A thermal spraying powder is characterized in that 90% particle size D90 of the thermal spraying powder is 15 μm or less. The thermal spraying powder is also characterized in that the ratio of the total volume of particles having a particle size of 1 μm or less to the total volume of all particles in the thermal spraying powder is 2% or less. A value obtained by dividing the bulk density of the thermal spraying powder by the theoretical density of material forming the thermal spraying powder is preferably 0.15 or more. The particle size dispersion index of the thermal spraying powder is preferably 0.7 or less. A thermal spray coating that is dense and has a small surface roughness is reliably formed using the thermal spraying powder.
THERMAL SPRAYING POWDER, THERMAL SPRAYING METHOD, AND METHOD FOR FORMING THERMAL SPRAY COATING

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a thermal spraying powder, a thermal spraying method, and a method for forming a thermal spray coating.

[0002] To impart useful properties such as corrosion resistance, wear resistance, and thermal resistance to metal components of various industrial machines and general machines, a technique to provide a thermal spray coating on surfaces of the components has been proposed. The thermal spray coating is formed by spraying, to base material, thermal spraying material that has been heated to be softened or melted. Therefore, the surface of the thermal spray coating is inherently not smooth but rough. Thus, in a case where a surface is required to be smooth, the thermal spray coating is polished until a target surface roughness is achieved. However, since the thermal spray coating having the above mentioned useful properties generally has a high hardness, polishing of the thermal spray coating is not easy in many cases. In particular, in a case of the thermal spray coating formed by spraying a cermet containing tungsten carbide and metal, the thermal spray coating must be polished using diamond abrasive grain, which increases manufacturing costs. Therefore, there is a demand for a technique for forming the thermal spray coating having a small surface roughness, which omits or simplifies the polishing after thermal spraying.

[0003] Furthermore, the thermal spray coating is inherently porous, and may include through holes that extend through the thermal spray coating from the base material to the surface of the thermal spray coating. However, the thermal spray coating is required to include no through holes depending on the use such as when the thermal spray coating is provided to prevent corrosion of the base material. In the prior art, when the thermal spray coating is required to include no through holes, the thermal spray coating is formed thick. However, as the thickness increases, the cost of the thermal spray coating is increased. Thus, the thickness of the thermal spray coating is desired to be as small as possible. Therefore, there is a demand for a technique for forming a thin thermal spray coating that includes no through holes. Also, a method for closing the through holes by sealing has been proposed to prevent through holes. However, the costs are increased in this case also since the manufacturing process is increased.

[0004] As one of techniques for responding to such demand for the thermal spray coating, the thermal spray coating may be formed from a fine thermal spraying powder. When fine thermal spraying powder is sprayed, a dense thermal spray coating the surface roughness of which is small and that does not include through holes is obtained. However, in this case, there is a high risk that supply of the thermal spraying powder from a powder feeder to a spray gun could become unstable. This is because as the thermal spraying powder becomes finer, the flowability of the thermal spraying powder is decreased. For example, when pulsation occurs while feeding the thermal spraying powder, the quality of the thermal spray coating is significantly decreased. Moreover, if the thermal spraying powder forms a bridge (powder bridging), the thermal spraying powder is not smoothly supplied to the spray gun, and the supply of the thermal spraying powder may be stopped in some cases.

[0005] For example, Japanese Laid-Open Patent Publication No. 2003-129212 discloses a technique for forming a thermal spray coating from a thermal spraying powder having 90% particle size $D_{90}$ of 20 $\mu$m or less. However, in the thermal spraying powder of the above publication, since the ratio of particles having a particle size of 1 $\mu$m or less in the thermal spraying powder is not specified, the thermal spraying powder could include a large amount of particles having a particle size of 1 $\mu$m or less. If the thermal spraying powder includes many particles having a particle size of 1 $\mu$m or less, in addition to decreasing the flowability of the thermal spraying powder, flocculation of the thermal spraying powder is likely to occur. If the thermal spraying powder that has been flocculated is mixed in the thermal spray coating, uniformity and density of the thermal spray coating may be decreased, through holes may be formed in the thermal spray coating, or the surface roughness of the thermal spray coating may be increased.

SUMMARY OF THE INVENTION

[0006] Accordingly, it is an objective of the present invention to provide a thermal spraying powder that reliably forms a dense thermal spray coating with a low surface roughness. It is also an objective of the present invention to provide a thermal spraying method using the thermal spraying powder, and a method for forming a thermal spray coating using the thermal spraying powder.

[0007] To achieve the foregoing and other objectives of the present invention, a thermal spraying powder is provided, in which 90% particle size $D_{90}$ of the thermal spraying powder is 15 $\mu$m or less, and the ratio of the total volume of particles having a particle size of 1 $\mu$m or less to the total volume of all particles in the thermal spraying powder is 2% or less.

[0008] The present invention also provides a thermal spraying method including spraying the above thermal spraying powder.

[0009] Further, the present invention provides a method for forming a thermal spray coating including spraying the above thermal spraying powder.

[0010] Other aspects and advantages of the invention will become apparent from the following description, illustrating by way of example the principles of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0011] One embodiment of the present invention will now be described.

[0012] The thermal spraying powder of the preferred embodiment is a granulated and sintered powder of cermet. Particles of the thermal spraying powder are composed of tungsten carbide and at least one of cobalt, chromium, and nickel.

[0013] When the content of tungsten carbide, which is a ceramic component in the thermal spraying powder, is greater than 92% by mass, in other words when the total content of cobalt, chromium, and nickel, which are metal
components in the thermal spraying powder, is less than 8% by mass, the brittleness of the thermal spray coating formed of the thermal spraying powder is increased and there is a risk that the thermal spray coating does not have a high wear resistance. Therefore, the content of the ceramic component in the thermal spraying powder is preferably 92% by mass or less, and the content of the metal components in the thermal spraying powder is preferably 8% by mass or more.

When 90% particle size $D_{90}$ of the thermal spraying powder is greater than 15 $\mu$m (that is, when the ratio of the total volume of particles having a particle size of 15 $\mu$m or less to the total volume of all particles in the thermal spraying powder is less than 90%), it is difficult to form the thermal spray coating that is dense and has a small surface roughness from the thermal spraying powder since particles having a particle size of greater than 15 $\mu$m are included in the thermal spraying powder by a large amount. Therefore, the 90% particle size $D_{90}$ of the thermal spraying powder must be 15 $\mu$m or less (that is, the ratio of the total volume of particles having a particle size of 15 $\mu$m or less must be 90% or more). However, even if the 90% particle size $D_{90}$ of the thermal spraying powder is 15 $\mu$m or less, if it is greater than 13 $\mu$m (that is, if the ratio of the total volume of particles having a particle size of 13 $\mu$m or less to the total volume of all particles in the thermal spraying powder is less than 90%), the surface roughness and the density of the thermal spray coating formed of the thermal spraying powder are not significantly improved. Therefore, the 90% particle size $D_{90}$ of the thermal spraying powder is preferably 13 $\mu$m or less (the ratio of the total volume of particles having a particle size of 13 $\mu$m or less is preferably 90% or more).

When the 90% particle size $D_{90}$ of the thermal spraying powder is less than 5 $\mu$m (that is, when the ratio of the total volume of particles having a particle size of 5 $\mu$m or less to the total volume of all particles in the thermal spraying powder is greater than 90%), and more specifically less than 7 $\mu$m (that is, when the ratio of the total volume of particles having a particle size of 7 $\mu$m or less to the total volume of all particles in the thermal spraying powder is greater than 90%), the flowability of the thermal spraying powder is slightly decreased since particles having a particle size of 5 $\mu$m (or 7 $\mu$m) or less is included in the thermal spraying powder by a large amount. Therefore, the 90% particle size $D_{90}$ of the thermal spraying powder is preferably 5 $\mu$m or more (the ratio of the total volume of particles having a particle size of 5 $\mu$m or less is preferably 90% or less), and the 90% particle size $D_{90}$ of the thermal spraying powder is more preferably 7 $\mu$m or more (the ratio of the total volume of particles having a particle size of 7 $\mu$m or less is more preferably 90% or less).

When the ratio of the total volume of particles having a particle size of 1 $\mu$m or less to the total volume of all particles in the thermal spraying powder is greater than 2% (that is, when 2% particle size $D_{2}$ of the thermal spraying powder is less than 1 $\mu$m), the flowability of the thermal spraying powder is significantly decreased since particles having a particle size of 1 $\mu$m or less is included in the thermal spraying powder by a large amount. As a result, supply of the thermal spraying powder from the powder feeder to the spray gun during spraying becomes unstable. Moreover, flocculation of the thermal spraying powder may occur, thereby decreasing the uniformity and the density of the thermal spray coating, generating through holes in the thermal spray coating, or increasing the surface roughness of the thermal spray coating. Therefore, the ratio of the total volume of particles having a particle size of 1 $\mu$m or less must be 2% or less (that is, the 2% particle size $D_{2}$ of the thermal spraying powder must be 1 $\mu$m or more). However, even if the ratio of the accumulated volume of particles having a particle size of 1 $\mu$m or less is 2% or less, if it is greater than 1.5% (that is, if 1.5% particle size $D_{1.5}$ of the thermal spraying powder is less than 1 $\mu$m), the stability of supplying the thermal spraying powder while spraying is not significantly improved. Therefore, the ratio of the total volume of particles having a particle size of 1 $\mu$m or less is preferably 1.5% or less (that is, the 1.5% particle size $D_{1.5}$ of the thermal spraying powder is preferably 1 $\mu$m or less).

When the particle size dispersion index of the thermal spraying powder is greater than 0.7, and more specifically greater than 0.67, the flowability of the thermal spraying powder is slightly decreased since the proportion of particles having a small particle size in the thermal spraying powder is increased. Alternatively, there is a risk that the density of the thermal spray coating formed of the thermal spraying powder could be slightly decreased or the surface roughness could be slightly increased since the proportion of particles having a large particle size in the thermal spraying powder is increased. Therefore, the particle size dispersion index of the thermal spraying powder is preferably 0.7 or less, and more preferably 0.67 or less.

When a value obtained by dividing the bulk density of the thermal spraying powder by the theoretical density of material forming the thermal spraying powder is less than 0.15, and more specifically less than 0.17, there are risks that the stability of supplying the thermal spraying powder while spraying could be slightly decreased, and the density of the thermal spray coating formed of the thermal spraying powder could be slightly decreased. Therefore, the value obtained by dividing the bulk density of the thermal spraying powder by the theoretical density of material forming the thermal spraying powder is preferably 0.15 or more, and more preferably 0.17 or more.

Next, a method for manufacturing the thermal spraying powder of the preferred embodiment, that is, a method for manufacturing the granulated and sintered cermet powder composed of tungsten carbide and at least one of cobalt, chromium, and nickel will now be described. First, a metal powder consisting of at least one of cobalt, chromium, and nickel and tungsten carbide powder are mixed in a dispersion medium to prepare slurry. An appropriate binder may be added to the slurry. Next, granulated powder is formed from the slurry using a roll granulator, a spray granulator, or a compression granulator. Thus obtained granulated powder is sintered, then crushed and classified to manufacture the granulated and sintered cermet powder composed of tungsten carbide and at least one of cobalt, chromium, and nickel. The sintering of the granulated powder may be performed either in vacuum or an inert gas atmosphere, and either an electric furnace or a gas furnace may be used.

The thermal spraying powder of the preferred embodiment is used for forming the thermal spray coating through, for example, high-velocity flame spraying. The thermal spray coating formed of the thermal spraying pow-
der of the preferred embodiment through high-velocity flame spraying has a sufficient wear resistance. A high-velocity flame spray gun that is capable of spraying the thermal spraying powder of this embodiment in a suitable manner includes high-output type high-velocity flame spray gun such as “JP-5000” manufactured by Praxair/TAF and “Diamond jet (hybrid type)” manufactured by Sulzer Metco, and “0-Gun” manufactured by WHITCO Japan Corporation.

[0021] The preferred embodiment has the following advantages.

[0022] Since the 90% particle size D_{90} of the thermal spraying powder is set to 15 μm or less, the thermal spray coating that is dense and has a small surface roughness is formed using the thermal spraying powder of this embodiment.

[0023] Furthermore, since the ratio of the total volume of particles having a particle size of 1 μm or less to the total volume of all particles in the thermal spraying powder is set to 2% or less, the thermal spray coating is reliably formed using the thermal spraying powder of this embodiment.

[0024] Since the value obtained by dividing the bulk density of the thermal spraying powder by the theoretical density of material forming the thermal spraying powder is set to 0.15 or more, the thermal spraying powder of this embodiment further reliably prevents the stability of supplying the thermal spraying powder while spraying from decreasing and the density of the thermal spray coating formed of the thermal spraying powder from decreasing.

[0025] Since the particle size dispersion index of the thermal spraying powder is set to 0.7 or less, the thermal spraying powder of this embodiment suppresses problems caused by irregular sizes of particles in the thermal spraying powder.

[0026] The granulated and sintered powder generally has sufficient fluidity and less risk of contamination by impurities during a manufacturing process as compared to a fused and crushed powder and a sintered and crushed powder. Therefore, the thermal spraying powder of this embodiment consisting of the granulated and sintered powder has the same advantages.

[0027] The particles in the thermal spraying powder of this embodiment consist of cermet. Therefore, the thermal spray coating having a sufficient wear resistance is formed using the thermal spraying powder of this embodiment.

[0028] The preferred embodiment may be modified as follows.

[0029] The particles in the thermal spraying powder may further include ceramics other than tungsten carbide such as chromium carbide instead of tungsten carbide or in addition to tungsten carbide.

[0030] The particles in the thermal spraying powder may further include metal other than cobalt, chromium, and nickel instead of cobalt, chromium, and nickel or in addition to cobalt, chromium, and nickel.

[0031] The thermal spraying powder may contain components other than the granulated and sintered powder of cermet composed of tungsten carbide and at least one of cobalt, chromium, and nickel. However, the content of the granulated and sintered powder in the thermal spraying powder is preferably 50% by mass or more, and more preferably 80% by mass or more.

[0032] The thermal spraying powder may be a fused and crushed cermet powder or a sintered and crushed cermet powder instead of the granulated and sintered cermet powder. In these cases, particles in the thermal spraying powder may or may not be composed of tungsten carbide and at least one of cobalt, chromium, and nickel. The fused and crushed powder is manufactured by melting a raw material powder and crushing and classifying the raw material powder after being cooled and solidified. The sintered and crushed powder is manufactured by sintering the raw material powder, and crushing and classifying the raw material powder.

[0033] The thermal spraying powder of the preferred embodiment may be used for forming the thermal spray coating through a thermal spraying method other than the high-velocity flame spraying.

[0034] Next, examples and comparative examples of the present invention will be described.

[0035] In examples 1 to 7 and comparative examples 1 to 4, granulated and sintered cermet powders containing 12% by weight of cobalt with the tungsten carbide as the main component were prepared as the thermal spraying powders. In example 8, fused and crushed cermet powder composed of tungsten carbide and cobalt was prepared as the thermal spraying powder. In example 9 and comparative example 5, granulated and sintered cermet powders containing 10% by weight of cobalt and 4% by weight of chromium with tungsten carbide as the main component were prepared as the thermal spraying powders. Specifics of the thermal spraying powders of examples 1 to 9 and comparative examples 1 to 5 are as shown in Table 1.

[0036] The column entitled “Ratio of particles having particle size of 1 μm or less” in Table 1 shows the ratio of the total volume of particles having a particle size of 1 μm or less to the total volume of all particles in the thermal spraying powder. The ratio was measured using a laser diffraction/scattering type of particle size distribution measuring instrument “LA-300” manufactured by HORIBA Ltd.

[0037] The columns entitled “10% particle size D_{10}”, “50% particle size D_{50}”, and “90% particle size D_{90}” in Table 1 show the 10% particle size D_{10}, the 50% particle size D_{50}, and the 90% particle size D_{90} of the thermal spraying powders measured using the laser diffraction/scattering type of particle size distribution measuring instrument “LA-300” manufactured by HORIBA Ltd. The 10% particle size D_{10} of the thermal spraying powder is the size of the particle that is lastly summed up when the volume of particles in the thermal spraying powder is accumulated from particles of the smallest size in ascending order until the accumulated volume reaches 10% of the total volume of all the particles in the thermal spraying powder. The 50% particle size D_{50} of the thermal spraying powder is the size of the particle that is lastly summed up when the volume of particles in the thermal spraying powder is accumulated from particles of the smallest size in ascending order until the accumulated volume reaches 50% of the total volume of all the particles in the thermal spraying powder. The 90% particle size D_{90} of the thermal spraying powder is the size of the particle that is lastly summed up when the volume of particles in the
thermal spraying powder is accumulated from particles of the smallest size in ascending order until the accumulated volume reaches 90% of the total volume of all the particles in the thermal spraying powder.

[0038] The column entitled “Dispersion index” in Table 1 shows the particle size dispersion index D of the thermal spraying powders calculated in accordance with the equation: \( D = (D_{90}-D_{10}) / (D_{90} + D_{10}) \). In the equation, \( D_{90} \) represents the 90% particle size of the thermal spraying powder, and \( D_{10} \) represents the 10% particle size of the thermal spraying powder.

[0039] The column entitled “Bulk density/theoretical density” in Table 1 shows values obtained by dividing the bulk density of each thermal spraying powder measured using a bulk specific gravity measuring instrument (refer to JIS Z 2504) by the theoretical density of material forming the thermal spraying powder.

[0040] The thermal spray coatings having a thickness of 200 \( \mu \)m were formed by high-velocity flame spraying of the thermal spraying powders according to examples 1 to 4, 6 to 9, and comparative examples 1 to 5 under a first spraying condition shown in Table 2 and high-velocity flame spraying of the thermal spraying powder according to example 5 under a second spraying condition shown in Table 2. Then, depending on whether the thermal spray coatings were formed, the thermal spraying powders were evaluated according to a two rank scale: good (1) and poor (2). That is, when the thermal spray coating was formed, the thermal spraying powder was ranked good, and when the supply of the thermal spraying powder from the powder feeder to the spray gun was stopped and the thermal spray coating was not formed, the thermal spraying powder was ranked poor. The evaluation results are shown in the column entitled “Formation of coating” in Table 1.

[0041] The surface roughnesses \( R_a \) of any 15 spots on each of the thermal spray coatings formed by high-velocity flame spraying of the thermal spraying powders according to examples 1 to 9 and comparative examples 1 to 5 were measured under a condition shown in Table 3. Based on the average value of the surface roughnesses \( R_a \) of the measured 15 spots, the thermal spraying powders were evaluated according to a three rank scale: excellent (1), good (2), and poor (3). That is, when the average value of the surface roughnesses \( R_a \) was less than 1.3 \( \mu \)m, the thermal spraying powder was ranked excellent, when it was 1.3 \( \mu \)m or more and less than 1.6 \( \mu \)m, the thermal spraying powder was ranked good, and when it was 1.6 \( \mu \)m or more, the thermal spraying powder was ranked poor. The evaluation results are shown in the column entitled “Surface roughness of thermal spray coating before polishing” in Table 1.

TABLE 1

<table>
<thead>
<tr>
<th>Composition of thermal spraying powder</th>
<th>Manufacturing method of thermal spraying powder</th>
<th>Ratio of particles having particle size of 1 ( \mu )m or less</th>
<th>10% particle size ( D_{10} ) [( \mu )m]</th>
<th>50% particle size ( D_{50} ) [( \mu )m]</th>
<th>90% particle size ( D_{90} ) [( \mu )m]</th>
<th>Dispersive index</th>
<th>Bulk density/theoretical density [%]</th>
<th>Formation of coating</th>
<th>Surface roughness of thermal spray coating before polishing</th>
<th>Surface roughness of thermal spray coating after polishing</th>
<th>Variance of surface roughness</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex. 1 WC/12Co granulated-sintered</td>
<td></td>
<td>0.24%</td>
<td>2.7</td>
<td>5.6</td>
<td>8.5</td>
<td>0.52</td>
<td>27.1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ex. 2 WC/12Co granulated-sintered</td>
<td></td>
<td>0.30%</td>
<td>2.9</td>
<td>5.9</td>
<td>10.4</td>
<td>0.56</td>
<td>27.2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
As shown in Table 1, in examples 1 to 9, each of the evaluations for the surface roughness and the density of the thermal spray coatings before polishing was either excellent or good. The results suggest that the thermal spray coatings that are dense and have a small surface roughness are formed with the thermal spraying powders according to examples 1 to 9.

1. A thermal spraying powder, wherein 90% particle size D90 of the thermal spraying powder is 15 μm or less, and the ratio of the total volume of particles having a particle size of 1 μm or less to the total volume of all particles in the thermal spraying powder is 2% or less.

2. The thermal spraying powder according to claim 1, wherein the 90% particle size D90 of the thermal spraying powder is 13 μm or less.

3. The thermal spraying powder according to claim 1, wherein the ratio of the total volume of particles having a particle size of 1 μm or less to the total volume of all particles in the thermal spraying powder is 1.5% or less.

4. The thermal spraying powder according to claim 1, wherein a value obtained by dividing the bulk density of the thermal spraying powder by the theoretical density of material forming the thermal spraying powder is 0.15 or more.

5. The thermal spraying powder according to claim 1, wherein the particle size dispersion index of the thermal spraying powder is 0.7 or less.

6. The thermal spraying powder according to claim 1, wherein the thermal spraying powder is a granulated and sintered powder.

7. The thermal spraying powder according to claim 7, wherein particles in the thermal spraying powder consist of cermet.

8. The thermal spraying powder according to claim 7, wherein the content of a ceramic component in the thermal spraying powder is 92% by mass or less.
9. The thermal spraying powder according to claim 7, wherein the content of a metal component in the thermal spraying powder is 8% by mass or more.

10. The thermal spraying powder according to claim 7, wherein the cermet includes tungsten carbide.

11. The thermal spraying powder according to claim 7, wherein the cermet includes at least one of cobalt, chromium, and nickel.

12. The thermal spraying powder according to claim 1, wherein the thermal spraying powder is used for forming a thermal spray coating through high-velocity flame spraying.

13. A thermal spraying method, comprising spraying a thermal spraying powder, wherein 90% particle size D90 of the thermal spraying powder is 15 μm or less, and the ratio of the total volume of particles having a particle size of 1 μm or less to the total volume of all particles in the thermal spraying powder is 2% or less.

14. A method for forming a thermal spray coating, the method comprising spraying a thermal spraying powder, wherein 90% particle size D90 of the thermal spraying powder being 15 μm or less, and the ratio of the total volume of particles having a particle size of 1 μm or less to the total volume of all particles in the thermal spraying powder is 2% or less.

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