resulting solution was added to a solution prepared according to steps (*a*) to (*d*) of Example I. This solution and the various intermediate products were treated similarly to those under Example I, except that the reduction of the oxides was carried out at 1350° C. The resulting product, which was stainless steel with 5% aluminum oxide, exhibited suitable properties for metallurgical processing.

Example III.—Aluminum titanate, refractory material

51 parts aluminum oxide and 80 parts titanium dioxide were dissolved in excess sulfuric acid according to the following formulas:

$$Al_2O_3+3H_2SO_4\rightarrow Al_2(SO_4)_3+3H_2O$$

$$TiO_2+2H_2SO_4\rightarrow Ti(SO_4)_2+2H_2O$$

The several solutions were mixed together and the resulting solution was fed dropwise onto a hot metal surface which was maintained at 450° C. and left there for thirty seconds. The volatilized sulfur was condensed and was found to have been in the form of 78% H_2SO_4 and 22% SO_2. The dry product contained 55% of the original sulfates, when compared to the formulas $Ti(SO_4)_2$ and $Al_2(SO_4)_3$. The dry product was calcined at 800° C. for forty minutes in which time the remainder of the sulfur was evolved as SO_2 and the product $Al_2O_3TiO_2$ was formed. The product was then ground to the desired fineness.

Example IV.—Tungsten-molybdenum alloy, 50% W, 50% Mo

63 parts WO_3 and 76 parts MoO_3 were dissolved in excess aqueous ammonia and mixed. The resulting solution was fed dropwise onto a hot metal surface maintained at 150° C. and left there for thirty seconds. The evolved gases were condensed and collected. The ammonia was quantitatively recovered. The resulting solid product was a molecular mixture of molybdenum and tungsten oxides. The solid mixture was ground to minus 100 mesh, and was reduced in a tube furnace which was slowly raised from 300° C. to 1100° C. The total reduction time was ninety minutes. The powder, an alloy of 50% tungsten and 50% molydenum, had sintered slightly; when the powder was added to a hammer mill, the powder broke up into its prereduction size.

Example V.—Monel powder

60 parts nickel turnings were dissolved in excess nitric acid; 33 parts copper turnings were dissolved in excess nitric acid; and 7 parts iron turnings were dissolved in excess nitric acid. The three solutions were mixed and then dropped on a metal surface which was maintained at 350° C. The solid product remained on the surface for thirty seconds and was then removed. The solid product still contained 10% of the original nitrates. The solid was ground to pass through a 100 mesh screen. The product was then calcined at 800° C. for ten minutes after which decomposition was substantially complete. The product was reduced for thirty minutes at 900° C. under a hydrogen atmosphere. A slightly sintered powder remained. The powder was ground up in a hammer mill to the prereduction size of the particles. The resulting product was a powdered Monel of exactly 60% Ni, 33% Cu and 7% iron and no other elements. The powder had excellent strength when compacted under moderate pressures.

Example VI.—Spinel, $MgAl_2O_4$

78 parts $Al(OH)_3$ were dissolved in excess nitric acid, 40 parts MgO were dissolved in nitric acid as follows: about ten parts were added to an aluminum nitrate solution until the pH reached a value of 3; the remaining 30 parts were dissolved in a stoichiometric amount of nitric acid. The resulting solutions were mixed and concentrated to 120° C. The solution was then fed dropwise onto a heated metal surface which was maintained at 250° C. The product remained on the surface for fifteen seconds. The product contained about 30% of the original nitrates. 95% of the nitrogen which was evolved was recovered directly as nitric acid. The product was then heated at 500° C. for five minutes, 600° C. for the next five minutes, and 800° C. for the final five minutes. The product now contained no nitrogen. The nitrogen which was evolved was in the form of nitric acid, NO_2 and NO. The product was densified by heating for approximately thirty minutes. The product as analyzed was found to be spinel.

Example VII.—Aluminous cement

An aluminous cement containing 40%, CaO, 40% Al_2O_3, 15% Fe_2O_3, 5% SiO_2 was prepared by the following steps:

(*a*) 10.5 parts iron was dissolved in excess nitric acid,

(*b*) 61.3 parts $Al(OH)_3$ was dissolved in excess nitric acid,

(*c*) 40 parts CaO were dissolved in nitric acid; one portion was added to the iron solution until the pH rose to 1; another portion was added to aluminum nitrate solution until the pH rose to 1; and the remainder was added to a stoichiometric amount of nitric acid.

(*d*) 5 parts SiO_2 as a 30% colloidal solution was prepared.

(*e*) The solutions were all mixed together and then concentrated to 120° C.

(*f*) The solution was then fed dropwise onto a heated metal surface which was maintained at 350° C. The material was allowed to remain on the surface for fifteen seconds. The material contained 35% of the original nitrates.

(*g*) The product from step (*e*) was then heated for thirty minutes at a rising temperature which began at 500° C. and reached 800° C. after the thirty minutes. Substantially all the nitrates were evolved as HNO_3, NO_2 and NO; and the product contained no nitrates.

(*h*) The product was ground until it all passed a screen of 200 mesh.

Example VIII.—Ferroxcube IV

A ferrite material, which could be used for transformer cores and is of a composition 50% $NiFe_2O_4$ and 50% $ZnFe_2O_4$ was prepared by the following steps:

(*a*) 58.7 parts nickel turning were dissolved in excess nitric acid.

(*b*) 11.7 parts iron turnings were dissolved in excess nitric acid.

(*c*) 81.4 parts zinc oxide were dissolved in nitric acid; one portion being added to the nickel solution until the pH rose to 1; another portion added to the iron until the pH rose to 1; and the third portion in a stoichiometric amount of nitric acid.

(*d*) The solutions were mixed and then concentrated to 120° C.

(*e*) The solution was added dropwise to a metal surface which was maintained at 350° C. The material was removed from the hot zone after fifteen seconds. The product has 15% of the original nitrates left in it. The nitrogen which was evolved was 92% in the form of nitric acid, and the remainder in the form of lower oxides of nitrogen.

(f) The product was then calcined for thirty minutes in a rising temperature which started at 500° C. and reached 800° C. after thirty minutes. The nitrogen which was evolved was in the form of HNO_3, NO_2 and some NO. The resulting product, a ferrite known as ferroxcube IV, had good magnetic and electrical properties.

Example IX—Brass powder

Ninety parts copper metal was dissolved in excess nitric acid. 12.2 parts zinc oxide was dissolved in nitric acid by adding one portion of the zinc oxide to the copper nitrate solution until the excess acid was neutralized, and second portion to a stoichiometric amount of nitric acid. The solutions were mixed and concentrated to a temperature of 140° C. The resulting solution was fed dropwise onto a metal surface maintained at 400° C. and left there ten seconds. The evolved nitrogen was collected and found to have been 85% in the form of nitric acid, and the remainder as NO_2 and NO. The solid product contained 4% of the original nitrate content. The solid product was then calcined at 800° C. for ten minutes and then reduced to a brass metal powder by heating at 800° C. for thirty minutes under a hydrogen-carbon monoxide atmosphere. The resulting powder had good compressibility and excellent flow and density characteristics.

Example X.—Zircon, $ZrSiO_4$

167 parts basic zirconium carbonate was dissolved in excess nitric acid. The solution was added to another solution containing sixty parts silica in colloidal suspension. The resulting solution was added dropwise onto a hot metal surface maintained at 300° C. and left there for thirty seconds. The resulting solid product was then calcined at 1000° C. for sixty minutes. The product was analyzed and found to be $ZrSiO_4$.

Example XI.—Ferrotitanium, 50% Fe, *50%* Ti

71 parts Fe_2O_3 was dissolved in excess sulfuric acid. 83 parts TiO_2 was dissolved in excess sulfuric acid. The two solutions were mixed. The resulting solution was then fed dropwise onto a hot metal surface maintained at 450° C. The material was left for thirty seconds on this surface and then removed. The evolved sulphur was condensed and found to have been 80% in the form of H_2SO_4 and 20% in the form of SO_2. The solid product still contained 50% of the sulphur when figured as $Fe(SO_4)_3$ and $Ti(SO_4)_2$. This solid product was calcined at 800° for thirty minutes in which time all the sulphur was volatilized as SO_2. The solid product was then reduced at 1600° for one hundred twenty minutes under very dry hydrogen. A metal product was obtained which was analyzed and found to be 50% Fe and 50% Ti. Reduction is accomplished at a temperature readily attainable with gas burners or the like. Accordingly, the illustrative process exhibits marked advantages as compared to conventional techniques which require temperatures of the order of 2000° C., usually attained with an electric arc.

Example XII.—Ferroaluminum, 70% Fe, *30%* Al

70 parts Armco iron filings were dissolved in excess nitric acid. 86.5 parts aluminum hydroxide were dissolved in excess nitric acid. The two were mixed and concentrated to a boiling point of 119° C. The solution was fed dropwise onto a hot metal surface maintained at 300 C. and left there for fifteen seconds. The evolved nitrogen was 98% in the form of nitric acid and 2% in the form of lower oxides of nitrogen. This gas was condensed and recovered as a strong nitric acid solution. The solid product contained 31% of the original nitrates, when figured as $Fe(NO_3)_3$. The solid product was ground in a hammer mill and then heated in a rising temperature which started at 500 C. and reached 800 C. after fifteen minutes. The product contained no nitrogen. The nitrogen which was evolved was in the form of nitric acid, NO_2 and NO. The solid product was then reduced at 1600° C. for one hundred twenty minutes under very dry hydrogen. The resulting metal was analyzed and found to be 70% iron and 30% aluminum.

From the foregoing, it will be appreciated that the process of the present invention is exceptionally versatile and lends itself to the production of many and varied alloy metal powders, ceramic-metal powders, synthetic minerals, and ceramic-type mixtures. Further, the various powders can be made to exacting specifications, with relative freedom of impurities. Still further, difficult to reduce metals may be prepared in regulus form. Further variants and numerous other products may be prepared in accordance with the teachings of the present invention, as will occur to those skilled in the science and art of metallurgy. A latitude of variation, substitution and modification is intended in the foregoing disclosure and in some instances certain features of the invention will be used without a corresponding use of other features.

What I claim is:

1. In a method for manufacturing homogeneous compositions of alloy metals, cermets and ceramics the steps of preparing a homogeneous solution of the several elements in the composition in a volatile solvent including constituents selected from the group consisting of nitric acid, sulfuric acid, ammonia and water, subjecting said solution to quick drying to drive off substantially all of said volatile solvent under conditions selected to preclude segregation of the several elements and to assure the formation of a homogeneous molecular mixture of said several elements in solid form, further heating said molecular mixture to drive off any residue of said volatile solvent, and recovering said volatile solvent driven off during at least said quick drying for reuse.

2. The method according to claim 1 including the further step of treating said molecular mixture to obtain a powder.

3. The method according to claim 1 including the further step of reducing said molecular mixture to a metal in regulus form.

4. The method according to claim 1 including the further step of recovering said volatile solvent driven off during said further heating of said molecular mixture.

5. In a method for manufacturing homogeneous compositions of alloy metals, cermets and ceramics, the steps of preparing a homogeneous solution of the several elements in the composition in a volatile solvent including constituents selected from the group consisting of nitric acid, sulfuric acid, ammonia and water, subjecting said solution to quick drying at a temperature within the range of 150° C. to 450° C. to drive off substantially all of said volatile solvent under conditions selected to preclude segregation of the several elements and to assure the formation of a homogeneous molecular mixture of said several elements in solid form, further heating said molecular mixture to drive off any residue of said volatile solvent, and recovering said volatile solvent driven off during at least said quick drying for reuse.

6. The method according to claim 5 including the further step of treating said molecular mixture to obtain a powder.

7. The method according to claim 6 including the further step of reducing said mixture.

8. In a method for manufacturing a homogeneous composition of several metals, the steps of preparing a homogeneous solution of said several metals in a volatile solvent including constituents selected from the group consisting of nitric acid, sulfuric acid, ammonia and water, subjecting said solution to quick drying to drive off substantially all of said volatile solvent under conditions selected to preclude segregation of said several metals and to assure the formation of a homogeneous molecular mixture of said several metals in solid form, heating said molecular mixture in a reducing atmosphere to drive off

any residue of said volatile solvent, and recovering said volatile solvent driven off during at least said quick drying for reuse.

9. In a method for manufacturing a homogeneous composition of several metals comprising the steps of preparing a homogeneous solution of said several metals in a volatile solvent including constituents selected from the group consisting of nitric acid, sulfuric acid, ammonia and water, subjecting said solution to quick drying at a temperature in the range of 150° C. to 450° C. to drive off substantially all of said volatile solvent under conditions selected to preclude segregation of said several metals and to assure the formation of a homogeneous molecular mixture of said several metals in solid form, further heating said molecular mixture to drive off any

any residue of said volatile solvent, and recovering said volatile solvent driven off during at least said quick drying for reuse.

References Cited in the file of this patent

UNITED STATES PATENTS

1,950,459	Seifert	Mar. 13, 1934
2,077,873	Braselton	Apr. 20, 1937
2,119,489	Beer	May 31, 1938
2,254,976	Powell	Sept. 2, 1941
2,497,268	Grenoble	Feb. 14, 1950

FOREIGN PATENTS

658,241	Great Britain	Oct. 3, 1951