United States

Fustukian

[11] **3,914,507**

[45] **Oct. 21, 1975**

[54] **METHOD OF PREPARING METAL ALLOY COATED COMPOSITE POWDERS**

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[22] Filed: **Nov. 20, 1973**

[21] Appl. No.: **417,689**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 122,098, March 8, 1971, abandoned.

[30] **Foreign Application Priority Data**

Mar. 20, 1975 Canada 077934

[52] **U.S. Cl.** ..... **428/404**; 29/192 CP; 75/0.5 BA; 75/0.5 BB; 75/0.5 BC; 427/217; 106/1

[51] **Int. Cl.²** **B22F 1/02**

[58] **Field of Search** ..... 117/22, 31, 100, 71 R, 117/131, 71 M, 160 R; 75/0.5 BA, 0.5 BB, 0.5 BC; 29/192 CP

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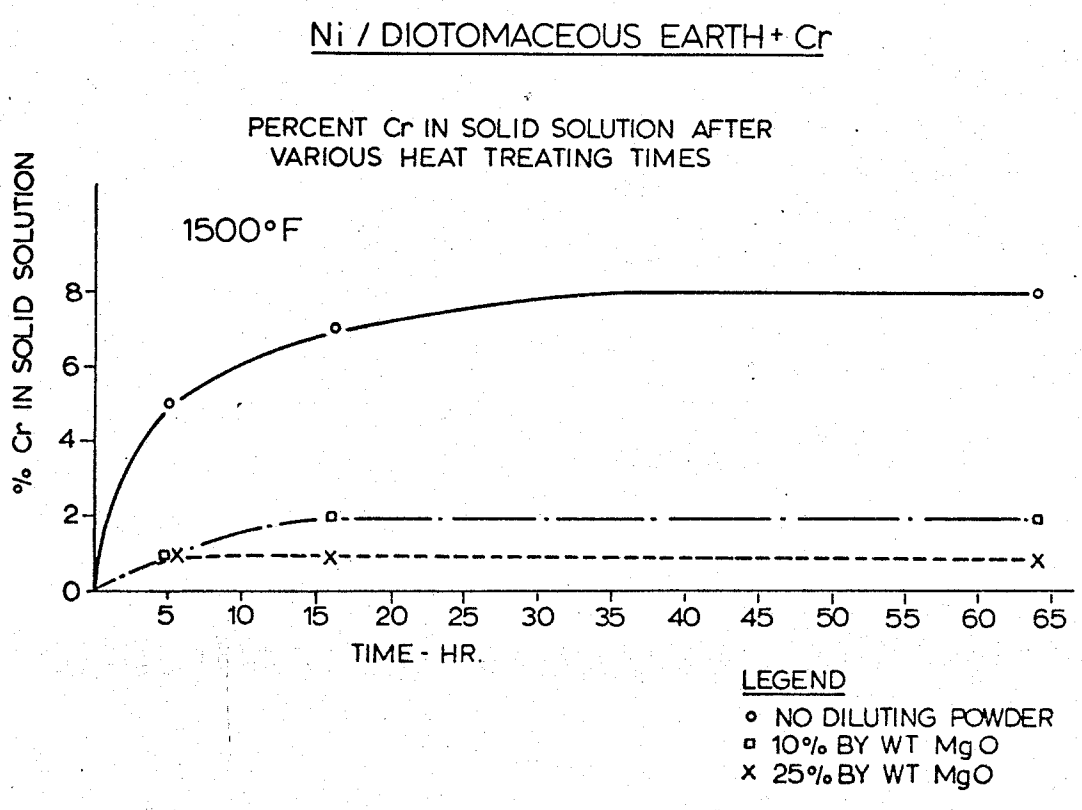
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[57] **ABSTRACT**

Composite alloy coated particles are produced by blending finely divided metal coated composite particles, such as nickel coated graphite or cobalt coated tungsten carbide, with finely divided particles of at least one alloying metal, such as chromium or aluminum. The powder blend is heated in a protective atmosphere at a temperature and for a time sufficient to cause the alloying metal to alloy with the metal coatings of the composite powder particles without extensive sintering of the powder particles.

18 Claims, 2 Drawing Figures



Ni / DIOTOMACEOUS EARTH + Cr

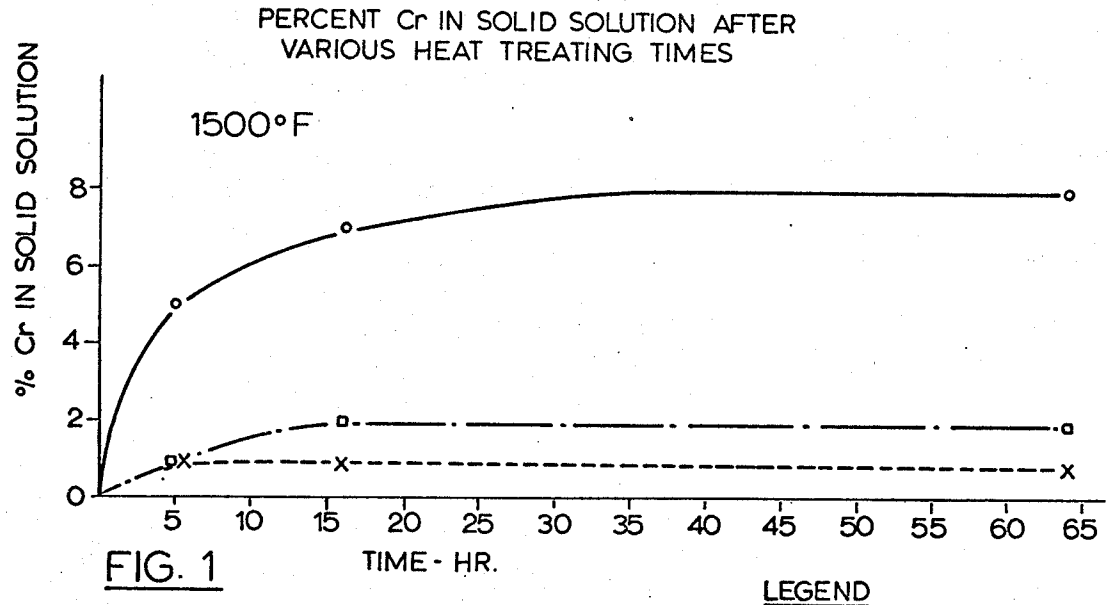


FIG. 1

LEGEND
- ○ NO DILUTING POWDER
- □ 10% BY WT MgO
- × 25% BY WT MgO

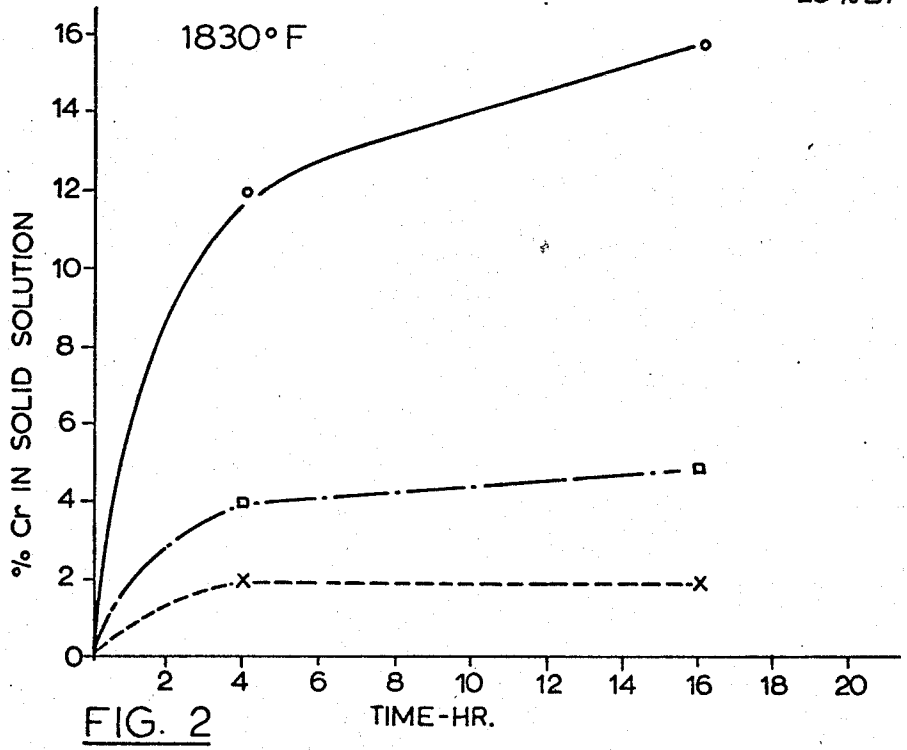


FIG. 2

METHOD OF PREPARING METAL ALLOY COATED COMPOSITE POWDERS

This application is a continuation-in-part of application Ser. No. 122,098 filed Mar. 8, 1971 and now abandoned.

This invention relates to a process for preparing composite powders having a metallic or non-metallic central core and a metallic alloy layer coating the core. The invention also relates to the product of such process.

Composite powder particles comprising a central core coated with a mono-component metal layer are known and in commercial use in for example the flame and plasma spraying fields, nickle-coated graphite and nickel-coated diatomaceous earth particles are flame sprayed to make abradable seals for turbine engines. As another example, cobolt-coated tungsten carbide is plasma sprayed on carving knife blades to provide a hard cutting edge which is resistant to wear.

A variety of these powders is commercially available. They can be made using hydrometallurgical techniques such as are described in U.S. Pat. Nos. 2,853,398; 2,853,401; 2,853,403; 3,062,680; 3,218,192; and 3,241,949. However, these methods describe production only of composite powders with a mono-component coating and there is a need for composite powder particles having metal alloy coatings on the core material because such particles, owing to their heterogeneous nature, are capable of being formed from an unusual combination of materials. By appropriate choice of materials it is possible to tailor the properties of the composite particles closely to meet the requirements of their end use. By contrast, much less variation in properties is possible in composite particles having a mono-component coating.

It is therefore an object of this invention to provide a practical method for producing composite powder particles which have a metal alloy coating on a metallic or non-metallic core.

It is another object to provide composite powder particles which have central core and a metal alloy coating on the core, the constituents of the alloy coating being substantially uniformly distributed in one another.

It is another object to alter the properties of the mono-component metal coating of prior art composite powders by alloying such coating with one or more other constituents.

The method of the invention comprises: providing composite powder particles of a size within the range of 10–850 microns each such composite particles having a central core coated with a layer of metal; forming a powder mixture which lacks a diluting or parting agent and which comprises the composite particles and finely divided particles of alloying metal chosen from the group comprising: chromium, and aluminum, said alloying metal being capable of alloying with the metal coating of the composite particles when the mixture of composite particles and alloying metal particles is heated; and heating the mixture under non-oxidizing condition at a temperature of from about 1650°F. to about 2300°F where said alloying metal is chromium and from about 1100°F. to about 1220°F. where said alloying metal is aluminum, and continuing said heating step for a period of time sufficient to ensure that a required quantity of said alloying metal diffuses into and alloys with the metal coating of the composite particles without gross sintering taking place.

The specific composition of the composite powder particles used as the starting material of the process is not important. The core material of these particles may be any substance which can be coated with a mono-component metal layer and which is stable at the temperature required for the alloying step of the process. The core material may be graphite, diatomaceous earth and refractory materials such as aluminum oxide, tungsten carbide, titanium carbide, tungsten-titanium carbide, chromium carbide and chromium oxide.

Where the finished particles are to be used as abradable seals the core material must be both abradable and erosion resistant. In addition corrosion resistance of the core material in the environment in which the seals are used is also required. For example where the seals are used in turbine engines to minimize the clearance between the compressor blades and the casing and between the stator vanes and the rotor, the seals must be resistant to corrosion by the turbine exhaust gases.

Because graphite oxidizes at low temperatures, its use as a core material in alloy-coated composite particles in engine seals is limited to engine temperatures up to about 1022°F. For higher service temperatures, composite powders having more refractory abradable cores are required. Diatomaceous earth and calcium fluoride are preferred for this purpose.

The metal coatings on the composite particles may be nickel, cobolt, copper or molybdenum deposited on the core by the hydrometallurgical methods described in the above noted patents, or it may be another metal such as zirconium, zinc or aluminum bonded to the core surface using a technique such as ball milling.

The starting composite particles must be within the general size range of 10–850 microns with the precise particle size being chiefly governed by the use to which the alloy coated product particles are put. For example, flame-spraying processes generally require that the feed powder be about 50–200 microns in size; on the other hand, plasma-spraying applications usually require 10 – 50 microns size feed particles.

For most applications, the mono-component metal coating on the starting powder particles is very thin, e.g. in the order of 10 microns or less. This is usually the case because of the composition required for the intended application. For example, flame sprayers of nickel-coated graphite particles specify a graphite content of 15%. Since graphite has a low density, its volume in comparison with the metal coating is large so the nickel coating is relatively thin. An 85/15% by weight nickel-graphite composite particle of 50 microns in size has a nickel coating thickness in the order of 10 microns. As another example, plasma sprayers use 20/80% by weight cobolt coated tungsten carbide particles having a size of about 10 microns. These particles have a cobalt coating about 1 micron thick.

The operability of the process of the invention is dependent on the previously unrecognized fact that when thinly coated composite particles are heated to a high alloying temperature in close contact with particles of chromium or aluminum, the latter metals will form an alloy with the coating metal. The finished product will not be sintered at all or will be only lightly sintered so that it can be ground or otherwise broken down to particles which are of a size closely resembling the initial unheat-treated powder size and which have a complete

alloy coating. When a mixtuure of fine particles of the coating metal and particles of chromium or aluminum are heated to the same temperature however, rather than forming an alloy the mixture will be grossly sintered. For purposes herein the product is "grossly sintered" where it cannot be broken down to a size closely resembling the initial unheat-treated powder size without causing fractures to form through the particles making up the product as opposed to between adjacent particles.

To illustrate the foregoing, if a mixture of 2 – 10 nickel and chromium particles is heated at 1650°F. for 30 minutes, a solid mass is produced. This mass cannot be broken down short of grinding it. If a grinding precedure is followed, the nickel and chromium particles making up the mass are fractured so that the original character of the powder particles is destroyed. By contrast where a mixture of nickel-coated graphite composite particles and chromium are heated to the same temperature, the mass is only slightly sintered and can easily be broken down without fracturing the chromized composite particles.

Thus a mixture of chromium or aluminum and composite particles can be heated to a higher temperature without gross sintering taking place than can a mixture of chromium or aluminum and particles of the same metal as the metal which coats the composite particles. This fact gives rise to significant results. Since at higher temperatures, the rate of alloying is much more rapid than at lower temperatures, the coating metal or composite particles can be alloyed with chromium or aluminum much more quickly than can particles of the coating metal per se which must be heated at a lower temperature to avoid gross sintering. The marked effect which temperature has on the rate of alloying is shown in the drawing and is described in Example 12.

It is known that in the presence of a diluting or "parting agent" such as alumina or magnesia, particles of the alloying metal and particles of the coating metal per se can be heated without sintering to temperatures which, in the absence of the parting agent would result in gross sintering. A number of problems are however caused by parting agents. First the agents retard the rate at which alloying takes place and hence the time required for the operation (the drawing illustrates the retarding effect which magnesia has on the rate of alloying). Secondly, the agents by definition dilute the quantity of active metal or non-metal in a given volume of powdered mixture and accordingly there is less transfer of the alloying metal into a substrate than from the same volume of mixture containing no parting agents. Thirdly, the agents must be separated from the finished alloyed particles prior to use. In many cases, complicated and costly procedures are required to remove the parting agents from the alloyed powder particles.

In view of the foregoing it is undesirable to use a parting agent to prevent sintering. In the absence of a parting agent, as pointed out before, the coating metal of composite powder particles can be alloyed at a much faster rate than can single component particles of the coating metal. Furnaces required for prolonged heat treatment of single component particles are accordingly not required where composite particles are being treated.

Binary or ternary alloy coated composite particles can be produced by the process of the invention. For example finely divided metal coated composite particles such as nickel-coated graphite particles, and particles of for example chromium, can be heated at alloying temperatures for a period of time to obtain uniform solid state diffusion or reaction alloying. Similarly, coated composite particles can be mixed with both chromium and aluminum and heated to yield ternary alloy coated composite particles. Gross sintering of the alloy coated particles does not occur. The product obtained is either a powder or a lightly sintered cake which can be easily broken up to provide composite alloy coated particles of substantially the same size and shape as the starting composite particles.

The rate of transfer of the alloying metal into the coating of the composite powder can be greatly increased by the addition of a small amount of halogen-bearing compound activator such as chromium chloride, bromide or fluoride or ammonium chloride, bromide or iodide. The temperature at which alloying of the composite powder and alloying metal occurs is also somewhat lessened by the presence of the activator. The compound is added to the mixture of composite powder and alloying metal prior to the heating operation. In general no more than 2% of the compound by weight based on the total weight of the mixture is required for this puurpose. To prevent contamination of the alloy coating, it is preferable that the cation of the halogen-bearing compound be the same as one of the metals making up the alloy coating. For example, chromium chloride is the preferred activator when the alloying metal is chromium. Alternatively the cation should volatilize upon decomposition of the halogen-bearing compound e.g. NH_4.

The particles of alloying metal or metals which are mixed with the composite particles should be smaller in size than the composite particles and preferably should be less than 50 microns. The smaller the alloying metal particles, the faster the alloying reaction rate, so it is desirable to utilize the smallest alloying metal particles that are available. The alloying metal particles must be formed of a metal which is capable of alloying quickly with the composite particle coating metal when a mixture of the particles is heated to alloying temperatures.

The selection of the composite powder and the alloying metal particles is a matter of choice, depending on the properties desired in the final alloy coated composite powder product. However, the process of the invention is particularly effective for alloying chromium and aluminum with nickel, cobalt or copper coated on non-metallic core particles.

The mixing step of the invention can be carried out by any of the known metal powder blending techniques, such as tumbling, which ensure substantially uniform blending of the powder constituents.

The powder mixture is heated to and maintained at alloying temperature for a predetermined period of time selected to ensure that the required degree of alloying occurs without appreciable sintering. The precise heating time and temperature have to be determined for each case although 48 hours is usually about the maximum time that can be expended on the heating step in any case while still providing an economically desirable process. If the coating material of the composite particles and chromium are being alloyed, heating should be carried out at about 1650°F. to 2300°F. Above 2300°F. no significant increase in alloying rate is obtained with increases in temperature and sintering starts to become a problem.

While alloying of chromium with the coating metal will occur at temperatures as low as 1500°F. it is desirable to heat the powder mixture to temperatures in excess of about 1650°F. Where the powder mixture is heated at temperatures below 1650°F., the rate of diffusion of chromium into the coating material increases rapidly in the initial stage of heating but then as time passes the rate decreases and eventually virtually ceases. Thus at these temperatures there is a maximum chromium level which can be reached and prolonging the heat treatment will not serve to increase this level. For many applications finished composite particles having such a low chromium level in the coating material are not suitable. By contrast, a much higher chromium level can be attained where heating is conducted at temperatures of above about 1650°F. By appropriate control of heating time the level of chromium in the coating material can be adjusted within a very wide range to suit the application intended for the finished particles.

In the particular case of composite nickel-diatomaceous earth particles and chromium powder alloying should preferably be conducted at no higher than 1900°F. Since at higher temperatures the chemical constituents of the diatomaceous earth begin to react with the metals.

In the case where nickel coated composite particles and aluminum are being alloyed, the heating should be carried out between about 1100°F. and about 1220°F. Below 1100°F. the alloying reaction is too slow. Above 1220°F. the aluminum melts. From the foregoing, it is seen that each system of components has its own requirements. The specific temperature used in alloying has to be tailored for each system by carrying out routine experimentation.

The heating step is carried out in any suitable furnace which permits the provision of a protective atmosphere to avoid oxidation. Preferably, hydrogen, having a dew-point below −40°F. is flowed through the heating zone throughout the alloying operation.

Where ternary alloy coated particles are being produced, the chromium and aluminum particles may be mixed simultaneously with particles of the composite powder before the mixture is passed to the heating operation. Alternatively, the production of the particles may be carried out in two stages. In the first stage, the composite powder is mixed with one alloying metal and the mixture is heated to effect alloying of the coating of the powder with the alloying metal. In the second stage, finely divided particles from the first stage are mixed with the second alloying metal and heated as before. For example the starting composite particles may first be mixed with particles of chromium and heated to an alloying temperature of 1650°F. to 2300°F. After chromizing has occurred, the resulting particles may be heated in contact with aluminum particles to temperatures as high as 1400°F.

The temperature within the furnace and the duration of the heating step will depend upon the constituents of the ternary alloy coated powder, and whether the composite powder starting material is blended simultaneously with both alloying metals or whether each alloying metal is blended separately with the composite powder.

In some cases, the product from the heating step is in the form of a powder. In other cases, it is in the form of a lightly sintered mass which can be easily comminuted to separate the chromized or aluminized composite particles from one another.

The product of the invention comprises a plurality of particles of a size within the range of 10–800 microns, each particle having a central core with a firmly bonded coating of alloyed metals attached thereto. The product particles are slightly larger but similar in shape to the starting composite particles. Magnetic and microprobe analysis of the alloy coating shows complete alloying of the metal constituents in the alloy coating.

EXAMPLE I

This example illustrates preparation of nickel-chromium coated diatomaceous earth composite powder. The starting material for this example was nickel coated diatomaceous earth composite powder containing 85% nickel by weight. The powder which was prepared in accordance with U.S. Pat. No. 3,062,680 had the following physical characteristics.

TABLE I

Standard Tyler screen analysis: Fraction	Percent
− 48 + 100	1.6
−100 + 150	5.6
−150 + 200	13.0
−200 + 250	10.0
−250 + 325	31.4
−325	38.4

Apparent density: 0.83 grams/cubic centimetre
Flow rate: 107.2 seconds/gram
Fisher Number: 14

100 grams of the composite powder were blended with 16 grams of commercial grade, a micron size chromium powder. The powders were blended by manually shaking them together in a bag and then mixing them in a highspeed blender for 2 minutes.

After blending, the powder mixture was placed in a nickel boat and positioned in the cooling zone of an electrically heated laboratory tube furnace. At this stage, the bed of powder was purged with hydrogen to remove entrapped oxygen. This was done by passing hydrogen, having a dew point of −40°F. through a 2½ inch diameter chamber of the furnace at 1½ cubic feet per minute for 20 minutes. The hydrogen has been preheated by passing it through the hot zone of the furnace.

The boat was then moved to the hot zone of the furnace. This zone was maintained at 1900°F. Hydrogen was passed through the zone at 1½ cubic feet per minute. Heating was continued for 4 hours.

The boat was then returned to the cooling zone and left there for a period of 1 hour. The boat was then removed from the furnace and the powder mixture, in the form of a sinter cake, was broken into pieces and placed in a high speed blender for 1 minute. It easily broke up in the blender to a powder product having a following physical characteristics:

TABLE II

Standard Tyler screen analysis: Fraction	Percent
− 48 + 100	8.4
−100 + 150	9.8
−150 + 200	15.4
−200 + 250	5.7
−250 + 325	18.5

TABLE II-Continued

Standard Tyler screen analysis: Fraction	Percent
−325	42.2

Apparent density: 1.08 grams/cubic centimetre
Fisher Number: 12.1.

The coating of the product powder was examined for alloying using electron microprobe analysis and relative ferro-magnetism testing. The coating was found to be comprised of a uniform alloy of nickel and chromium.

Conventional metallographic examination of a polished section of powder particles showed that the individual particles consisted of a core and a uniform metallic coating.

A qualitative microanalysis of the particles was carried out using an electron microprobe and revealed that the metallic coatings were comprised of a homogeneous mixture of chromium and nickel and the cores were comprised of a compound containing silicon and oxygen (diatomaceous earth).

Comparison of the ferromagnetic nature of the blend before heat treatment and after heat treatment indicated that the heat-treated powder was non-magnetic. Therefore the intimate mixture of chromium and nickel in the coating was in fact a solid solution of chormium in nickel.

Ferro-magnetism tests were carried out by first balancing the sample weight, then determining the force of attraction to a fixed magnetic field. Pure iron powder was used as the standard (100%). The nickel-coated diatomaceous earth blended with chromium had relative ferro-magnetism of 19% relative to pure iron.

The effects of time, when treating at 1900°F. on the magnetic properties of the nickel-coated diatomaceous earth and chromium blend were studied in detail. The results shown in Tale III indicate that alloying was taking place. The virtual elimination of ferro-magnetism was an indication of the completeness of the alloying reaction.

TABLE III

Time (Minutes)	Ferromagnetism of the blend relative to iron, %
0	19
4	7.2
16	0.8
35	0.1

EXAMPLE 2

This example illustrates preparation of nickel-aluminum alloy coated diatomaceous earth composite powder.

100 grams of the composite powder of Example 1 was blended with 42.5 grams of aluminum powder having a Fisher number of 28.1 and apparent density of 0.99 grams/cubic centimetre. The blend of powders was treated in accordance with the procedure of Example 1 with the exception that the furnace was operated at 1170°F. and the blend was heated for only 30 minutes. The screen analysis of the product after light grinding in a mechanical blender was as follows:

TABLE IV

Standard Tyler screen analysis: Fraction	Percent
− 48 + 100	23.9
−100 + 150	16.3
−150 + 200	18.2
−200 + 250	2.6
−250 + 325	13.5
−325	25.5

Apparent density: 2.13 grams/cubic centimetre

Qualitative microanalysis and ferro-magnetic comparison in accordance with Example 1 showed that the desired complete alloying of the aluminum and nickel was achieved.

EXAMPLE 3

This Example illustrates preparation of nickel-chromium alloy coated graphite composite powder.

Nickel coated graphite composite powder containing 25% core material by weight was provided. The powder had the following physical characteristics:

TABLE V

Standard Tyler screen analysis: Fraction	Percent
− 48 + 100	0.4
−100 + 150	3.2
−150 + 200	14.4
−200 + 250	18.4
−250 + 325	38.4
−325	25.2

Apparent density: 1.95 grams/cubic centimetre
Flow rate: 91.0 seconds/gram.

100 grams of the composite powder were blended with 18.75 grams of the chromium powder of Example 1. The blend of powders was treated in accordance with the procedure of Example 1 with the exception that the furnace was operated at 2200°F. and the blend was heated for 16 hours.

No screen analysis was carried out on the powder product. However, qualitative microanalysis and ferro-magnetic comparison in accordance with Example 1 showed that the desired alloying of chromium and nickel was achieved.

EXAMPLE 4

This Example illustrates preparation of nickel-chromium alloy coated boron nitride composite powder.

Hydrometallurgically produced, nickel-coated boron nitride composite powder containing 48% by weight of the core material was provided. The powder had the following physical characteristics:

TABLE VI

Standard Tyler screen analysis: Fraction	Percent
+150	56.0
−150 + 170	4.0
−170 + 200	1.6
−200 + 250	0.8
−250 + 270	1.6
−270	36.0

Apparent density: 1.17 grams/cubic centimetre

200 grams of the composite powder were blended with 29.2 grams of the chromium powder of Example 1. The blend of powders was treated in accordance with the procedure of Example 1 with the exception that the furnace was operated at 1900°F. and the blend was heated for 38 hours.

Qualitative microanalysis and ferro-magnetic comparison in accordance with Example 1 showed that the desired alloying of chromium and nickel was achieved.

EXAMPLE 5

This Example illustrates preparation of cobalt-chromium alloy coated tungsten carbide powder.

Hydrometallurgically produced cobalt coated tungsten carbide composite powder containing 80% core material by weight was provided. The powder had the following physical characteristics:

TABLE VII

Buckbee Mears screen analysis (in microns): Fraction	Percent
+44	0.0
−44 + 30	7.0
−30 + 20	30.0
−20 + 10	43.0
−10 + 5	10.0
− 5	10.0

Apparent density: 4.54 grams/cubic centimetre
Fisher Number 12.7.

100 grams of the composite powder were blended with 5 grams of commercial grade, 8 micron size chromium powder using the procedure described in Example 1.

After blending, the powder was treated in accordance with the procedure of Example 1 with the exception that the heating was continued for 21.5 hours at 1900°F. The coating of the product powder was examined using electron microprobe analysis and relative ferro-magnetism. Comparison of the ferro-magnetic nature of the blend before heat treatment and after heat treatment indicated that the heat treated powder was substantially less magnetic indicating that the intimate mixture of chromium and cobalt in the coating was in fact a solid solution of chromium in cobalt.

EXAMPLE 6

This Example illustrates preparation of nickel-chromium coated calcium fluoride composite powder. The starting material for this example was nickel calcium fluoride composite powder containing 75% by weight nickel. The powder was prepared in accordance with U.S. Pat. No. 3,062,680 and had the following physical characteristics.

TABLE VIII

Standard Tyler screen analysis: Fraction	Percent
− 48 + 100	1.8
−100 + 150	9.3
−150 + 200	5.6
−200 + 250	18.0
−250 + 325	19.5
−325	45.8

Apparent density: 1.20 grams/cubic centimetre.

100 grams of the composite powder were blended with 19 grams of commercial grade, 8 micron size chromium powder. The powders were blended by manually shaking them together in a bottle.

After blending, the powder mixture was heat treated as in Example 1 except that heating was continued in the hot zone of the furnace for 16 hours.

The powder was removed from the furnace and was observed to be in the form of a sinter cake. The cake was easily broken into pieces and was pulverized in a high speed blender to yield a finely divided powder substantially 100% - 100 mesh in size.

The coating of the product powder was examined for alloying and relative ferro-magnetism and was found to be comprised of a uniform alloy of nickel and chromium.

Conventional metallographic examination of a polished section of powder particles showed that the individual particles consisted of a core and a uniform metallic coating.

Comparison of the ferro-magnetic nature of the blend before and after heat treatment indicated that the heat-treated powder was non-magnetic. Thus the intimate mixture of chromium and nickel in the coating was in fact a solid solution of chromium in nickel.

EXAMPLE 7

This Example illustrates the preparation of a composite powder composed of a diatomaceous earth core with a ternary alloy. The elements making up the ternary alloy are nickel, chromium and aluminum.

A composite powder having a diatomaceous earth core encased in a nickel-aluminum coating was used as the starting material. The composite powder was prepared in accordance with the procedure described in Example 2 except that the temperature within the furnace was 1200°F. and the heat treatment was continued for 1½ hours. Following the heat treatment, the nickel-aluminum coated diatomaceous earth particles were removed from the furnace and placed in a high speed blender to break the particles down into a finely divided powder. 100 grams of the powder was blended with 16 grams of commercial grade 8 micron size chromium powder and heat treated in the manner described in Example 1 except that the temperature within the furnace was maintained at 1800°F. and the heat treatment was continued for 16 hours. The heat treated particles were broken down as above to yield a composite powder composed of a diatomaceous earth core coated with a nickel-chromium-aluminum alloy.

The effect of the above described treatment on the magnetic properties are set out in the following table.

TABLE IX

Material	Ferromagnetism (Iron 100%)
Pure Nickel reference	31.5 %
Blend of Nickel coated Diatomaceous earth plus aluminum:	
Before heat treatment	22.8 %
After heat treatment	7.7 %
Blend of Diatomaceous earth core coated with nickel aluminum alloy plus chromium:	
Before heat treatment	7.6 %
After heat treatment	.01%

The negligible ferro-magnetism of the heat treated blend of chromium and the composite powder composed of a diatomaceous earth core and a nickel alumi-

num alloy coating indicates the virtually complete formation of the ternary alloy around the diatomaceous earth core particles.

EXAMPLE 8

This Example illustrates the improvement in the rate of transfer of the alloying metal into the coating of the composite powder caused by the addition of a vaporizable halide prior to heat treatment. In the first test, hydrated chromium chloride was blended with a mixture of chromium and composite powder. In each case, the resulting mixture contained approximately 81.8% by weight composite powder, 16.2% by weight chromium and 2.0% by weight hydrated chromium chloride. The mixtures were heat treated at various temperatures and for varying lengths of time in purified hydrogen. The degree of alloying as well as the relative ferromagnetism were determined according to the procedures outlined in Example 1. The results are summarized in the following table X.

TABLE X

Temperature °F	Powder Chromium Additive Time hr	75 Nickel/Graphite 25 Coarse Cr (40 microns) $CrCl_3$ % Cr/relative Ferromagnetism	75 Nickel/Graphite 25 Coarse Cr (40 microns) Nil % Cr/ rel. fer.	75 Nickel/Graphite 25 Medium Cr (8 microns) $CrCl_3$ % Cr/ rel. fer.	75 Nickel/Graphite 25 Medium Cr (8 microns) Nil % Cr/ rel. fer.	82 Nickel/Diatomaceous earth 8 Coarse Cr (40 microns) $CrCl_3$ % Cr/ rel. fer.	82 Nickel/Diatomaceous earth 8 Coarse Cr (40 microns) Nil % Cr/ rel. fer.
1800	20	10.9/ 3.81	3 /10.6	15 /10.0	4.5/10.7		
	4	9.5/ 2.76	3 /14.4	7.4/ 3.1	2.6/29.0		
	1	8.5/ 1.6 2.3	2.6/15	8.5/ 1.3 1.2	2.8/31	16.1/ 0.51	
	0.5	10.0/ 1.80	2.6/24.7	7.0/ 1.60	1 /28.3		
1650	0.5	7 / 5.50	1 /35.0	9 / 2.60	0 /33.6		
1500	18	4.5/ 7.30		10.9/ 0.87			
	16					12.2/ 1.17	1.6/32.3
	2	5 /10.10		7 / 2.96		13.6/ 0.61	0.0/34.9
	1.25	6.2/ 5.14		7 / 4.70			
	0.5	5.4/ 8.13	1 /30.4	5.4/ 8.60	0.6/35.5		
1300	64	2.4/11.3		2.0/26.0		5.0/ 2.2	
	4	0.0/14.5		1.5/11.5		/ 5.1	
	2	2.4/19.0		1.5/11.48			
	0.5	6.2/19.6		12.8/15.8		12.2/10.0	
0	0	n.d./34.7	n.d./35.0	n.d./35.0	n.d./36.3	n.d./38	

It is apparent from the results tabulated above that in every case the addition of chromium chloride dramatically increases the diffusion rate of chromium in the nickel coating of the composite powder. Substantial diffusion at temperatures as low as 1300°F. occurs. Further tests establish that the time required to achieve a given amount of alloying in a sample containing $CrCl_3$ and heat treated at the same temperature is significantly less than for a sample containing no $CrCl_3$ and heat treated at the same temperature.

The effect of the presence of ammonium chloride on the diffusion rate of the alloying metal in the coating of composite powder was also treated. Deoxidized 75 nickel/graphite 25 composite powder was blended with chromium powder and ammonium chloride. The blend analyzed 82.5% by weight 75 Ni/C25, 16.3% by weight Cr and 1.2% NH_4Cl. The blend was heated for 30 minutes at 1800°F. then analyzed. About 10% of the chromium was alloyed with the nickel coating and the relative ferro-magnetism was 5.3%.

EXAMPLE 9

This example illustrates the preparation of nickel-chromium coated titanium carbide powder.

4500 grams of composite powder (NI 20.9%, TiC 79.1%) were blended with 225 grams of chromium powder having an average size of 8 microns and 11 grams of chromium chloride.

The powder mixture was placed in a nickel boat and positioned in the cooling zone of an electrically-heated laboratory tube furnace. The powder was purged with hydrogen for 30 minutes to remove entrapped oxygen. The hydrogen had been preheated by passing it through the hot zone of the furnace.

The boat was then moved to the hot zone of the furnace. This zone was maintained at 1900°F. Hydrogen was passed through the zone at 1½ cubic feet per minute. Heating was continued for 4 hours.

The boat was then returned to the cooling zone and left there for a period of 1 hour following which the boat was removed from the furnace. It was found that the powder was present in the form of a sinter cake.

The screen analysis of the product after light grinding in a mechanical blender was as follows:

TABLE XI

Powder Size in Microns Fraction	Percent
+44	7.1
−44 +30	25.0
−30 +20	40.0
−20 +10	18.6
−10 +5	7.4
−5	1.9

Apparent density: 1.86 grams/cubic centimetre

Qualitative microanalysis and ferro-magnetic comparison in accordance with Example 1 showed that the desired complete alloying of chromium and nickel had been achieved.

EXAMPLE 10

This example illustrates the preparation of nickel-chromium coated chromium carbide powder.

4770 grams of powder (Ni 16%, Cr_3C_2 84%) were blended with 258 grams of chromium powder (average size 8 microns) and 50 grams of $CrCl_3$. The blend of

powders were treated in acccordance with the procedure of Example 9.

The screen analysis of the product after light grinding in a mechanical blender was as follows:

Fraction screen analysis:

TABLE XII

Fraction	Percent
−200 +250	2.3
−250 +325	76.2
−325 +400	21.5

Apparent density: 2.78 grams/cubic centimetre

Qualitative microanalysis and ferro-magnetic comparison in accordance with Example 1 showed that the desired complete alloying of the aluminum and nickel had been achieved.

EXAMPLE 11

This example illustrates the preparation of nickel-chromium and nickel-chromium-aluminum coated tungsten-titanium carbide powders.

800 gms of Ni/$WTiC_2$ (15/85) were blended with 25 gms of fine chromium powder (average particle size about 8 microns) and 8 gms of $CrCl_3$ powder. The blend was placed in a covered boat and purged in the cold zone of a muffle furnace. The blend was purged with dry hydrogen for 30 min. Following this the blend was heated for 2½ hours at 1950°F. in a dry hydrogen atmosphere and then cooled to room temperature.

The blend was found to have sintered lightly, but was easily broken up into powder. Most of the powder passed through a 250 mesh screen and was found to be satisfactory for plasma spraying. An experimental plasma spray coating was found to have D.P.H. microhardness of 1290.

A sample of the nickel-chromium coated tungsten-titanium carbide powder was further treated to produce a more complex oxidation resistant composite powder.

400 gms of the NiCr/$WTiC_2$ powder was blended with 5 gms of fine leafing-grade aluminum. The blend was treated in a similar manner as above with the exception that the heating temperature was 1400°F. and the heating time was 1 hour.

The resultant powder was found to be satisfactory for plasma spraying. An experimental plasma spray coating of the NiCrAl/$WTiC_2$ powder had D.P.H. microhardness of 950.

EXAMPLE 12

This Example illustrates the marked effect which temperature has on the rate at which the alloying metal diffuses into and becomes alloyed with the coating material of the composite particles. The starting material was nickel-coated diatomaceous earth containing 88% nickel by weight. A powder mixture was prepared by blending the starting material with chromium powder (Fisher No. 14) to a composition of 4 parts Ni, 1 part Cr. Part of the mixture was blended with a magnesia parting agent to produce first and second samples, the first containing 10% MgO and the second containing 25% MgO (by weight). Third sample contained no parting agent. 1/2% by weight $CrCl_3$ activator was combined with each sample.

The samples were subjected to various heat treatments and the amount of chromium in the nickel coating was determined at various times during the treatments by following the shift in the 220 line according to the standard XRD technique. The accuracy of this technique is about ± 1%. The results are shown in FIGS. 1 and 2 of the drawing.

At 1500°F. in the sample containing no parting agent there is an initial fairly rapid increase in chromium level of the nickel coating followed by a more gradual increase followed thereafter by negligible or no increase in the chromium level. In samples containing parting agent there is a much less rapid increase in the chromium level of the nickel coating to only 2% followed by no increase even after 64 hours of heat treatment.

At 1830°F. the rate of chromizing without a parting agent is much more rapid than at 1500°F. Furthermore the level of chromium in the nickel coating in the absence of a parting agent increases with heating time and does not reach a maximum at the same point in time as does the chromium level in the sample heated at 1500°F.

Both at 1830°F. and at 1500°F. the rate of chromizing is greatly influenced by the level of parting agent in the sample. Not only is the chromizing rate greatly retarded by magnesia but the magnesia appears to impose a maximum level of chromium in the nickel coating.

EXAMPLE 13

This example illustrates the effect of heat treatment on various powder mixtures. Samples were prepared as follows:

1 - a blend of iron and chromium powders (80% Fe, 20% Cr) and 2% ammonium fluoride.
2 - a blend of nickel and chromium powders (80% Fe, 20% Cr) and 2% NH_4F.
3 - a blend of nickel and aluminum powders (67% Ni, 33% Al)
4 - the same as Sample 3 except that 10% by weight MgO was added to the blend
5 - a blend of nickel-coated diatomaceous earth composite particles, aluminum particles (67% Ni/De; 33% Al) and 1/2% $CrCl_3$.

The five samples were heated under the conditions specified below and the resulting products were examined for degrees of sintering. The extent of alloying was also checked in products which were not grossly sintered. The results are set out in the following table:

TABLE XIII

Sample	Heating Conditions	Condition of heated product
1. (Fe + Cr)	1650°F. for 20 minutes	grossly sintered
2. (Ni + Cr)	1650°F. for 20 minutes	grossly sintered
3. (Ni + Al)	1100°F. for 1 hour in presence of H_2	grossly sintered
4. (Ni + Al +MgO)	1100°F. for 1 hour in presence of H_2	no sintering; no alloying
5. (Ni/De + Al)	1100°F. for 1 hour in presence of H_2	no sintering; extensive alloying

The results show that when single component particles are mixed with chromium and aluminum particles and are heated to the lowest temperature recommended for chromizing and aluminizing according to the subject process, gross sintering occurs. Where a

parting agent (MgO) is added to the mixture containing aluminum particles, gross sintering does not take place but, on the other hand, aluminizing also does not occur. By contrast where a mixture of composite particles and aluminum are heated under the same conditions alloying occurs. The results of Example 12 show that the same is also true of chromium containing mixtures.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A process for producing powder particles having a central core coated with an alloy which comprises the steps of: providing finely divided particles of an alloying metal and composite particles of a size within the range of 10 to 850 microns, said alloying metal being chosen from the group consisting of chromium and a mixture of chromium and aluminum, each said composite particle having a central core coated with a layer of material which is metallic, which is different from the material of the core and which is capable of alloying with said alloying metal when a mixture of said compositve particles and said alloying metal particles is heated; forming a powder mixture which consists of said composite particles and said alloying metal particles; and heating said powder mixture under non-oxidizing conditions at a temperature of from about 1650°F to about 2300°F; and continuing said heating step for a period of time sufficient to ensure that a required quantity of said alloying metal diffuses into and alloys with the metal coating of the composite particles without gross sintering taking place.

2. The process defined in claim **1** including the additional step of mixing the alloy coated particle with a second alloying metal and heating the resulting mixture under non-oxidizing conditions at a temperature and for a period sufficient to ensure that said second alloying metal forms an alloy with the alloy coating of the composite particles without gross sintering taking place.

3. The process defined in claim **1** wherein the particles of alloying metal are less than 50 microns in size.

4. The process as defined in claim **1** wherein the product from the heating step is comminuted to powder form.

5. The process defined in claim **1** wherein the metal coated on said central core is chosen from the group consisting of nickel, cobalt and copper.

6. The process as claimed in claim **1** wherein the heating step is carried out at a temperature above about 1830°F.

7. The process defined in claim **1** wherein the central core is chosen from the group consisting of graphite, calcium fluoride, diatomaceous earth, aluminum oxide, tungsten carbide, titanium carbide, tungsten-titanium carbide, chromium carbide and chromium oxide.

8. The process as defined in claim **7** wherein the metal coated on said central core is nickel.

9. The process defined in claim **8** wherein the core is diatomaceous earth and the heating step is carried out at a temperature between 1650°F. and 1900°F.

10. A process for producing powder particles having a central core coated with an alloy which comprises the steps of: providing finely divided particles of an alloying metal consisting of aluminum and composite particles of a size within the range of 10 to 850 microns, each said composite particle having a central core coated with a layer of material which is metallic, which is different from the material of the core and which is capable of alloying with said alloying metal when a mixture of said composite particles and said alloying metal particles is heated; forming a powder mixture which consists of said composite particles and said alloying metal particles; and heating said powder mixture under non-oxidizing conditions at a temperature of from about 1100°F to about 1220°F; and continuing said heating step for a period of time sufficient to ensure that a required quantity of said alloying metal diffuses into and alloys with the metal coating of the composite particles without gross sintering taking place.

11. The process defined in claim **10** including the additional step of mixing the alloy coated particle with a second alloying metal and heating the resulting mixture under non-oxidizing conditions at a temperature and for a period sufficient to ensure that said second alloying metal forms an alloy with the alloy coating of the composite particles without gross sintering taking place.

12. A process for producing powder particles having a central core coated with an alloy which comprises the steps of: providing finely divided particles of an alloying metal and composite particles of a size within the range of 10 to 850 microns, said alloying metal being chosen from the group consisting of chromium and a mixture of chromium and aluminum, each said composite particle having a central core coated with a layer of material which is metallic, which is different from the material of the core and which is capable of alloying with said alloying metal when a mixture of said composite particles and said alloying metal particles is heated; forming a powder mixture which consists of said composite particles, a halogen-bearing compound and said alloying metal particles; and heating said powder mixture under non-oxidizing conditions at a temperature of from about 1650°F to about 2300°F; and continuing said heating step for a period of time sufficient to ensure that a required quantity of said alloying metal diffuses into and alloys with the metal coating of the composite particles without gross sintering taking place.

13. A process for producing powder particles having a central core coated with an alloy which comprises the steps of: providing finely divided particles of an alloying metal consisting of aluminum and composite powder particles of a size within the range of 10 to 850 microns, each said composite particle having a central core coated with a layer of material which is metallic, which is different from the material of the core and which is capable of alloying with said alloying metal when a mixture of said composite particles and said alloying metal particles is heated; forming a powder mixture which consists of said composite particles, a halogen-bearing compound and said alloying metal particles; and heating said powder mixture under non-oxidizing conditions at a temperature of from about 1100°F to about 1220°F; and continuing said heating step for a period of time sufficient to ensure that a required quantity of said alloying metal diffuses into and alloys with the metal coating of the composite particles without gross sintering taking place.

14. A powder composition comprising non-grossly sintered particles within the size range of 10–850 microns and each consisting essentially of single central core chosen from the group consisting of diatomaceous earth, graphite and calcium fluoride, a continuous coating firmly bonded to the core, said coating com-

prising an alloy in the form of a solid solution of at least two constituents, one constituent being chosen from the group consisting of chromium and aluminum.

15. The powder composition defined in claim **14** wherein said alloy is in the form of a solid solution of chromium, aluminum and another constituent.

16. The powder composition defined in claim **14** wherein said alloy is in the form of a solid solution composed of nickel and chromium.

17. The powder composition defined in claim **14** wherein said alloy is in the form of a solid solution composed of nickel and aluminum.

18. The powder composition defined in claim **14** wherein said alloy is in the form of a solid solution composed of nickel, chromium and aluminum.

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