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Kizer

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[54] **PROCESS FOR MAKING SINTERED ARTICLES**

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[51] **Int. Cl.** **B22f 1/00**
[58] **Field of Search** 75/212

[56] **References Cited**

UNITED STATES PATENTS

3,223,523 12/1965 Adler 75/212

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[57] **ABSTRACT**

A process for making sintered articles from powdered particles of high-temperature nickel-base or cobalt-base alloys which contain from 3.0 to 30.0 weight percent of refractory elements having a melting point at least 450°C. above that of the base metal, the particles being characterized by a concentration at their surface of refractory elements or intermetallic compounds which constitutes a barrier to the diffusion of alloying elements, which process comprises coating said particles with a thin layer of a diffusion-promoting metal which is a constituent of the alloy to be sintered and is selected from the group consisting of cobalt, nickel, titanium, zirconium, iron, and vanadium, the quantity of said diffusion-promoting metal being insufficient to materially change the composition and properties of the alloy to be sintered, compacting the particles into an article of the desired shape, and sintering the compacted article in a non-reactive environment at normal sintering temperatures.

10 Claims, 2 Drawing Figures

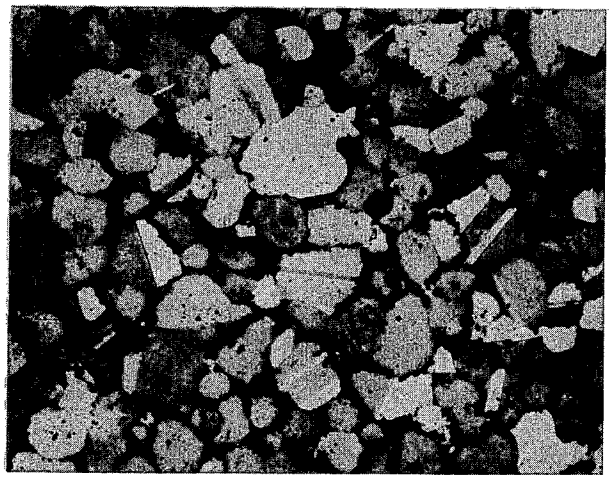


FIG. 1

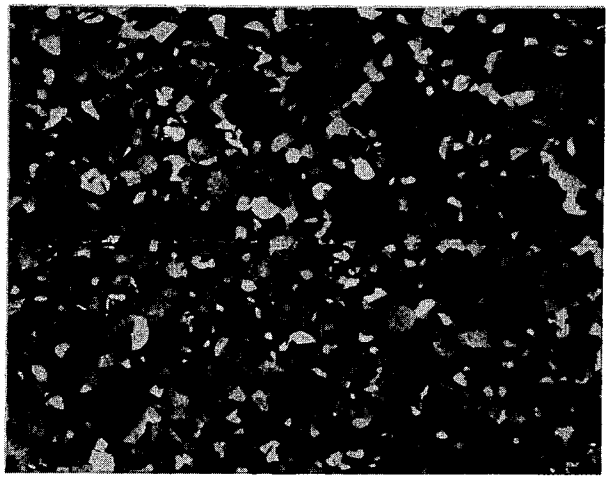


FIG. 2

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PROCESS FOR MAKING SINTERED ARTICLES

BACKGROUND OF THE INVENTION

This invention relates to processes for making sintered articles from metal powders and more particularly to processes for making sintered articles from pre-alloyed powders which contain significant amounts of refractory metal alloying elements or intermetallic compounds.

Advances in the art of powder metallurgy have made possible the manufacture of high quality sintered articles from a wide variety of metals and alloys. According to wellknown conventional techniques, finely divided metal particles are first compacted under pressure into a body of the desired shape and the body is then sintered to bond the particles and densify the structure. This process has been applied with little or no difficulty to particles of the more common metals and to binary or ternary alloys which have alloying elements with melting points which do not differ significantly from those of the base metals. However, when the process is applied to more complex alloys, and especially those containing elements with widely differing melting points, the quality of the resulting products is significantly decreased.

One method of producing sintered alloy articles is to start with powders of the individual metals of the alloy and to form a uniform mixture of such powders. The mixture is then compacted into shape and sintered to produce the desired article. This process has been used successfully to produce articles of certain nickel-base and cobalt-base alloys which contain high melting point elements. The quality of such sintered alloys has been found to be comparable to that of cast material but only when very fine (below 10 microns) virgin metal powders are used and when sintering is done within specified temperature ranges and in a vacuum. In spite of the success of this process, articles produced in a similar manner from compacts of fused alloy powders (pre-alloyed powders) were inferior in quality and did not match the properties of the articles made from individual metal powders.

It is believed that the difficulties encountered in sintering pre-alloyed powders of nickel-base and cobalt-base alloys containing elements with widely differing melting points are mainly due to concentrations of refractory alloying elements or intermetallic compounds at the surface of the powder particles. The problem is aggravated in certain alloy structures by additional concentrations of carbides at the surface. It is believed that sintering of the pre-alloyed powders is impeded when the concentration of these refractory elements at the particle surfaces is sufficient to constitute a substantially continuous barrier to the diffusion of lower melting point elements. When such barriers are present the refractory materials constituting the barriers will not diffuse into the metal structure. Such substantially continuous barriers are generally present due to either the "coring" phenomenon or to the alloy composition.

Coring is generally the result of the process used in manufacture of the pre-alloyed powders. One such method involves atomization of molten metal in a stream of gas, liquid, or mixture of gases and liquids. The atomized molten droplets solidify rapidly with the solidification proceeding from the outside toward the center of the particles. As a result, when this process is used in the manufacture of certain high-temperature

alloy powders, especially nickel-base and cobalt-base superalloy powders containing significant amounts of refractory metal elements such as molybdenum, the high melting point (refractory) phases or elements segregate out of solution and become concentrated at the surface of the particle during solidification. Generally, the more rapidly the particles are cooled, the greater the concentration gradient resulting from such segregation. The resulting inhomogeneous structure is the product of the phenomenon called "coring" which occurs in the absence of sufficient time for diffusion of elements within the solidifying particles.

In addition to gas atomization, coring also occurs in other methods by which metal powders are produced directly from molten alloy, including those methods which employ spinning discs or rotating electrodes. Coring is an inevitable result of the mechanism of rapid freezing in solid-solution systems. Coring does not present any significant problem in alloy systems which do not contain elements having widely differing melting points or which contain only very small percentages of such elements. Nor is there a problem in alloy systems which do not form high melting point phases such as intermetallic compounds. However, when the amount of alloying elements having melting points significantly higher than the other elements in an alloy system exceeds about 3.0 percent, coring will significantly affect subsequent densification and sintering of the pre-alloyed powders. Thus, conventional molten metal processes used in the manufacture of powder particles (which are generally more efficient and produce a more uniform product), cannot be used effectively in the production of many high-temperature alloy powders.

Powder particles of certain complex alloys which contain unusually large amounts of high-melting point elements, usually in excess of 10 percent, will have significant concentrations of high melting point elements at their surfaces by virtue of their composition, regardless of whether coring has occurred during particle formation. These powders are also very difficult to fabricate into fully dense articles.

Pre-alloyed powder particles having an inhomogeneous structure as a result of the coring phenomenon are difficult, and in some cases impossible, to facilitate into useful articles by known powder metallurgy techniques. Significant concentrations of refractory elements or intermetallic compounds at the outer surface of the particles do not permit sufficient metal-to-metal bonding between particles either during green pressing (compaction of particles into the desired shape prior to sintering) or during sintering at normal sintering temperatures and times. In addition, powder particles produced by the gas atomization process are generally spherical in shape and such shapes are inherently difficult to green compact by conventional techniques.

In many cases stable oxides or other contaminants will form on the particle surfaces and when combined with the refractory elements at the surface they form a substantially impervious barrier which prevents cohesion of the particles during green pressing, even at high pressures. The resulting green pressed bodies are crumbly and unmanageable. It has in the past been necessary to add an organic binder material to such powdered particles before green pressing in order to produce a cohesive body for further processing. The addition of binders is generally disadvantageous because they must

be removed by heating the article prior to sintering and this increases production time. Also, binders may leave residual contamination such as carbon and oxygen within the sintered article. Such residual contamination generally will adversely affect the mechanical properties of the sintered article.

It is known in the art that the green pressed properties of certain metal powders, such as stainless steel powders, can be improved by coating the particles with a softer and more readily compressible metal such as nickel. However, sintering compacts of coated stainless steel particles has not been shown to produce any significant increase in density and no grain growth has been reported (see U.S. Pat. No. 3,223,523). Also, stainless steels do not contain significant quantities of refractory metal additions and most contain little or no intermetallic compounds at ordinary temperatures and therefore sintering of stainless steel compacts is considerably less difficult than sintering most high temperature complex alloys of nickel and cobalt.

The presence of significant concentrations of refractory elements, phases, or compounds at the surface of high-temperature alloy particles will generally retard sintering and inhibit grain growth, especially where stable oxides have also formed on the particle surfaces. The resulting sintered articles have low strength brittle bonds between particles. Although many attempts have been made to densify and sinter pre-alloyed powders of high-temperature alloys, especially nickel- and cobalt-base superalloys which have significant concentrations of refractory elements or phases at the particle surfaces, there has been little or no success in producing fully dense articles. In many cases the final product has a density of less than 60 percent of theoretical and exhibits little or no grain growth.

I have found that coating pre-alloyed particles of high-temperature nickel-base or cobalt-base alloys having significant concentrations of high melting point elements, phases, or compounds at the particle surfaces with a thin layer of a diffusion-promoting metal such as nickel will significantly enhance the densification and sintering of the particles and, in addition, provide unexpected grain growth during sintering which is desirable for maximizing resistance to high temperature creep. To the best of my knowledge such densification accompanied by grain growth has not been achieved with previous processes. Articles having substantially 100 percent of theoretical density have been produced from powders which exhibit coring by means of the present invention using normal sintering times and temperatures. In addition, the diffusion-promoting metal coatings employed are soft, ductile, and readily cold weld to themselves. This generally eliminates the need for a binder in green pressing and lowers the pressures required for green pressing.

SUMMARY OF THE INVENTION

A process for making a sintered article from powdered particles of a high-temperature nickel-base or cobalt-base alloy which contains from about 3.0 to about 30.0 weight percent of at least one refractory metal alloying element having a melting point at least 450° C. above the melting point of the base metal, the particles being characterized by a concentration at their surface of at least one of the group consisting of refractory alloying elements and intermetallic compounds, the concentration constituting a substantially continuous barrier to the diffusion of alloying elements, which process comprises coating the particles with a thin layer of a diffusion-promoting metal which is a constituent of the alloy to be sintered and is selected from the group consisting of cobalt, nickel, titanium, zirconium, iron, and vanadium, the quantity of the diffusion-promoting metal being insufficient to materially change the composition and properties of the alloy to be sintered, compacting the particles into an article of the desired shape, and sintering the compacted article in a non-reactive environment at normal sintering temperatures. The article is typically heated further to homogenize the structure. The particles are preferably coated with from about 0.25 to 5.0 weight percent of the diffusion promoting metal by either chemical vapor deposition during particle formation or thermal decomposition of a compound in a fluidized bed.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a photomicrograph (100X) of a cross-section of a sintered article made from B-1900 alloy powder having a thin coating of nickel.

FIG. 2 is a photomicrograph (100X) of a cross-section of a sintered article made from uncoated B-1900 alloy powder.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of the present invention allows production of fully dense, bonded articles from pre-alloyed powdered particles of high-temperature nickel-base or cobalt-base alloys. This invention is only concerned with prealloyed powders which have significant concentrations of high melting point elements, phases, or compounds at their surfaces such that the powders do not readily green press into a cohesive body and diffusion during sintering is inhibited.

High-temperature nickel-base and cobalt-base alloys are generally complex alloys containing more than three elements. The alloys of concern for purposes of this invention are typically complex alloys which contain from about 3.0 to about 30.0 percent of refractory metal alloying elements which have melting points significantly higher than those of the base metal. The most common refractory metal alloying elements are tungsten, molybdenum, niobium, tantalum, hafnium, ruthenium, and rhodium. The alloy may contain 3.0 or more percent of any one of the refractory elements or it may contain a total of 3.0 or more percent of a combination of several of the elements, either individually or in compound form. Where the quantity of refractory metals in the alloy exceeds about 3.0 percent (the exact percentage will vary somewhat from alloy to alloy), the coring phenomenon which occurs when powder particles are produced by molten metal production processes will effect a sufficiently high concentration of refractory metals at or near the particle surface to provide a substantially impervious barrier or shell which envelops the particle. This barrier inhibits diffusion of alloying elements, especially the lower melting point elements, during sintering and therefore impedes the formation of metal-to-metal bonds between particles. The high melting point elements remain fixed in the barrier and do not diffuse into the structure. Powders of certain alloys which contain relatively large amounts of refractory metal additions, usually in excess of 10.0 percent, have significant concentrations of those ele-

ments at their surfaces by virtue of the alloy composition, regardless of the method of manufacture. Alloys containing more than about 30.0 percent refractory metal additions would generally not be classified as nickel-base or cobalt-base alloys.

The high-temperature nickel-base and cobalt-base alloys of concern generally include as alloying additions intermetallic compound forming elements. For example, many nickel-base superalloys contain aluminum which forms intermetallic compounds of the NiAl type such as Ni_3Al. These compounds are refractory in nature and are very stable at ordinary sintering temperatures of the alloy. Such compounds, like the refractory metals, segregate to the surface of the powder particles by the coring phenomenon and due to their refractory nature inhibit diffusion of the lower melting point phases or elements at normal alloy sintering temperatures. If densification can be accomplished by techniques such as hot pressing, the resultant structure has an undesirable distribution of the intermetallic compound strengthening phase.

Many of the complex nickel-base and cobalt-base alloys also contain carbon which often is added to form carbide strengtheners such as $Cr_{23}C_6$ (for nickel-base alloys). These carbides are also stable and are preferably uniformly dispersed throughout the metal microstructure. In forming pre-alloyed powders from the melt, both the intermetallic compounds and the carbides (and in some cases borides and nitrides also) will become concentrated at the particle surfaces by means of the coring phenomenom and will effectively prevent diffusion of the lower melting point elements. When cored particles containing carbide strengtheners are formed into compacts, the result is an undesirable distribution of strengtheners in the structures.

The present invention allows pre-alloyed powders which previously could not be effectively sintered to be sintered to essentially full density. Examples of alloys which may be sintered according to the invention include nickel-base superalloys such as B-1900, IN 100, M-252, Rene 41, Udimet 500, Udimet 700, Waspaloy, and Unitemp 1753, and cobalt-base superalloys such as S-816, WI-52, HS 31, HS 151, J-1570, and J-1650. The powder particles are preferably no larger than U.S. standard mesh No. 100 in size because it is believed that larger particles would core more severely and as a result diffusion distances would be increased significantly making the process undesirable economically.

In the process of this invention the powder particles are first coated with a thin layer of a diffusion-promoting metal. The diffusion-promoting metal is preferably a soft, ductile, metal which readily cold welds to itself such that bonding between the particles is improved and increased which in turn provides increased green strength and improved sinterability. I have found that in order to sinter powder compacts of high temperature alloys having significant concentrations high melting point elements at the particle surfaces, the diffusion-promoting coating metal must be capable of initiating localized diffusion around and between the particle surfaces (sometimes called surface diffusion). In order to promote this type of diffusion, the diffusion-promoting metal must have a lower melting point than the refractory phases at the surfaces and it must have a high solubility for those refractory phases. It must also have a relatively high diffusivity compared to the alloy and must not be readily embrittled or hardened by alloying. The diffusion-promoting metal serves as an agent or vehicle for moving the refractory elements and facilitates neck growth between particles—allowing the mechanisms of sintering to occur. It is also preferable that the coating metal be one which does not readily form stable oxides at its surface.

The following metals are suitable for coating powder particles according to this invention: cobalt, nickel, titanium, zirconium, iron, or vanadium. It is preferred that the metal used also be a constituent of the alloy to be sintered and that the amount used not materially change the composition or properties of the alloy. In some cases it may be necessary to prepare the pre-alloyed powder with less than the required amount of alloying addition of the diffusion-promoting metal as the balance will be supplied by the metal coating.

The particles are preferably coated with from about 0.25 to 5.0 weight percent of the diffusion-promoting metal. In most cases when amounts less than 0.25 percent are used the coating metal does not promote bonding or diffusion to any significant extent. However, this depends to a large extent on the coating metal used and the alloy being coated and in some cases less than 0.25 percent may be adequate. When amounts greater than 5.0 percent are used the coating metal may not diffuse sufficiently into the metal during sintering and will affect the alloy composition to some extent in addition to being uneconomical.

The diffusion-promoting metal coatings may be applied by thermal decomposition of a compound, by chemical vapor deposition in a fluidized bed, by sputtering techniques, by vacuum evaporation of the coating material and subsequent deposition directly on the powder, or by mechanical coating techniques such as ball milling or planetary milling of the hard alloy powders with the soft diffusion-promoting metal. Of these processes, thermal decomposition and chemical vapor deposition may be employed concurrently with the production of alloy powders by the gas atomization process. The gaseous components required for chemical vapor deposition or decomposition can be added to the powder production atmosphere and when the molten particles have cooled to the temperature required the desired deposition reaction will occur. For example, a nickel coating can be readily applied by adding $(NiCO)_4$ (g) to the powder production atmosphere. Upon cooling of the molten particles, the $(NiCO)_4$ (g) will be thermally decomposed to solid nickel and CO gas. As another example, titanium can be deposited by adding $TiCl_4$ and hydrogen to the atomization atmosphere. Many other similar methods can be used for coating the particles during production. Coating the particles during production avoids the necessity of removing any oxide or nitride films which may form at the particle surfaces prior to coating.

After coating, the powder particles are compacted or green pressed into an article of the desired shape. The compacting may be done using conventional methods such as die pressing, or by hydrostatic or isostatic pressing techniques. The coated particles readily green press into manageable, cohesive articles or preforms at pressures as low as 40,000 psi. Uncoated complex alloy particles generally will not form cohesive bodies even when green pressed at pressures as high as 100,000 psi.

The compacted article is then sintered in a non-reactive environment at normal sintering temperatures and times. Normal sintering temperatures are consid-

ered to be about three-fourths to seven-eighths of the solidus temperature of the alloy. Sintering times of less than 10 hours should be adequate for full densification of most alloys. To define a specific sintering schedule applicable to all current or potential alloys is impossible as is setting a firm sintering schedule for a specific alloy which would be suitable for all available powder sizes and all diffusion-promoting metal coatings due to the complex interacting mechanisms involved in sintering.

Further, the diffusion-promoting metal coating accelerates one or more sintering mechanisms in relation to other mechanisms involved, i.e., accelerates the surface diffusion mechanism to vaporization concentration of creep mechanism. Selecting a suitable sintering schedule is complicated by the fact that the various sintering mechanisms become operable at different temperatures and their rates vary as the temperature changes. To establish a suitable sintering schedule for an alloy with a particular diffusion-promoting metal coating it is recommended that green pellets be sintered at incremental temperatures covering the range of three-fourths of the alloy melting temperature to the reported solidus temperature. It is judged that sintering times of less than four hours will be sufficient for full densification of most alloys at the appropriate sintering temperature. Slow heating or an intermediate hold at a temperature below the final sintering temperature may be desirable to completely avoid or minimize incipient melting during sintering. Incipient melting may be detrimental to the properties of the sintered product by causing excess segregation of the alloy or by resulting in the formation of porosity at incipient melting sites due to solidification shrinkage. After establishment of the sintering schedule it may be desirable, depending on the alloy, to heat treat to further homogenize and transform the structure to achieve the desired mechanical properties.

The following example illustrates the invention with respect to producing a fully dense article from B-1900 alloy powder. B-1900 alloy is a complex nickel-base super-alloy having the following nominal composition (percentages are weight percent): 0.1 percent carbon, 8 percent chromium, 10 percent cobalt, 6 percent molybdenum, 1 percent tianium, 6 percent aluminum, 0.015 percent boron, up to 0.35 percent iron, 0.08 percent zirconium, up to 0.20 percent manganese, up to 0.015 percent sulfur, up to 0.25 percent silicon, up to 0.10 percent tungsten, up to 0.10 percent niobium, 4.25 percent tantalum, and the balance nickel.

Minus 100 plus 200 mesh (United States Standard mesh) particles of B-1900 alloy were produced by gas atomization of the molten alloy. The particles were coated with 2.9 weight percent nickel by thermal decomposition of $(NiCO)_4$ in a fluidized bed. The coated particles were die pressed at 40,000 psi into 1.0 inch diameter by 0.5 inch long cylindrical specimens. Uncoated B-1900 alloy particles of the same size could not be successfully die pressed into cohesive pellets even with pressures as high as 100,000 psi. It was necessary to add 1.0 weight percent of parawax as a binder before the uncoated particles could be green pressed into a cohesive pellet. The density of the specimens after green pressing was approximately 55 percent of theoretical.

Both specimens were vacuum sintered for 1 hour at 2,250° F. plus one hour at 2,300° F. As shown by FIG. 1, the nickel coated powder specimen sintered to essentially full density (99.6 percent of theoretical) and, in addition, the structure had an unexpectedly large grain size of 4.4 ASTM. LIttle or no densification occurred in the uncoated powder specimen as shown in FIG. 2 and no noticeable grain growth resulted. The uncoated particles had a grain size of 12 ASTM after sintering.

Subsequent sintering of identical specimens of coated B-1900 alloy powders resulted in densities measured at 99.7 and 99.8 percent of theoretical. Grain sizes in these specimens were 3.9 and 3.5 ASTM, respectively. Improved homogeneity of the sintered specimen was achieved by further heating the specimen in an argon atmosphere for 16 hours at 2,275° F. plus 8 hours at 2,330° F.

The homogenized structure exhibited improved corrosion resistance. This sintered material exhibited a weight gain of only 24.6 mg/cm² during 100 minutes at 1,832° F. in oxygen while cast material exhibited a weight gain of 28.7 mg/cm².

The process of the present invention allows production of fully dense sintered articles from complex, high-temperature nickel-base and cobalt-base alloy powders that could not previously be fabricated by powder metallurgy techniques. It allows molten metal powder production methods to be used in production of prealloyed powders of these alloys without concern for the problem of coring. It also makes possible the use in powder metallurgy production processes of new alloys containing greater amounts of high melting point elements and of intermetallic compound forming elements. The process will have many applications in production of components for jet or rocket engines, turbines, and other areas where high-temperature, high-strength metals are needed.

It will be understood, of course, that while the forms of the invention herein shown and described constitute preferred embodiments of the invention, it is not intended to illustrate all possible forms of the invention. It will also be understood that the words used are words of description rather than of limitation and that various changes may be made without departing from the spirit and scope of the invention herein disclosed.

What is claimed is:

1. A process for making a sintered article from powdered particles of a high-temperature alloy selected from the group consisting of nickel-base and cobalt-base alloys, said alloy containing from about 3.0 to about 30.0 weight percent of at least one refractory metal alloying element having a melting point at least 450° C. above the melting point of the base metal, said particles being characterized by a concentration at their surface of at least one of the group consisting of refractory alloying elements and intermetallic compounds, said concentrations constituting a substantially continuous barrier to the diffusion of alloying elements, which comprises:

a. coating said particles with a thin layer of a diffusion-promoting metal which is a constituent of the alloy to be sintered and is selected from the group consisting of cobalt, nickel, titanium, zirconium, iron, and vanadium, the quantity of said diffusion-promoting metal being insufficient to materially change the composition and properties of the alloy to be sintered;

b. compacting said particles into an article of the desired shape; and

c. sintering the compacted article in a non-reactive environment at normal sintering temperatures.

2. The process of claim **1** including the step of further heating the sintered article to homogenize the structure.

3. The process of claim **1** wherein said refractory alloying element is selected from the group consisting of tungsten, molybdenum, niobium, tantalum, hafnium, ruthenium, and rhodium, and combinations thereof.

4. The process of claim **1** wherein said particles are coated with from about 0.25 to 5.0 weight percent of said diffusion-promoting metal.

5. The process of claim **1** wherein said particles are produced by atomization of a molten metal stream and wherein said particles are coated with said diffusion-promoting metal during cooling of the particles.

6. The process of claim **5** wherein said particles are coated by chemical vapor deposition.

7. The process of claim **1** wherein said particles are coated by thermal decomposition of a compound in a fluidized bed.

8. The process of claim **1** wherein said particles are no longer than about United States Standard mesh No. 100.

9. The process of claim **1** wherein said complex alloy is consists essentially of 0.1 percent carbon, 8 percent chromium, 10 percent cobalt, 6 percent molybdenum, 1 percent titanium, 6 percent aluminum, 0.015 percent boron, up to 0.35 percent iron, 0.08 percent zirconium, up to 0.20 percent manganese, up to 0.015 percent sulfur, up to 0.25 percent silicon, up to 0.10 percent tungsten, up to 0.10 percent niobium, 4.25 percent tantalum, and the balance nickel.

10. The process of claim **9** wherein said diffusion-promoting metal is nickel.

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