Title: WEAR RESISTANT ALLOY POWDERS AND COATINGS

Abstract: This invention relates to alloys and wear resistant alloy powders useful for deposition through thermal spray devices. The alloys comprise from about 20 to 65 weight percent chromium, about 20 to 65 weight percent molybdenum, about 0.5 to 3 weight percent carbon, and about 10 to 45 weight percent nickel. The wear resistant alloy powders are useful for forming coatings having the same composition.
WEAR RESISTANT ALLOY POWDERS AND COATINGS

Field of the Invention

This invention relates to chromium-molybdenum alloys and wear resistant alloy powders useful for deposition through thermal spray devices. The wear resistant alloy powders are useful for forming coatings having the same composition.

Background of the Invention

Hard surface coating metals and alloys are known in the art. For example, chromium metal has been used as an electroplated coating for many years to restore worn or damaged parts to their original dimensions, to increase wear and corrosion resistance, and to reduce friction. Hard chromium electroplate, however, has a number of limitations. When the configuration of the part becomes complex, obtaining a uniform coating thickness by electro-deposition is difficult. A non-uniform coating thickness necessitates grinding to a finished surface configuration, which is both difficult and expensive with electroplated chromium because of its inherent brittleness and hardness. The rate of deposition by electroplating is relatively low, and thus a substantial capital investment in plating equipment is required. It is often necessary to apply one or more undercoats, or to use expensive surface cleaning and etching procedures to prepare substrates. Disposal of spent plating baths also adds significantly to the cost of the process.

An alternative method of depositing chromium metal is by metal spraying such as with a plasma, high
velocity oxygen fuel (HVOF) or detonation gun. This method allows the coating to be applied to almost any metallic substrate without using undercoats. The coating thickness can be controlled very closely so that any subsequent finishing can be kept to a minimum. However, considerable finishing may be required for certain coatings with wear resistance tailored for specific applications.

U.S. Patent No. 3,846,084 discloses coatings made by the plasma or detonation gun process that are superior to hard chromium electroplate in compatibility, frictional characteristics and wear resistance by incorporating a dispersion of chromium carbide particles in a chromium matrix. Coatings of this type can be made from mechanical mixtures of powders. However, there are certain limitations to the quality of coatings made from them. Plasma, HVOF and detonation-gun coatings result in a multilayer structure of overlapping lamellae or “splats.” Each splat is derived from a single particle of the powder used to produce the coating. There appears to be little, if any, combining or alloying of two or more powder particles during the coating deposition process.

U.S. Patent No. 6,562,480 B1 discloses a wear resistant coating for protecting a surface undergoing sliding contact with another surface such as piston rings and cylinder liners of internal combustion engines. The wear resistant coating is applied by HVOF deposition of a powder which comprises a blend of about 13 weight percent to about 43 weight percent of a nickel-chromium alloy, about 25 weight percent to about
64 weight percent chromium carbide, and about 15 weight percent to about 50 weight percent molybdenum.

U.S. Patent No. 6,503,290 B1 discloses a corrosion resistant powder useful for deposition through thermal spray devices. The powder comprises about 30 to 60 weight percent tungsten, about 27 to 60 weight percent chromium, about 1.5 to 6 weight percent carbon, a total of about 10 to 40 weight percent cobalt plus nickel and incidental impurities plus melting point suppressants. The corrosion resistant powder is useful for forming coatings having the same composition.

A need continues to exist for powders and coatings that can be deposited by thermal spray devices and that exhibit excellent wear and/or corrosion resistance. Therefore, a need continues to exist for developing new powders and for exploring their potential for thermal spray deposition of wear and corrosion resistant coatings. It would therefore be desirable in the art to provide powders and coatings that can be deposited by thermal spray devices and that exhibit excellent wear and corrosion resistance.

Summary of the Invention

This invention relates to alloys comprising about 20 to 65 weight percent chromium, about 20 to 65 weight percent molybdenum, about 0.5 to 3 weight percent carbon, and about 10 to 45 weight percent nickel. The alloys include precipitated carbides (and optionally nitrides) of chromium and molybdenum interspersed throughout. This invention also relates to wear resistant alloy powders useful for deposition through
thermal spray devices. The powders comprise an alloy of about 20 to 65 weight percent chromium, about 20 to 65 weight percent molybdenum, about 0.5 to 3 weight percent carbon, and about 10 to 45 weight percent nickel. The wear resistant alloy powders are useful for forming coatings having the same composition.

Detailed Description of the Invention

As indicated above, this invention relates to wear resistant alloy powders useful for deposition through thermal spray devices such as plasma, HVOF or detonation gun. The powders are made from alloys comprising about 20 to 65 weight percent chromium, about 20 to 65 weight percent molybdenum, about 0.5 to 3 weight percent carbon, and about 10 to 45 weight percent nickel. The alloys include precipitated carbides and optionally nitrides of chromium and molybdenum interspersed throughout. The alloys are useful for forming wear resistant powders and coatings having the same composition.

The alloys herein rely upon a large concentration of chromium and molybdenum for excellent wear resistance. Advantageously, the alloys contain at least about 20 weight percent chromium, preferably at least about 30 weight percent chromium, and more preferably at least about 35 weight percent chromium. Powders containing less than about 20 weight percent chromium may exhibit inadequate wear resistance for many applications. Chromium levels in excess of about 65 weight percent may tend to detract from the wear resistance of the coating because the coating may become too brittle.
Similarly, the alloys contain at least about 20 weight percent molybdenum, preferably at least about 25 weight percent molybdenum, and more preferably about 30 or 35 weight percent molybdenum. Powders containing less than about 20 weight percent molybdenum may exhibit inadequate wear resistance for many applications. Molybdenum levels in excess of about 65 weight percent may tend to detract from the wear resistance of the coating because the coating may become too brittle.

In an embodiment of this invention, the alloys comprise about 20 to 65, preferably about 30 to 60, and more preferably about 35 to 55, weight percent chromium; about 20 to 65, preferably about 25 to 60, and more preferably about 30 to 55, weight percent molybdenum; about 0.5 to 3, preferably about 1 to 2.5, and more preferably about 1.5 to 2, weight percent carbon; and about 10 to 45, preferably about 15 to 35, and more preferably about 20 to 35, weight percent nickel. These alloys are useful for forming wear resistant powders and coatings having the same composition.

In another embodiment of this invention, the alloys comprise about 50 to 90, preferably about 60 to 80, and more preferably about 65 to 75, weight percent chromium and molybdenum; about 0.5 to 3, preferably about 1 to 2.5, and more preferably about 1.5 to 2, weight percent carbon; and about 10 to 45, preferably about 15 to 35, and more preferably about 20 to 35, weight percent nickel. These alloys are useful for forming wear resistant powders and coatings having the same composition.
The carbon concentration controls the hardness and wear properties of coatings formed with the powders. A minimum of about 0.5 weight percent carbon may be necessary to impart adequate hardness into the coatings. If the carbon exceeds about 3 weight percent, the melting temperature of the powder may become too high and it may become too difficult to atomize the powder.

In another embodiment of this invention, cobalt may be included in the alloys, powders and coatings. The powders may contain about 10 to 45, preferably about 15 to 35, and more preferably about 20 to 35, weight percent nickel plus cobalt. This may facilitate the melting of the chromium/molybdenum/carbon combination that, if left alone, would form carbides having too high of melting temperatures for atomization. Increasing the concentration of cobalt and nickel may also tend to increase the deposition efficiency for thermal spraying the powder. Because total nickel plus cobalt levels above about 45 weight percent may tend to soften the coating and limit the wear resistance of the coating, the total concentration of nickel plus cobalt may best be maintained below about 45 weight percent. In addition, the alloys may contain only nickel or cobalt since coatings with only nickel (e.g., about 10 to 45 weight percent nickel) or only cobalt (e.g., about 10 to 45 weight percent cobalt) may form powders with wear resistance tailored for specific applications. But for most applications, cobalt and nickel appear to be interchangeable.

In another embodiment of this invention, boron, silicon and/or manganese may be included in the alloys,
powders and coatings. The alloys may contain about 0.5 to 3, preferably about 1 to 2.5, and more preferably about 1.5 to 2, weight percent carbon plus boron, silicon and/or manganese. To facilitate melting for atomization, the alloys may optionally contain melting point suppressants such as boron, silicon and manganese. An excessive amount of melting point suppressants may tend to decrease both corrosion and wear resistance.

As indicated above, the alloys include precipitated carbides (and optionally nitrides) of chromium and molybdenum interspersed throughout. The alloys may contain a volume fraction of the precipitated carbides and optionally nitrides in excess of 0.25. Preferably, the volume fraction of the precipitated carbides and optionally nitrides dispersed in the alloys may be 0.25 or greater and more preferably between 0.35 and 0.80. Preferably, the precipitated carbide and optionally nitride grains may be of micrometer and submicrometer size, for example, between 0.5 or less and 20 micrometers, more preferably between 1 and 10 micrometers in its largest dimensions. The size and volume fraction of the precipitated carbides and optionally nitrides can be adjusted by varying the chromium, molybdenum and carbon content.

The alloys of this invention may be blended with molybdenum to form powders with wear resistance tailored for specific applications. The amount of molybdenum that may be blended with the alloys of this invention is not narrowly critical and may range from about 10 to 50, preferably about 15 to 45, and more preferably about 20 to 40, weight percent of the total
alloy/molybdenum blend composition. The amount of blended molybdenum is in addition to the amount of alloy molybdenum. The amount of blended molybdenum will depend upon the desired application.

Advantageously, the powders of this invention may be produced by means of inert gas atomization of a mixture of elements in the proportions stated herein. Preferred atomization methods that may be employed in making the powders of this invention are described in U.S. Patent 5,863,618, the disclosure of which is incorporated herein by reference. The alloys of these powders are typically melted at a temperature of about 1600°C and then atomized in a protective atmosphere (e.g., argon, helium or nitrogen). Most advantageously the atmosphere is argon. A nitrogen atmosphere may be employed which may result in the formation of additional hard phases interspersed throughout the alloys, e.g., nitrides. As indicated above, to facilitate melting for atomization, the alloy may optionally contain melting point suppressants like boron, silicon and manganese.

Alternatively, sintering and crushing, sintering and spray drying, sintering and plasma densification are possible methods for manufacturing the powders. Gas atomization however represents the most effective method for manufacturing the powder. Gas atomization techniques typically produce a powder having a size distribution of about 1 to 500 microns. For thermal spray applications, the powder is classified to a size of about 1 to 100 microns.
Coatings may be produced using the alloys of this invention by a variety of methods well known in the art. These methods include thermal spray (plasma, HVOF, detonation gun, etc.), laser cladding; and plasma transferred arc (PTA). Thermal spray is a preferred method for deposition of powders to form the coatings of this invention. The wear resistant alloy powders of this invention are useful for forming coatings having the same composition.

The alloy powders of this invention are useful for forming coatings or objects having excellent wear properties, for example, wear resistant coatings for protecting surfaces undergoing sliding contact with other surfaces such as piston rings and cylinder liners of internal combustion engines.

The examples that follow are intended as an illustration of certain preferred embodiments of the invention, and no limitation of the invention is implied.

Example 1

The alloy powders listed in Table I were made by processes alike to those described in U.S. Patent 5,863,618.
Table I

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>C</th>
<th>Other</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>45</td>
<td>20</td>
<td>32</td>
<td>2</td>
<td>1 B</td>
</tr>
<tr>
<td>B</td>
<td>42</td>
<td>23</td>
<td>33</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>40</td>
<td>35</td>
<td>22.5</td>
<td>2.5</td>
<td></td>
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<tr>
<td>D</td>
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<td>20</td>
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</tr>
<tr>
<td>F</td>
<td>34</td>
<td>22</td>
<td>43</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>30</td>
<td>30</td>
<td>39</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>50</td>
<td>21</td>
<td>3(+20Co)</td>
<td>0.5</td>
<td>0.4B, 2.3Fe, 2.2 Si</td>
</tr>
<tr>
<td>I</td>
<td>51</td>
<td>22</td>
<td>13(+10Co)</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>J</td>
<td>35</td>
<td>35</td>
<td>27.5</td>
<td>1.5</td>
<td>0.5 B</td>
</tr>
</tbody>
</table>
Other variations and modifications of this invention will be obvious to those skilled in the art. This invention is not limited except as set forth in the claims.
Claims

1. An alloy comprising from about 20 to 65 weight percent chromium, about 20 to 65 weight percent molybdenum, about 0.5 to 3 weight percent carbon, and about 10 to 45 weight percent nickel.

2. The alloy of claim 1 comprising about 10 to 45 weight percent nickel plus cobalt.

3. The alloy of claim 1 comprising about 0.5 to 3 weight percent carbon plus boron, silicon and/or manganese.

4. The alloy of claim 1 further comprising precipitated carbides and optionally nitrides of chromium and molybdenum interspersed throughout.

5. The alloy of claim 4 in which the volume fraction of the precipitated carbides and optionally nitrides dispersed throughout the alloy is 0.25 or greater.

6. The alloy of claim 4 in which the size of the precipitated carbides and optionally nitrides is between 0.5 or less and 20 micrometers in its largest dimensions.

7. A wear resistant powder useful for deposition through thermal spray devices, the powder comprising an alloy of about 20 to 65 weight percent chromium, about 20 to 65 weight percent molybdenum, about 0.5 to 3
weight percent carbon, and about 10 to 45 weight percent nickel.

8. The wear resistant powder of claim 7 in which the alloy further comprises about 10 to 45 weight percent nickel plus cobalt.

9. The wear resistant powder of claim 7 in which the alloy further comprises about 0.5 to 3 weight percent carbon plus boron, silicon and/or manganese.

10. The wear resistant powder of claim 7 in which the alloy further comprises precipitated carbides and optionally nitrides of chromium and molybdenum interspersed throughout.

11. The wear resistant powder of claim 10 in which the volume fraction of the precipitated carbides and optionally nitrides dispersed throughout the alloy is 0.25 or greater.

12. The wear resistant powder of claim 10 in which the size of the precipitated carbides and optionally nitrides is between 0.5 or less and 20 micrometers in its largest dimensions.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : B22F 1/00, C09C 1/62, C22C 27/04, 27/06
US CL : 75/255; 106/403; 420/428, 429, 588
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 75/255; 106/403; 420/428, 429, 588

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please see Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>US 3,030,206 A (BUCK) 17 April 1962 (17.04.1962)</td>
<td>1-12</td>
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<tr>
<td>A</td>
<td>US 4,556,607 A (SASTRI) 03 December 1985 (03.12.1985)</td>
<td>1-12</td>
</tr>
<tr>
<td>Y</td>
<td>US 4,692,305 A (RANGASWAMY et al.) 08 September 1987 (08.09.1987)</td>
<td>1,3, 7-9</td>
</tr>
<tr>
<td>A</td>
<td>US 6,248,292 B1 (ANDO et al.) 19 June 2001 (19.06.2001)</td>
<td>4-6 and 10-12</td>
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<tr>
<td>A,P</td>
<td>US 6,887,585 B2 (HERBST-DEDERICHS) 03 May 2005</td>
<td>1-12</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C. See patent family annex.

Date of the actual completion of the international search
16 August 2005 (16.08.2005)

Date of mailing of the international search report
27 OCT 2005

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Form PCT/ISA/210 (second sheet) (January 2004)
Continuation of B. FIELDS SEARCHED Item 3:
EA$T(\text{all databases})$: (Cr or chromium) with (molybdenum or m) with (nickle or ni)) same (graphite or carbon or c) and (wear$1$ resist$2$ or anti$1$ wear or wear near$1$ (resistant$2$ or prevent$3$)) and coat$3$ near$5$ (powder or alloy)