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<p>(21) International Application Number: PCT/US82/01653 (22) International Filing Date: 22 November 1982 (22.11.82) (31) Priority Application Number: 325,416 (32) Priority Date: 27 November 1981 (27.11.81) (33) Priority Country: US (71) Applicant: GTE PRODUCTS CORPORATION [US/US]; One Stamford Forum, Stamford, CT 06904 (US). (72) Inventors: HOUCK, David, L. ; 3 Walnut Street, Towanda, PA 18848 (US). CHENEY, Richard, F. ; 50 Hemlock Road, Birchwood Apts., Sayre, PA 18840 (US). (74) Agent: WALTER, Robert, E.; 100 Endicott Street, Danvers, MA 01923 (US).</p>		<p>(81) Designated States: BE (European patent), DE (European patent), FR (European patent), GB (European patent), NL (European patent), SE (European patent). Published <i>With international search report.</i></p>
<p>(54) Title: NICKEL-CHROMIUM CARBIDE POWDER AND SINTERING METHOD</p> <p>(57) Abstract</p> <p>A powder which consists essentially of chromium and nickel with the balance being from 50 to 95 percent by weight chromium carbide, with the chromium and nickel being present in a weight ratio of about 1 part by weight chromium to 4 parts by weight nickel. Also, producing the powder by the process, of agglomerating a blend of the constituents and sintering the agglomerates in a high temperature reactor.</p>		

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NICKEL-CHROMIUM CARBIDE POWDER AND SINTERING METHOD

BACKGROUND OF INVENTION

This invention relates to a powder for thermal spray applications and a process to produce it.

5 These powders require various agglomeration methods to make free flowing powders from normally non-flowing small particles. One such agglomeration method is spray drying. Agglomerates are formed in spray drying by atomizing a slurry of powder, binder and liquid into a drying chamber where the liquid is evaporated. The result is a generally spherical agglomerate held together by the binder. U.S patent 3,617,358 describes an agglomeration process using an organic binder.

10 Other agglomeration processes have been developed to overcome what may be undesirable effects caused by the presence of organic binders. In some cases, the organic binder may cause fouling of the plasma gun due to vaporization of the organic. The presence of organics may even decrease the apparent density of the powder or affect the flame spray coating. In U.S. patent 15 3,881,911 to Cheney et al., the agglomerates are presintered to remove the binder. U.S. Patent 3,973,948 to Laferty et al. uses a water soluble ammonia complex as a binder and U.S patent 4,025,334 to Cheney et al. uses an aqueous nitrate solution.

SUMMARY OF INVENTION

Chromium carbide (Cr_3C_2) in combination with nickel-20% chromium powders are used to produce plasma-spray coatings for jet turbine engine applications.

30 These powders, as presently produced, are mechanical

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blends of the two components. As a result they have a tendency to become segregated both during shipment and during thermal spraying, yielding coatings which are not completely homogeneous. It is therefore desirable to have a powder which is comprised of particles each of which contains like amounts of both constituents.

In accordance with the present invention, there is provided an agglomerated powder which can be plasma densified to a thermal spray powder of a substantially uniform composition consisting essentially of nickel and chromium with the balance being about 50 to about 95 percent chromium carbide, said nickel and chromium being present in a weight ratio of about 1 part chromium to about 4 parts nickel. The chromium may be partially or completely combined with the nickel to form a nickel-chromium alloy.

DETAILED DESCRIPTION

For the thermal spray powders of the present invention, a powder blend is prepared consisting of 1 part chromium to 4 parts nickel with the balance chromium carbide. The amount of chromium carbide present may be varied from 50 to 95 percent. The nickel and chromium in the blend may be present as a mixture of elemental nickel powder and elemental chromium powder or as an alloy of nickel and chromium provided the ratio of chromium to nickel is about 1:4. Preferably the overall powder blend has an average particle size less than about 10 microns. The ratio of chromium to nickel is described in terms of the ratio of chromium to nickel excluding the chromium in the chromium carbide.

The powders are mixed by methods known in the art, such as by V-blending, tumbling or even by milling to obtain suitable particle sizes if size reduction is desired. The uniform powder blend is next agglomerated by methods known in the art. Such agglomeration tech-



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5 niques include forming powder compacts and subsequently crushing and screening them. However, agglomeration by spray drying is in general preferred for its flexibility and economy of operation on a production scale as well as its close control over the size of the agglomerated particles produced.

10 Conditions under which slurries are formed and spray dried are well known. For example, U.S. patent 3,617,358, issued November 2, 1971 describes formation of slurries. Other suitable methods for agglomerating are described in U.S. patents 3,881,911; 3,973,948 and 4,025,734, hereinafter discussed.

15 The agglomerates may be conveniently classified to obtain a desired particle size distribution. It is generally desired to have at least 80% of the particles within a 50 micron average particle size range.

20 The classified agglomerates are passed through a furnace at low temperatures to decompose the binders used for agglomeration and further treated at high temperatures to strengthen them for subsequent handling.

25 An alternative method for the incorporation of the nickel and chromium into the powder is through the binder used for the agglomeration. Conventional binders include such materials as waxes and polyvinyl alcohols. As previously mentioned, these materials decompose during heat treatment, and thus contribute nothing to the constitution of the powder. Alternative binders include soluble salts of nickel and chromium. These can be introduced into the slurry for spray drying. Upon 30 drying, these salts serve to bind the fine powders together to form agglomerates. When the agglomerates are passed through a high temperature furnace under a reducing atmosphere the binder decomposes to yield the desired quantity of nickel and chromium.

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The sintered agglomerates can be subsequently screened to yield a particle size distribution suitable for creating thermal sprayed coatings. Typically these distributions fall within two ranges, -200 +325 mesh or 5 -270 mesh. The coarser distribution powder typically contains 10% +200 and 10% -325 material. The finer distribution powder generally has a restriction on the percentage of ultra fine particles allowable, e.g. a maximum of 20% -20um.

10 Alternatively, the agglomerated and sintered particles can also be subsequently plasma densified so as to produce fine, spherical, densified particles. The densification process comprises entraining agglomerated powders in a carrier gas and feeding the entrained particles through a high-temperature reactor. The particles pass through the reactor at such a flow rate that interparticle contact and coalescence are avoided but that at least the outer surfaces of the particles are melted. After melting, the particles fall through a 20 distance sufficient to permit solidification and cooling prior to contact with a solid surface or each other. Because the particles are melted while entrained in a carrier gas, the solidified particles are substantially spherical, have smooth surfaces and thus excellent flow- 25 ability. In addition, the solidified particles have the same general size range as the starting material. However, depending on the porosity of the starting material, they may have a smaller mean particle size, due to densification during melting. Preferably the melting 30 during densification is to such an extent that each particle becomes prealloyed, i.e., the nickel and chromium alloy together and achieve intimate contact with the



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densified chromium carbide. Some solution of the constituents in one another may also take place. A major portion and preferably substantially all of the densified powder consists essentially of particles wherein each particle has a substantially uniform composition. The powder particles preferably have essentially the same composition so that the powder is uniform particle to particle.

The plasma densification is preferably carried out in a plasma flame reactor. Details of the principles and operation of such plasma flame reactors are well known. The temperature within the plasma flame can be adjusted between 10,000 F and 30,000 F. The temperature which the particles experience is a function of the rate at which they are fed through the reactor. Commercially available feeding devices allow rates between approximately 1/2 and 30 pounds per hour, depending on the bulk density of the material being fed. Conditions for plasma densification are established such that the particles reach a temperature at least above the melting point of the highest melting component and preferably below the vaporization point of the lowest vaporizing component.

The melted particles must be cooled at a rate sufficient to solidify at least an outer layer of the particles prior to their contact with a solid surface or with each other in order to maintain their sphericity and particle integrity. While any of several methods may be used to achieve this result, it has been found convenient to feed the melted particles into a liquid cooled chamber containing a gaseous atmosphere. The chamber may conveniently serve as a collection vessel.

After the powders have been plasma densified they can be classified to achieve the desired particle size distribution for use in thermal spray applications. Particle size distributions similar to those for the agglomerated and sintered particles are desired.

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Alternatively, the plasma densified powders can be crushed and classified to yield a powder with a finer particle size distribution, preferably one for which all the particles pass through a 270-mesh U.S. screen and at least 60 percent of the particles are less than 20 microns in average diameter. A typical particle size distribution has less than 10 percent of the particles below about 5 microns. The bulk density is from about 1.5 to about 3.0 grams/cc.

10 EXAMPLE 1

A sintered agglomerated powder is prepared by blending 80/20 nickel-chromium alloy powder, with a particle size less than approximately 10 micron with chromium carbide powder of the same particle size in amounts sufficient to result in a blend comprising 25% of the nickel-chromium alloy and 75% chromium carbide. A slurry is prepared by combining the resulting powder blend with polyvinyl alcohol in the ratio of 98:2 respectively, with enough water to make a 50-80% solids concentration. Spray drying is carried out by pumping the slurry at low pressure through a two fluid nozzle located at the top of a commercially available spray dryer. The slurry is continually agitated throughout the spray drying run. The atomization air pressure to the nozzle is 40-60 psi. The inlet air temperature is 370 C to 430 C with an outlet temperature of 140 to 150 C. The spray dried powder is slowly passed through a hydrogen furnace at 450 C to remove the organic binder. It is then fired for approximately 7 hours at 1000 C to strengthen the agglomerated particles. The resulting particles are screened to yield powders with a -200+325 or a -270+20 um particle size distribution. These particles can then be used as thermal spray powders.

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EXAMPLE 2

The agglomerated spray dried and sintered particles of Example 1 are fed through a commercially available plasma torch into a jacketed water cooled collection tank. A mixture of 126 cubic feet per hour of argon and 70 cubic feet per hour of hydrogen is fed to the plasma torch. The torch power is about 28KVA. Nitrogen gas is fed to a powder feeder at the rate of 7 cubic feet per hour to entrain the powder which is fed through the torch. The powder produced is then screened as in Example 1. Analysis of the -270 powder indicated 15%-15 um particles. These prealloyed powder particles can then be used as a thermal spray powder.

EXAMPLE 3

A plasma densified spray powder as produced in Example 2 is comminuted and air classified to produce a powder having the following distribution: 60-90% less than 20 um and no more than 15% less than 5 microns.

EXAMPLE 4

A sintered agglomerate is prepared according to the process described in Example 1 by substituting nickel powder and chromium powder in the ratio of 4 to 1 for the 80/20 nickel-chromium alloy. Similar results are obtained.

EXAMPLE 5

The sintered agglomerate powder of Example 4 is plasma densified according to the process as set forth in Example 2. The results were similar.

EXAMPLE 6

The densified plasma spray powder of Example 5 is comminuted and classified as in Example 3 with similar results.

EXAMPLE 7

A sintered agglomerate is prepared according to the process described in Example 1 by substituting nickel acetate and chromic acetate or nickel nitrate and chro-

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mic nitrate for the nickel-chromium alloy. The quantity of these salts is chosen such that upon decomposition they yield the proper ratios of nickel to chromium and chromium carbide. Polyvinyl alcohol is not required.

5 EXAMPLE 8

The agglomerated spray dried and sintered particles of Example 7 are fed through a commercially available plasma torch into a jacketed water cooled collection tank. A mixture of 126 cubic feet per hour of argon and
10 70 cubic feet per hour of hydrogen is fed to the plasma torch. The torch power is about 28 KVA. Nitrogen gas is fed to the powder feeder at the rate of 7 cubic feet per hour to entrain the powder which is fed through the torch. The powder produced is then screened as in
15 Example 7. Analysis of the -270 powder indicates 15%-15um particles. These prealloyed powder particles can then be used as a thermal spray powder.

EXAMPLE 9

20 A plasma densified spray powder as produced in Example 7 is comminuted and air classified to produce a powder having the following distribution: 60-90% less than minus 20 microns, less than 15% less than 5 microns.



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CLAIMS

1. A thermal spray powder consisting essentially of nickel and chromium with the balance being from about 50 to about 95 percent by weight chromium carbide, said chromium and nickel being present in a weight ratio of about 1 part by weight chromium to 4 parts by weight nickel wherein said powder being a substantially uniform composition.
2. A thermal spray powder according to claim 1 wherein at least a major portion of said densified powder consist essentially of particles wherein each particle has a substantially uniform composition.
3. A thermal spray powder according to claim 2 having a particle size distribution of about 60 to 90 percent minus 20 microns, and less than about 15 percent minus 5 microns.
4. A thermal spray powder according to claim 2 having a particle size distribution of about 100 percent minus 270 mesh and less than 15 percent -15 microns.
5. A thermal spray powder according to claim 2 having a particle size distribution of about minus 200 plus 325.
6. A process for producing a thermal spray powder comprising preparing a uniform powder blend consisting essentially of chromium and nickel being present in a weight ratio of about 1 part by chromium to 4 parts by weight nickel with the balance being from about 50 to about 95 percent by weight chromium carbide, said powder blend having an average particle size less than about 10 microns, agglomerating the powder to produce agglomerated particles, sintering the agglomerated particles, entraining the sintered agglomerated powder in a carrier gas, feeding the entrained agglomerated powder through a high temperature reactor having a temperature above the

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melting point of the highest melting component of the powder material to densify said particles.

7. A process for producing a thermal spray powder according to claim 5 wherein said densified particles
5 consist essentially of particles wherein each particle has a substantially uniform composition.

8. A process for producing a thermal spray powder according to claim 6 wherein said densified particles
10 have a particle size distribution of about 60 to 90 percent minus 20 microns, and less than about 15 percent minus 5 microns.

9. A process for producing a thermal spray powder according to claim 6 wherein said densified particles
15 have a particle size distribution of about 100 percent minus 270 mesh and less than 15 percent minus 15 microns.

10. A process for producing a thermal spray powder according to claim 6 wherein said uniform powder blend
is spray dried to form said agglomerates.

20 11. A process for producing a thermal spray powder according to claim 10 wherein said chromium comprises a water soluble chromium salt and said nickel comprises a water soluble nickel salt.

25 12. A powder for thermal spraying consisting essentially of an agglomerated powder consisting essentially of nickel and chromium with the balance being from about 50 to about 95 percent by weight chromium carbide, said chromium and nickel being present in a weight ratio of about 1 part by weight chromium to 4
30 parts by weight nickel.

13. A powder for thermal spraying according to claim 12 having a particle size distribution of about 100 percent minus 270 mesh and less than 15 percent minus 15 microns.



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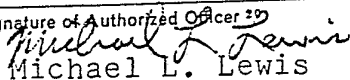
14. A powder for thermal spraying according to claim 13 having a particle size distribution of about minus 200 plus 325.

SUBSTITUTE SHEET



INTERNATIONAL SEARCH REPORT

International Application No PCT/US 82/01653

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. CL ³ B22F 1/00, 7/00		
U.S. CL 75/0.5 BA, 251 428/570		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
US	75/0.5BA, 0.5 BB, 0.5BC, 251-255; 419/31, 32, 35 427/34, 423 428/570	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
Chemical Abstracts Metals Abstracts	Engineering Index	
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
Y	US,A, 3,150,938, 29 September 1964, (Pelton, et al)	1, 2, 4-7, 9, 10, 12-14
A	US,A, 3,617,358, 02 November 1971, (Dittrich)	11
Y	US,A, 3,973,948, 10 August 1976, (Laferty, Jr., et al)	11
Y	US,A, 3,974,245, 10 August 1976, (Cheney, et al)	1, 2, 4-7, 9, 10, 12-14
A	US,A, 4,039,296, 02 August 1977, (Levinstein)	
Y	US,A, 4,075,371, 21 February 1978, (Patel)	3, 8
<p>* Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ²	
23 February 1983	15 MAR 1983	
International Searching Authority ¹	Signature of Authorized Officer ²	
ISA/US	 Michael L. Lewis	