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METHOD OF MAKING METAL ALLOY POWDERS
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ABSTRACT OF THE DISCLOSURE

A method of making a metal alloy in powder form
comprising heating a powder mixture comprising a sub-
strate metal, a mobile metal, and a halide capable of
reacting with said mobile metal to a temperature at which
a halide is formed from said mobile metal, cooling the
resulting mixture to a temperature at which a reaction
occurs producing a mobile metal in fluid form from said
mobile metal halide, thereby depositing a metal film on
the particles of said substrate metal, and repeating the
heating and cooling cycle until an alloy powder of the
desired composition is obtained.

BACKGROUND OF THE INVENTION

This invention was made in the course of, or under,
a contract with the United States Atomic Energy Com-
mission.

My invention relates to methods of making metal alloys
and particularly to methods of making such alloys in
powder form.

Alloys in powder form are useful in powder metal-
lurgical and in flame-spraying processes. The production
of alloys in powder form heretofore has required steps
of fusing the metal constituents in the desired proportion,
breaking up the fused mass, and ball-milling the resulting
pieces into powder. There is no assurance in such a proc-
ess of obtaining a powder having either the desired com-
position or particle size.

SUMMARY OF THE INVENTION

It is accordingly one object of my invention to provide
an improved method of making a metal alloy powder.

It is another object to provide a method of making a
metal alloy powder wherein the composition can be care-
fully controlled.

It is still another object to provide a method of making
a metal alloy powder having a closely controlled average
particle diameter.

Other objects of my invention will be apparent from
the following description and the attached claims.

In accordance with my invention I have provided a
method of making an alloy powder comprising the steps
of (a) providing a powder mixture comprising particles
of a substrate metal, a mobile metal, and a halide; (b)
heating the resulting mixture to a temperature high enough
to form a mobile metal halide; (c) cooling the resulting
mixture to a temperature at which at least a portion of
the metal values in said mobile metal halide are reduced
to the metallic state thereby depositing a film of said
mobile metal onto the particles of said substrate metal,
and repeating the heating and cooling steps until an alloy
of the desired composition is obtained.

My method produces a metal alloy powder having a
controlled particle size and a controlled composition. The
particle diameter of the product is determined by the
initial substrate particle diameter and the ultimate com-
position is determined by the relative amounts of differ-
ent metals present and the number of heating cycles.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For convenience in describing my invention the terms

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"mobile metal" and "substrate metal" are used in the
specification and in the claims and are descriptive of the
functions of the materials used in carrying out my process.

The term "mobile metal" refers to the constituent which
deposits onto and diffuses into another constituent dur-
ing the formation of the alloy.

The term "substrate metal" refers to the constituent
of the alloy which functions as a base onto which at
least one other constituent is deposited, and may be either
an element or an alloy. It must have a high enough melt-
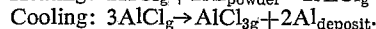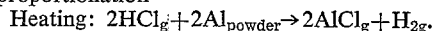ing point so that it does not melt at the process tem-
peratures.

The characteristics of other elements comprising the
alloy determine whether or not a specific element is a
mobile or a substrate metal. An element characterized
as a mobile metal in a process of making one alloy can
be a substrate metal in a process of making another alloy.
One factor governing the ability of elements to function
as a mobile or substrate metal is the free energy of forma-
tion of the halide, and the following list begins with ele-
ments most likely to form mobile metals and ends with
those most likely to be substrate metals. Each element
will be a substrate with respect to those elements pre-
ceding it in the list and will be a mobile metal with re-
spect to elements following it. For example, thorium
should deposit and alloy with all elements below it on
the list; palladium, however, can only be a substrate.
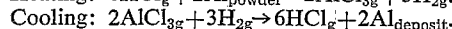
TABLE I

1. Magnesium	10. Plutonium	19. Cadmium
2. Thorium	11. Manganese	20. Cobalt
3. Zirconium	12. Zinc	21. Copper
4. Hafnium	13. Chromium	22. Silver
5. Aluminum	14. Tin	23. Nickel
6. Beryllium	15. Iron	24. Niobium
7. Boron	16. Silicon	25. Tungsten
8. Carbon	17. Lanthanum	26. Molybdenum
9. Titanium	18. Vanadium	27. Palladium

The mechanism involved in the movement and deposi-
tion of the mobile metal is believed to depend to some
extent on the specific metal under consideration. While
I do not wish to be bound by any theory, it is likely
that elements having multiple valence states are deposited
by a disproportion mechanism, although an oxidation-
reduction reaction may be involved. For those metal halides
which do not exist in multivalent forms an oxidation-
reduction reaction probably governs the alloying. The fol-
lowing equations are presented to illustrate the dispropor-
tionation reaction and the oxidation-reduction reaction
using aluminum as an illustrative mobile metal.

Disproportionation

Heating: $2HCl_g + 2Al_{powder} \rightarrow 2AlCl_g + H_{2g}$.
Cooling: $3AlCl_g \rightarrow AlCl_{3g} + 2Al_{deposit}$.

Oxidation-Reduction

Heating: $6HCl_g + 2Al_{powder} \rightarrow 2AlCl_{3g} + 3H_{2g}$.
Cooling: $2AlCl_{3g} + 3H_{2g} \rightarrow 6HCl_g + 2Al_{deposit}$.

My invention is described in more detail below with re-
spect to a metal capable of forming a halide in more than
one valent state as the mobile metal.

The mixture of components comprising a mobile metal,
its higher valent halide, and the particles of substrate
metal is heated to a temperature at which the higher valent
halide reacts with the mobile metal to form a halide in a
lower oxidation state. This reaction may be represented
by the following general equation in which the mobile
metal, represented by M, has oxidation states of 1 and 3:

$$2M + MX_3 \xrightarrow{\Delta} 3MX$$

The resulting mixture is then cooled to a temperature
at which the lower valent halide disproportionates into

the metal and the higher valent halide in accordance with the formula

$$3MX \rightarrow MX_3 + 2M$$

In this step the metal formed deposits onto the substrate and in subsequent cycles diffuses into it.

In these subsequent cycles the mobile metal deposited onto the substrate is unexpectedly non-reactive to the higher valent halide to the extent that it is not removed from the substrate particles in accordance with the first equation above. Consequently, the concentration of mobile metal within the substrate metal can be increased to form an alloy containing a large proportion of the mobile metal.

My invention will be described in more detail with a process wherein nickel is the substrate material and aluminum is the mobile material.

In carrying out my invention, nickel particles are first heated in the presence of aluminum particles and $AlCl_3$ to a temperature high enough to produce AlCl. The selection of an average particle size for the nickel powder is determined by the desired average particle diameter of the alloy powder formed.

The $AlCl_3$ may be provided as a powder; however, in the preferred method of carrying out my invention, it is formed in place during the heating step. In this preferred method, aluminum, preferably in the form of a powder, and NH_4Cl are mixed with the nickel powder. As the powder mixture is heated, NH_4Cl breaks down into NH_3 and HCl and the HCl reacts with the aluminum powder to form $AlCl_3$. The composition of the final alloy is easily controlled by providing aluminum and nickel powders in a ratio equal to the ratio in the desired alloy and repeating the heating and cooling cycles until the aluminum is consumed.

The following table gives the composition and nickel-aluminum phases present in some typical alloy powders produced in accordance with my method.

TABLE II

Constituents, wt. percent		Ni-Al phase produced
Ni	Al	
95.0	5.0	Zeta.
93.2	6.8	Do.
92.2	7.8	Zeta (65%) epsilon (30%).
90.7	9.3	Zeta (30%) epsilon (65%).
85.0	15.0	Epsilon (Ni₃Al).
83.0	17.0	Epsilon-delta.
79.0	21.0	Do.
77.6	22.4	Do.
74.4	25.6	Delta.
49.0	51.0	Delta plus Ni₂Al₃.

The concentration of NH_4Cl in the mixture is not critical, and a concentration of from 1 to 3 percent is preferred.

Inasmuch as the temperatures employed are high enough to sinter the particles, in order to prevent the particles from sintering an inert powder must be dispersed throughout the powder mixture in an amount equal to at least 50 percent by weight of the nickel powder. Al_2O_3 is preferred

in making an alloy of nickel and aluminum since its use introduces no extraneous impurities. This inert powder is preferably present in an amount of 50 to 200 percent by weight of the nickel powder. While the Al_2O_3 particle size is not critical, in order to easily separate it from the product it should be larger than the nickel particles, and preferably the average particle diameter is in the range of 60 to 100 microns.

The powder mixture is heated to a temperature of at least 1000° C., whereupon the $AlCl_3$, whether added to the mixture or formed in situ, forms AlCl. The powder mixture is preferably heated to a temperature within the range of 1000 to 1010° C. Higher temperatures tend to cause agglomeration of the particles.

After this heating step the powder mass is cooled to a temperature at which AlCl disproportionates into $AlCl_3$ and aluminum metal. This metal forms deposits on the nickel particles and alloys with the nickel. The powder mass in this step is cooled to a temperature below 1000° C. and preferably to a temperature of 980 to 990° C.

The foregoing heating and cooling cycle is repeated until an alloy of the desired composition is obtained. In a typical case no more than 20 cycles will be enough to alloy all of the aluminum present with the nickel.

The heating and cooling periods are not critical, and the length of time for these steps is determined by equipment limitations.

The pressure at which these reactions are carried out is not critical and is also determined by equipment limitations.

Having thus described my invention, the following examples are given to illustrate it in more detail.

EXAMPLE I

A powder mixture containing by weight 85 parts nickel powder having an average particle diameter of 5 microns, 15 parts of aluminum powder having an average particle diameter of 5 microns, 130 parts of alpha Al_2O_3 having an average particle diameter of 80 microns, and 10 parts by weight of NH_4Cl was placed in a ceramic container in a furnace which was evacuated to a pressure of 100 microns mercury to remove oxygen and moisture. The temperature was raised to about 1000° C. after which it was cooled to 930° C. and the temperature was cycled from about 1020° C. to 930° C. for 20 cycles. During these steps the pressure built up to about 75 p.s.i.g. as a result of evolution of hydrogen from the reaction between HCl and aluminum. The resulting powder was removed from the furnace, screened to remove Al_2O_3, and washed in distilled water to remove traces of chloride.

The resulting powder had a composition of Ni_3Al (epsilon phase) and an average particle diameter of 15 microns.

EXAMPLES II–V

Other alloys were made in accordance with the general method described in Example I. The starting materials, process conditions, and compositions of alloys are given as Examples II–V in Table III below.

TABLE III

Example No.	Starting material, parts by wt.		Temperature, ° C.		Number of cycles	Alloy composition wt. percent
	Metal powders	Other materials	Lower	Upper		
II	240 Ni 60 Cr	10 NH₄Cl 2.5 NH₄I Al₂O₃	950	1,030	14	90 Ni 10 Cr
III	820 Ni 160 Cu 96 Al	20 NH₄Cl 1,500 Al₂O₃	950	1,030	31	84.2 Ni 8.8 Al 7.0 Cu
IV	544 Ni 56 Al 10 Nb	20 NH₄Cl 1,400 Al₂O₃	980	1,030	23	87.5 Ni 11.6 Al 0.9 Nb
V	198 Fe 60 Cr 30 Ni 9 Al	10 NH₄Cl 471 Al₂O₃	980	1,030	6	60.3 Fe 26.2 Cr 12.5 Ni 1.0 Al

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As can be seen from the data of Table III, alloys having more than two components can easily be made in accordance with my method.

The above examples are given to illustrate, not to limit, my invention.

I claim:

1. A method of making an alloy powder comprising:
   (a) providing a powder mixture comprising particles of a substrate metal, a mobile metal, and a halide;
   (b) heating the resulting mixture to a temperature high enough to form a mobile metal halide;
   (c) cooling the heated mixture to a temperature at which at least a portion of the metal values in said mobile metal halide are reduced to the metallic state thereby depositing a film of said mobile metal onto the particles of said substrate metal;
   (d) heating said mixture to diffuse, into said substrate metal, film deposited thereon in step (c) and to form more of said mobile metal halide; and
   (e) repeating steps (c) and (d) until an alloy of the desired composition is obtained.

2. The method of claim 1 wherein mobile metal is capable of forming a higher valent halide and a lower valent halide, in step (b) the mixture is heated to a temperature high enough to form a lower valent halide, and in step (c) the mixture is cooled to a temperature low enough for said lower valent halide to disproportionate into said mobile metal and its higher valent halide.

3. The method of claim 1 wherein said mobile metal is selected from the group consisting of aluminum, chromium, niobium, and copper.

4. The method of claim 1 wherein said substrate metal is nickel.

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5. The method of claim 1 wherein said mobile metal is aluminum and said substrate metal is nickel.

6. The method of claim 5 wherein nickel-aluminum particles are formed containing from 49 to 99 percent nickel by weight.

7. The method of claim 1 wherein said mixture contains nickel powder, aluminum powder, ammonium chloride, and alumina.

8. The method of claim 7 wherein the powder mixture is heated to a temperature in the range of 1000° C. to 1010° C. and is then cooled to a temperature in the range of 980° C. to 990° C.

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